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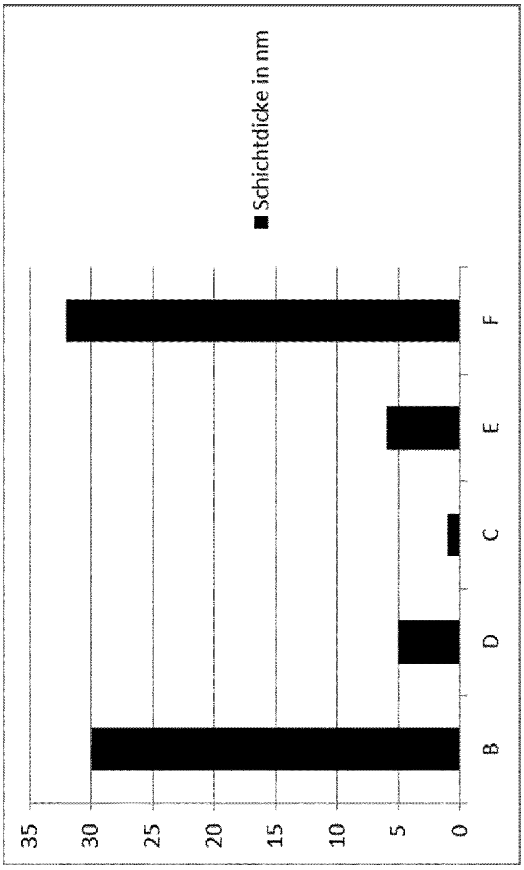
(54) Composition, use thereof and method for electrodepositing gold containing layers

(57) The present invention relates to a composition and method for electrodepositing gold containing layers using the composition and the use of mercapto triazole as additive. The composition contains a mercapto-triazole compound which acts as an anti-immersion additive. The composition and method are suited for depositing functional or hard gold or gold alloys that can be applied in the industry as contact material of electrical connectors for high reliability applications.

Figure 1



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Description

Field of the Invention

[0001] The present invention relates to a composition and method for electrodepositing gold containing layers using the inventive composition. The inventive composition contains a mercapto-triazole compound which acts as an anti-immersion additive. The composition and method are suited for depositing functional or hard gold or gold alloys that can be applied in the industry as contact material of electrical connectors for high reliability applications.

Background of the Invention

[0002] Hard gold or gold alloys of cobalt and nickel have been widely used as contact material of electrical connectors for high reliability applications. Connectors having hard gold end layers are therefore electroplated over electrically conductive metal layers, for example over nickel substrates such as nickel plated on copper. Usually, connectors are part of larger electrical devices or electrical wires. Selective electroplating techniques are used for depositing gold or gold alloy layers onto contact areas of connectors only while not plating the remaining part of the electrical circuit. Such selective plating techniques significantly reduce material cost of connectors by limiting the plating area of gold and other precious metals, such as palladium and palladium-nickel alloys.

[0003] As gold is a noble metal which is to be plated onto connectors that are usually made of less noble metal there arises the problem of gold displacement. Gold displacement is the deposition of gold by an exchange reaction. If the surface to be gold plated is for example a nickel surface, the displacement reaction is believed to occur as follows:

$$2\ Au^+ + Ni^0 \rightarrow 2\ Au^0 + Ni^{2+}$$

where the noble gold metal displaces the less noble nickel. Metal deposition by such an exchange or displacement reaction is also called immersion reaction or immersion plating.

[0004] On the one hand this problem occurs on the surface of parts or areas of substrates that is not to be plated and therefore is not electrically connected while the functional surface of the electronic part, i.e. a connector is electroplated. Additionally, the immersion reaction can occur when electroplating is stopped, for example during idle times. Then the connector surfaces remain in the gold deposition bath for some time without being electrically connected.

[0005] In both cases a gold layer is deposited on the non-connected surfaces by immersion reaction. Thus, a gold layer is deposited by immersion reaction at areas of the substrate where it is not desired. This immersion gold deposition is unwanted because it consumes more gold than is necessary for coating the connectors and other electronic parts and thus causes an extra consumption of gold leading to higher manufacturing costs.

[0006] The gold layer deposited on parts of printed circuit lines, connectors or other electronic devices that are unwanted to be plated can also cause defects in the substrate resulting in defective end products. The gold layer therefore has to be removed afterwards which is laborious, time consuming and costly.

[0007] In addition, the gold layer formed by immersion reaction has low adhesion to its subjacent surface. Parts of the immersed gold layer peel off from the underlying surface, with the risk of short cuts when accidentally connecting separate circuit lines or other contact metals.

[0008] Moreover, the problem of gold immersion increases with the age of the gold electrolyte.

[0009] Gold immersion may be reduced by improving the design of plating equipment. However, this requires costly expenditures to redesign and then manufacture new equipment parts.

[0010] European patent EP 2 309 036 B1 discloses a hard gold plating bath which decreases the gold displacement reaction. The effect is due to mercaptotetrazole compounds contained in the plating bath. However, the decrease of the gold displacement reaction is still insufficient. In addition,
EP 2 309 036 B1 is silent about the increasing gold displacement with proceeding age of the gold deposition bath.

[0011] Accordingly, there is still a need for inhibiting the gold immersion reaction in electrodeposition baths for functional pure gold and gold alloy layers.

Objective of the present Invention

[0012] Therefore, it is an objective of the present invention to provide a composition and a method for electrodepositing gold containing layers with further decreased gold immersion reaction.

[0013] It is a further objective of the present invention to provide a method for reducing the increasing gold immersion reaction during the lifetime of the composition for gold electrodeposition.

Summary of the Invention

[0014] These objectives are achieved by the following compositions and methods.

[0015] An electroplating composition comprising

(i) at least one source of gold ions, and
(ii) at least one mercapto-triazole or a salt thereof.

[0016] The mercapto-triazole or its salts according to (ii) significantly decrease or nearly inhibit the gold immersion reaction when electrodepositing gold containing layers.

[0017] A method comprising the steps:

(i) providing an electroplating composition as defined above;
(ii) contacting a substrate with the composition; and
(iii) applying an electrical current between the substrate and at least

one anode and thereby depositing a gold or gold alloy onto the substrate.

[0018] The method is suited for electrodepositing gold containing layers on substrates. The method significantly decreases or nearly inhibits the gold immersion reaction.

[0019] A method comprising:

(i) providing a used gold or gold alloy electroplating composition;
(ii) adding a mercapto-triazole as defined above to the used gold or gold alloy electroplating composition, and
(iii) contacting a substrate with the composition; and
(iv) applying an electrical current between the substrate and at least

one anode and thereby depositing a gold or gold alloy onto the substrate.

[0020] The method is suited for regenerating used gold or gold alloy electroplating compositions in which the gold immersion reaction has reached an extent that prevents effective operation and deposition of proper gold or gold alloy layers. The method significantly decreases or nearly inhibits the gold immersion reaction.

Brief Description of the Figures

[0021] Figure 1 shows the thickness of gold alloy layers deposited from electroplating baths containing different mercapto azole compounds by immersion reaction.

Detailed Description of the Invention

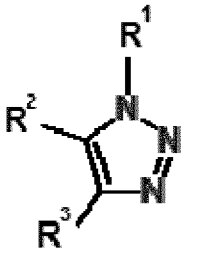
[0022] The present invention relates to an electroplating composition comprising

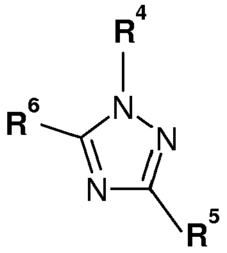
(i) at least one source of gold ions, and
(ii) at least one mercapto-triazole or a salt thereof.

[0023] The electroplating composition is suited for electrodepositing gold containing layers on substrates. The gold containing layers may be pure gold layers or gold alloy layers. Preferably, the gold containing layers are gold alloy layers. More preferably the gold containing layers are gold alloy layers which are used as so called functional or hard gold layers. Functional or hard gold layers have a high mechanical stability and are therefore particularly resistant against mechanical wear. Gold layers and in particular gold alloy layers are therefore suited for use in electrical connectors.

[0024] The mercapto-triazole or its salts according to (ii) significantly decrease or nearly inhibit the gold immersion reaction when electrodepositing gold containing layers.

[0025] In one embodiment the at least one mercapto-triazole has the following general formulae (I) or (II):


Formula (I)

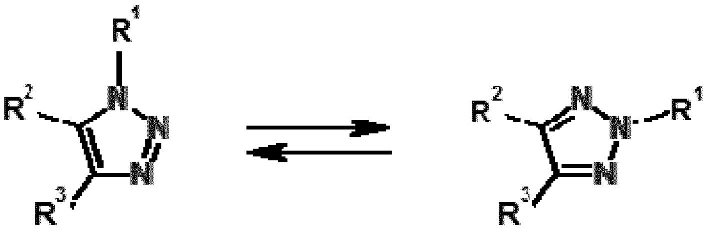

Formula (II)

wherein R^1, R^4 are independently of each other hydrogen; linear or branched, saturated or unsaturated (C_1 - C_{20}) hydrocarbon chain, (C_8 - C_{20}) aralkyl group; substituted or unsubstituted phenyl group, naphthyl group, amine group or carboxyl group; and
R^2, R^3, R^5, R^6 are independently of each other -S-X; hydrogen; linear or branched, saturated or unsaturated (C_1 - C_{20}) hydrocarbon chain, (C_8 - C_{20}) aralkyl group; substituted or unsubstituted phenyl group, naphthyl group, amine group or carboxyl group; and
X is hydrogen, (C_1 - C_4) alkyl group or a counter-ion selected from alkali metal ions, calcium ion, ammonium ion and quaternary amines, and at least one of R^2 and R^3 is -S-X, and at least one of R^5 and R^6 is -S-X.

[0026] In another embodiment the alkali metal ions are selected from sodium ion, potassium ion and lithium ion.

[0027] In another embodiment the substitutent groups of the substituted phenyl, naphthyl or amine group of R^1, R^2, R^3, R^4, R^5, R^6 are selected independently from branched or unbranched (C_1 - C_{12}) alkyl group, branched or unbranched (C_2 - C_{20}) alkylene group, branched or unbranched (C_1 - C_{12}) alkoxy group; hydroxyl group, and halogens. In another embodiment the halogens are selected from chlorine and bromine.

[0028] In solution the mercapto triazole of formula (I) may exist in two tautomeric forms:



[0029] Formula (I) therefore comprises both tautomeric forms.

[0030] In a preferred embodiment the at least one mercapto-triazole has the general formulae (I) or (II), wherein R^1, R^4 are independently of each other hydrogen or a linear (C_1 - C_4) alkyl group, and
R^2, R^3, R^5, R^6 are independently of each other -S-X, hydrogen or a linear (C_1 - C_4) alkyl group; and
X is hydrogen, a methyl group, an ethyl group, or a counter-ion selected from sodium ion and potassium ion; and
at least one of R^2 and R^3 is -S-X, and at least one of R^5 and R^6 is -S-X.

[0031] In another preferred embodiment the at least one mercapto-triazole has the general formulae (I) or (II), wherein R^1, R^4 are independently of each other hydrogen, methyl group or ethyl group, and
R^2, R^3, R^5, R^6 are independently of each other -S-X, hydrogen, methyl group or ethyl group, and
X is hydrogen, a sodium ion or a potassium ion; and
at least one of R^2 and R^3 is -S-X, and at least one of R^5 and R^6 is -S-X.

[0032] In another preferred embodiment the at least one mercapto-triazole has the general formulae (I) or (II), wherein R^1, R^4 are independently of each other hydrogen or a methyl group, and
R^2, R^3, R^5, R^6 are independently of each other -S-X, hydrogen or methyl group, and
X is hydrogen, a sodium ion or a potassium ion; and
at least one of R^2 and R^3 is -S-X, and at least one of R^5 and R^6 is -S-X.

[0033] In a more preferred embodiment the at least one mercapto-triazole has the general formula (I), wherein R^1, R^2, R^3 and X have the meanings as defined above.

[0034] In an even more preferred embodiment the at least one mercapto-triazole is selected from the group comprising 5-mercapto-1,2,3-triazole; 4,5-dimercapto-1,2,3-triazole; 5-mercapto-1,2,4-triazole; 3-mercapto-1,2,4-triazole; 3,5-

dimercapto-1,2,4-triazole and salts thereof.

[0035] In an even more preferred embodiment the at least one mercapto-triazole is selected from 5-mercapto-1,2,3-triazole and salts thereof. The mercapto-triazole compounds are commercially available or may be prepared by methods well known in the art.

[0036] In one embodiment the at least one mercapto-triazole has a concentration in the electroplating composition ranging from 1 mg/l to 1 g/l. Preferably the concentration is below 1g/l. More preferably the concentration ranges from 1 mg/l to 900 mg/l, even more preferably from 1 mg/l to 500 mg/l, even more preferably from 5 mg/l to 100 mg/l.

[0037] Addition of one or more mercapto-triazoles to a gold or gold alloy electroplating composition inhibits the gold immersion reaction, while not compromising gold alloy appearance. In addition, the functional properties of the gold or hard gold layers, such as contact resistance and hardness, are not compromised either. The contact resistance is maintained at the desired low levels and the gold layers are sufficiently hard for commercial electrical contacts for electronic devices.

[0038] The electroplating composition further comprises (i) at least one source of gold ions. The source of gold ions may be selected from sources of gold(I) ions and sources of gold(III) ions. Sources of gold(I) ions may be selected from the group of gold(I) salts comprising gold cyanide compounds, gold thiosulfate compounds, gold sulfite compounds, and gold(I) halides. Gold cyanide compounds may be selected from alkali gold cyanide such as potassium gold cyanide or sodium gold cyanide; and ammonium gold cyanide. Gold thiosulfate compounds may be selected from alkali gold thiosulfates such as trisodium gold thiosulfate or tripotassium gold thiosulfate. Gold sulfite compounds may be selected from alkali gold sulphites such as sodium gold sulphite or potassium gold sulphite; and ammonium gold sulfite. Gold(I) halides may be gold(I) chloride. Sources of gold(III) ions may be gold(III) halides such as gold(III) trichloride. Preferably, the source of gold ions is an alkali gold cyanide compound such as potassium gold cyanide or sodium gold cyanide. More preferably, the source of gold ions is a potassium gold cyanide, such as potassium dicyanoaurate(I) or potassium tetracyanoaurate(III); or a sodium gold cyanide, such as sodium dicyanoaurate(I) or sodium tetracyanoaurate(III). Even more preferably, the source of gold ions is potassium dicyanoaurate(I) or potassium tetracyanoaurate(III).

[0039] In one embodiment the at least one source of gold ions has a concentration in the electroplating composition ranging from 1 g/l to 50 g/l, preferably ranging from 5 g/l to 30 g/l, more preferably ranging from 5 g/l to 20 g/l, even more preferably ranging from 10 g/l to 20 g/l.

[0040] In one embodiment the electroplating composition may further comprise complexing agents for gold ions. The complexing agents for gold ions are selected from alkali metal cyanides such as potassium cyanide, sodium cyanide and ammonium cyanide; thiosulfuric acid and salts therof such as sodium thiosulfate, potassium thiosulfate, and ammonium thiosulfate; sulfurous acid and salts therof such as potassium sulfite, ammonium sulfite, carboxylic acids such as sorbic acid; hydroxy carboxylic acids, such as citric acid and malonic acid; amino carboxylic acids, such as ethylenediamine tetraacetic acid, iminodiacetic acid, nitrilotriacetic acid, 1,2-diamino cyclohexane tetraacetic acid, bis-2-amino ethylether tetraacetic acid, diethylene triamine pentaacetic acid; mineral acids, such as phosphoric acid, sulfuric acid, boric acid; phosphonic acids, such as 1-hydroxyethane-1,1-diphosphonic acid, 1-hydroxyethane-1,2-disphosphonic acid, aminotrimethylenephosphonic acid, ethylenediaminetetramethyl phosphonic acid, hexamethylene diamino tetramethyl phosphonic acid; and salts of the aforementioned acids, such as alkali metals salts and earth alkali metal salts; preferably sodium and potassium salts; amines, such as tetraethylenepentamine, triethylenetetramine, triethylamine, diethylenetriamine and ethylene diamine. The complexing agents may also function as conducting salts.

[0041] In one embodiment, in which the source of gold ions is an alkali gold cyanide compound, the complexing agent is preferably no cyanide compound, more preferably no alkali metal cyanide.

[0042] In one embodiment the complexing agents have a concentration in the electroplating composition ranging from 1 g/l to 200 g/l, preferably ranging from 1 g/l to 100 g/l, more preferably ranging from 10 g/l to 50 g/l.

[0043] In one embodiment the electroplating composition may further comprise at least one source of alloying metal ions. Metals of the alloying metal ions are selected from cobalt, nickel and iron. Gold-cobalt, gold-nickel and gold-iron alloys belong to hard gold alloys. Alloying metal ions are selected from cobalt(II) ions, nickel(II) ions, iron(II) ions and iron(III) ions. Sources of alloying metal ions are selected from cobalt carbonate, cobalt sulfate, cobalt gluconate, cobalt potassium cyanide, cobalt bromide, cobalt chloride, nickel chloride, nickel bromide, nickel sulfate, nickel tartrate, nickel phosphate, nickel nitrate, nickel sulfamate, iron chloride, iron bromide, iron citrate, iron fluoride, iron iodide, iron nitrate, iron oxalate, iron phosphate, iron pyrophosphate, iron sulfate, and iron acetate.

[0044] In one embodiment the at least one source of alloying metal ions has a concentration in the electroplating composition ranging from 0.001 g/l to 5 g/l, preferably ranging from 0.05 g/l to 2 g/l, more preferably ranging from 0.05 g/l to 1 g/l.

[0045] In one embodiment the electroplating composition may further comprise complexing agents for alloying metal ions. The complexing agents for alloying metal ions may be selected from sulfurous acid and salts therof such as potassium sulfite, ammonium sulfite, carboxylic acids, such as sorbic acid; hydroxy carboxylic acids, such as citric acid and malonic acid; amino carboxylic acids, such as ethylenediamine tetraacetic acid, iminodiacetic acid, nitrilotriacetic acid, 1,2-diamino cyclohexane tetraacetic acid, bis-2-amino ethylether tetraacetic acid, diethylene triamine pentaacetic acid; mineral acids, such as phosphoric acid, sulfuric acid, boric acid, thiosulfuric acid; phosphonic acids, such as 1-hydroxyethane-1,1-diphosphonic acid, 1-hydroxy ethane-1,2-disphosphonic acid, aminotrimethylenephosphonic acid, ethylenediaminetetramethylphosphonic acid, hexamethylene diamino tetramethyl phosphonic acid; and salts of the aforementioned acids, such as alkali metals salts and earth alkali metal salts; preferably sodium and potassium salts; amines, such as tetraethylenepentamine, triethylenetetramine, triethylamine, diethylenetriamine and ethylene diamine. The complexing agents may also function as conducting salts.

[0046] The complexing agents for alloying metal ions may have a concentration in the electroplating composition ranging from 1 to 200 g/l, preferably ranging from 20 to 150 g/l. If the same complexing agent is used for gold ions and for alloying metal ions, the concentration of the complexing agent is the sum of concentrations required for the gold ions and for the alloying metal ions.

[0047] In one embodiment the electroplating composition may further comprise at least one brightening agent. The at least one brightening agent is selected from pyridine and quinoline compounds. The pyridine and quinoline compounds are selected from substituted pyridine and substituted quinoline compounds. Preferably, the substituted pyridine and substituted quinoline compounds are selected from mono- or dicarboxylic acid, mono- or disulfonic acid, mono- or dithiol substituted pyridines, quinolines, pyridine derivatives or quinoline derivatives. The pyridine or quinoline derivatives may be substituted in one or more positions by the same or different substituents. More preferably, the pyridine derivatives or quinoline derivatives are selected from derivatives substituted in the 3-position of the pyridine ring. Even more preferably, the pyridine derivatives or quinoline derivatives are selected from pyridine or quinoline carboxylic acids, pyridine or quinoline sulfonic acids, and pyridine or quinoline thiols. Even more preferably, the pyridine or quinoline carboxylic acids are selected from the respective esters and amides thereof. Even more preferably, the pyridine or quinoline carboxylic acids are selected from pyridine-3-carboxylic acid (nicotinic acid), quinoline-3-carboxylic acid, 4-pyridine carboxylic acids, nicotinic acid methyl ester, nicotinamide, nicotinic acid diethyl amide, pyridine-2,3-dicarboxylic acid, pyridine-3,4-dicarboxylic acid and pyridine-4-thioacetic acid. Even more preferably, the pyridine or quinoline sulfonic acids are selected from 3-pyridinesulfonic acid, 4-pyridine sulfonic acid and 2-pyridinesulfonic acid. Most preferably, the at least one brightening agent is selected from pyridine-3-carboxylic acid (nicotinic acid), nicotinamide, and 3-pyridinesulfonic acid.

[0048] The at least one brightening agent may have a concentration in the electroplating composition ranging from 0.5 g/l to 10 g/l, preferably ranging from 1 g/l to 10 g/l.

[0049] The brightening agents advantageously cause deposition of bright gold layers over a wide current density range of between 2 A/dm^2 to 100 A/dm^2.

[0050] In one embodiment the electroplating composition may further comprise at least one acid. Preferably, the at least one acid is an organic or inorganic acid. More preferably, the at least one acid is selected from phosphoric acid, citric acid, malic acid, oxalic acid, formic acid and polyethylene amino acetic acid. The at least one acid is used to adjust the pH value of the electroplating composition. The at least one acid may also function as complexing agent and/or as conducting salt.

[0051] The at least one acid may have a concentration in the electroplating composition ranging from 1 g/l to 200 g/l.

[0052] In one embodiment the electroplating composition may further comprise at least one alkaline compound. The at least one alkaline compound is used to adjust the pH value of the electroplating composition. The at least one alkaline compound is selected from hydroxides, sulfates, carbonates, phosphates, hydrogen phosphates and other salts of sodium, potassium and magnesium. Preferably, the at least one alkaline compound is selected from KOH, NaOH, K_2CO_3, Na_2CO_3, K_2HPO_4, Na_2HPO_4, NaH_2PO_4 and mixtures thereof.

[0053] In one embodiment the electroplating composition is an acidic electroplating composition. The electroplating composition may have a pH value below 7, preferably between 1 to 6, more preferably between 3 to 6, even more preferably between 3.5 to 5.5.

[0054] In one embodiment the electroplating composition may comprise further additives, such as surfactants and/or grain refiners.

[0055] The present invention further relates to a method comprising the steps:

(i) providing an electroplating composition as defined above;
(ii) contacting a substrate with the composition; and
(iii) applying an electrical current between the substrate and at least

one anode and thereby depositing a gold containing layer onto the substrate.

[0056] The method is suited for electrodepositing gold containing layers onto substrates. The method utilizes the electroplating composition of the present invention containing at least one mercapto-triazole or salts thereof as anti-immersion additives. The method significantly decreases or nearly inhibits the gold immersion reaction. Therefore the method of the present invention significantly reduces the gold consumption and and increases the lifetime of the gold or gold alloy electroplating composition. The gold containing layers may be pure gold layers or gold alloy layers.

[0057] The gold containing layers may be deposited onto the entire surface of a substrate or onto parts of the surface of the substrate. Depositing metal layers onto parts of the surface of the substrate is also called selectively depositing or plating a metal layer. Thus, the gold containing layers may be selectively electroplated onto the substrate.

[0058] Selective plating may be performed by known methods, like a masking method, a spot plating method or a brush plating method. The masking method involves the use of a mask that covers the part of the substrate surface which is not to be plated. In the spot plating method only the part of the substrate to be metallized is electrically connected and thus plated. The brush plating method locally applies a brush covered anode to the area of the substrate to be plated wherein the brush contains a metal plating solution.

[0059] In both cases, metal deposition onto the entire surface of a substrate or selective metal deposition, the electrical conductive surface of the substrate or part of the substrate surface is contacted with the electroplating composition of the present invention. The surface of the substrate or part of the substrate surface is electrically connected as a cathode. A voltage is applied between this cathode and at least one anode so that a current flow is supplied to the substrate surface or part of the substrate surface.

[0060] The current densities of the current flow may range from 0.05 A/dm^2 to 100 A/dm^2, preferably from 1 A/dm^2 to 50 A/dm^2, more preferably from 5 A/dm^2 to 20 A/dm^2.

[0061] Plating times may vary. The amount of time depends on the desired thickness of the gold containing layer on the substrate. The thickness of the gold containing layer ranges from 0.01 μm to 5 μm, preferably from 0.05 μm to 3 μm, more preferably from 0.05 μm to 1.5 μm.

[0062] During plating the electroplating composition of the present invention may be held at a temperature ranging from 40°C to 70°C.

[0063] During plating the electroplating composition of the present invention may be unmoved or may be agitated. Agitation may be performed for example by mechanical movement of the aqueous plating bath like shaking, stirring or continuously pumping of the liquids or intrinsically by ultrasonic treatment or by elevated temperatures or by gas feeds such as purging the aqueous plating bath with an inert gas or simply with air.

[0064] The method for electrodepositing gold containing layers onto substrates may further comprise a pre-treatment step prior to contacting the substrate with the electroplating composition of the present invention. The pre-treatment step is an activation of the substrate surface using typically acids or fluoride containing acids.

[0065] The method for electrodepositing gold containing layers onto substrates may comprise further plating steps prior to contacting the substrate with the electroplating composition of the present invention. The further plating steps deposit further metal layers onto the substrate prior to electrodepositing gold or gold alloy layers onto the substrate. The metal of the further metal layers may be selected from iron, nickel, nickel-phosphorus alloy, copper, palladium, silver, cobalt and alloys thereof, preferably nickel, nickel-phosphorus alloy, and copper. Plating methods for the above mentioned metals are known in the art.

[0066] In one embodiment the substrate to be plated with a gold containing layer, i.e. a gold or gold alloy layer, is an electrically conductive material. The electrically conductive material may be a metal. The metal may be any metal where gold immersion reaction may occur. The metal may be selected from iron, nickel, nickel-phosphorus alloy, copper, palladium, silver, cobalt and alloys thereof. Preferably the substrate is made from iron or copper and covered with a nickel layer.

[0067] In one embodiment the substrate to be plated with a gold containing layer is an electrical connector. Preferably, the substrate is a contact interface of electrical connectors. More preferably the substrate is a plug connector. The substrate may be part of a printed circuit board, an electrical wire or an electrical device.

[0068] The present invention further relates to a method comprising the steps:

(i) providing a used gold or gold alloy electroplating composition;
(ii) adding a mercapto-triazole as defined above to the used gold or gold alloy electroplating composition, and
(iii) contacting a substrate with the composition; and
(iv) applying an electrical current between the substrate and at least

one anode and thereby depositing a gold or gold alloy onto the substrate.

[0069] The method is suited for regenerating used gold or gold alloy electroplating compositions. On the one hand a used electroplating composition may be an aged gold or gold alloy electroplating composition. Aged electroplating compositions mean herein compositions already used for electroplating in which the gold immersion reaction has reached an extent that prevents effective operation and deposition of proper gold or gold alloy layers. A criterion for assessing the extent of ageing is the rate of deposition by immersion reaction. In newly made up gold or gold alloy electroplating baths the deposition rate is about 5 nm/5min metal at 60º. The deposition rate increases with the lifetime of the electroplating bath. When the deposition rate arrives at 80 to 100 nm/5min metal at 60º the gold or gold alloy electroplating bath usually needs to be replaced. In contrast, the method of the present invention significantly decreases or nearly inhibits the gold immersion reaction in aged gold or gold alloy electroplating compositions. Therefore, the method of the present invention regenerates an aged gold or gold alloy electroplating composition and significantly increases the lifetime of a gold or gold alloy electroplating composition.

[0070] The thickness of gold layers may be measured with x-ray fluorescence (XRF) which is known in the art. The XRF thickness measurement makes use of the characteristic fluorescence radiation emitted from a sample (substrate, deposits) being excited with x-rays. By evaluating intensities and assuming a layered structure of the sample layer thicknesses can be calculated.

[0071] On the other hand a used electroplating composition may be a gold or gold alloy electroplating composition which has not been employed in the electroplating process for some time. Not being employed means that the gold or gold alloy electroplating composition is not electrically connected and no gold or gold alloy is electrodeposited from the composition. It was observed that the problem of gold immersion plating also increases while a gold or gold alloy electrodeposition composition is not employed in the electroplating process. Adding the mercapto-triazole of the present invention to a gold or gold alloy electrodeposition composition that was temporarily out of operation also significantly decreases or nearly inhibits the gold immersion reaction when the composition is in operation again.

[0072] The present invention further relates to a substrate electroplated with a gold containing layer obtainable by one of the methods of the present invention.

[0073] The present invention further relates to the use of mercapto-triazoles of the present invention as anti-immersion additives in electrodeposition compositions, preferably in electrodeposition compositions for gold containing layers.

[0074] The electroplating composition and the methods of the present invention significantly decrease or nearly inhibit the gold immersion reaction. Thus, gold is not deposited onto unwanted areas of substrate surfaces. This saves costs because loss of gold and production of defective end products is minimized. Moreover, the lifetime of gold or gold alloy electroplating compositions is significantly increased.

[0075] In contrast to the triazole compounds of the present invention, tetrazole compounds are significantly less effective in decreasing the gold immersion reaction. In addition, tetrazole compounds show less stability in gold or gold alloy electroplating compositions leading to higher consumption of tetrazole compounds, misfunctions due to the increasing concentrations of break down products during processing and thus to a reduced lifetime of the gold electrolyte.

Examples

Example 1

[0076] Copper panels electroplated with nickel were used as substrates. The substrates were pre-treated by rinsing with water, by oxidative activation (Uni-Clean 675, product of Atotech Deutschland GmbH) for 15 seconds at room temperature (about 20 ºC) and again rinsing with water and thereafter with deionized water.

[0077] Copper panel A was subjected to electroplating with a newly made up gold-cobalt alloy plating bath (Aurocor HSC, 15 g/l gold, pH 4.5, product of Atotech Deutschland GmbH) containing additionally 500 mg/l of the sodium salt of 5-mercapto-1,2,3-triazole as an anti-immersion additive. Electroplating was performed at a current density of 10 A/dm^2, a temperature of 60º, with agitation, for time 150 seconds.

[0078] After plating, the substrate was completely covered with a bright, uniform, well adhering gold-cobalt alloy layer of high hardness having a thickness of 5 μm.

Example 2

[0079] Copper panels electroplated with nickel and pre-treated as described in Example 1 were used as substrates. Half of the area of the substrates was covered with tesa tapes in order to mask the area that is not to be plated.

[0080] Copper panel B was contacted with a newly made up gold-cobalt alloy plating bath (Aurocor HSC, 15 g/l gold, pH 4.5, product of Atotech Deutschland GmbH) containing no mercapto triazole compound.

[0081] Copper panels C to F were contacted with separate portions of a newly made up gold-cobalt alloy plating bath (Aurocor HSC, 15 g/l gold, pH 4.5, product of Atotech Deutschland GmbH) containing 500 mg/l each of a mercapto triazole compound or a mercapto tetraazole compound as outlined in Table 1.

[0082] While being in contact with the gold-cobalt alloy plating baths the copper panels B to F were not electrically connected. Thus, no metal deposition by electroplating was possible. 50 ml of the gold-cobalt alloy plating baths containing the respective mercapto azole compound were used for each panel. The gold-cobalt alloy plating baths were held at a temperature of 60 ºC and constantly agitated with 400 rpm (rounds per minute). Contacting each panel was performed for 5 minutes.

[0083] After contacting the panels with the respective gold-cobalt alloy plating bath the thickness of the gold alloy layer deposited by immersion reaction was measured by XRF. The results are summarized in Table 1 and shown in Figure 1.

Table 1: Thickness of gold alloy layers deposited from electroplating baths containing different mercapto azole compounds by immersion reaction

Panel	mercapto azole	deposition thickness / nm/5min
B	None (comparative)	30
C	5-Mercapto-1,2,3-triazole (Na-salt) (according to invention)	1
D	1-Phenyltetrazol-5-thiol (comparative)	5
E	5-Mercapto-tetrazole-1-acetic acid (Na-salt) (comparative)	6
F	5-Methyl-1-mercapto-tetrazole (comparative)	32

[0084] Generally, a gold alloy layer was deposited onto the part of the substrate panel not covered by the tape, while no gold alloy was deposited to the part of the substrate panel which was covered with tape. From the gold alloy bath containing the mercapto triazole according to the invention a gold alloy layer of only minimal thickness was deposited by immersion reaction. In contrast, from the gold alloy baths containing no mercapto azole compound or comparative mercapto tetrazole compounds gold alloy layers of significant higher layer thickness are deposited by immersion reaction. Moreover, comparative compound D caused unwanted pricipitates in the gold alloy bath. In contrast to the triazole compounds of the present invention, tetrazole compounds show less stability in the gold alloy electrolyte leading to higher consumption of tetrazole compounds, misfunctions due to the increasing concentrations of break down products during processing and thus to a reduced lifetime of the gold electrolyte. Thus, the mercapto triazole compounds of the present invention significantly decrease or nearly inhibit the gold immersion reaction.

Example 3

[0085] Copper panels electroplated with nickel and pre-treated as described in Example 1 were used as substrates.

[0086] An aged pure gold electroplating bath (Aurocor HS, product of Atotech Deutschland GmbH) was first treated with active carbon for 30 min at 60 ºC.

[0087] In step 1, the gold plating bath was held at 60 ºC while the substrates were dipped in the gold plating bath for different time periods without being electrically connected. After 30 seconds in the bath, no gold was deposited onto a substrate. But after 2 minutes and after 3 minutes a gold layer was deposited onto the substrates by immersion reaction.

[0088] In subsequent step 2, 25 mg/l of the sodium salt of 5-mercapto-1,2,3-triazole was added to the gold plating bath and again substrates were dipped into the gold plating bath for different time periods without being electrically connected. No gold was deposited by immersion reaction onto a substrate after 30 seconds, 2 minutes, 3 minutes and not even after 5 minutes of contacting with the gold plating bath.

[0089] Thus, the mercapto triazole compounds of the present invention significantly decrease or nearly inhibit the gold immersion reaction in aged gold or gold alloy electroplating compositions. Therefore the mercapto triazole compounds of the present invention regenerate an aged gold or gold alloy electroplating composition and significantly increases the lifetime of a gold or gold alloy electroplating composition.

Example 4

[0090] On day 1, Example 3 was repeated with the same results. After step 2 the bath was left to stand for one day without being employed in plating.

[0091] On day 2, again substrates were contacted with the gold plating bath according to step 1 of Example 3. After 3 minutes in the bath, no gold was deposited onto a substrate. But after 5 minutes a gold layer was deposited onto the substrates by immersion reaction.

[0092] Afterwards step 2 of Example 3 was performed. No gold was deposited by immersion reaction onto a substrate even after 5 minutes of contacting with the gold plating bath.

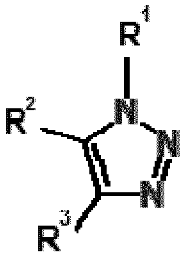
[0093] Thus, adding the mercapto-triazole compounds of the present invention to a gold or gold alloy electrodeposition composition that was temporarily out of operation also significantly decreases or nearly inhibits the gold immersion reaction when the composition is in operation again.

Claims

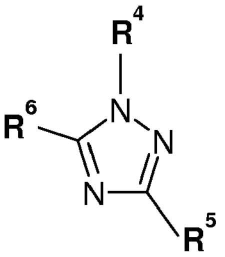
1. An electroplating composition comprising

   (i) at least one source of gold ions, and
   (ii) at least one mercapto-triazole or a salt thereof.

2. The composition according to claim 1, wherein the at least one mercapto-triazole has the following general formulae (I) or (II):



Formula (I)



Formula (II)

   wherein R^1, R^4 are independently of each other hydrogen, linear or branched, saturated or unsaturated (C_1-C_{20}) hydrocarbon chain, (C_8-C_{20}) aralkyl group; substituted or unsubstituted phenyl group, naphthyl group, amine group or carboxyl group; and
   R^2, R^3, R^5, R^6 are independently of each other -S-X, hydrogen, linear or branched, saturated or unsaturated (C_1-C_{20}) hydrocarbon chain, (C_8-C_{20}) aralkyl group; substituted or unsubstituted phenyl group, naphthyl group, amine group or carboxyl group; and
   X is hydrogen, (C_1-C_4) alkyl group or a counter-ion selected from alkali metal ions, calcium ion, ammonium ion and quaternary amines, and
   at least one of R^2 and R^3 is -S-X, and at least one of R^5 and R^6 is -S-X.

3. The composition according to any of the foregoing claims, wherein the at least one mercapto-triazole has the general formulae (I) or (II),
   wherein R^1, R^4 are independently of each other hydrogen or a linear (C_1 - C_4) alkyl group, and
   R^2, R^3, R^5, R^6 are independently of each other -S-X, hydrogen or a linear (C_1 - C_4) alkyl group; and
   X is hydrogen, a methyl group, an ethyl group, or a counter-ion selected from sodium ion and potassium ion; and at least one of R^2 and R^3 is -S-X, and at least one of R^5 and R^6 is -S-X.

4. The composition according to any of the foregoing claims, wherein the at least one mercapto-triazole has a concentration ranging from 1 mg/l to 1 g/l.

5. The composition according to any of the foregoing claims, further comprising at least one source of alloying metal ions, wherein the metal of the alloying metal ions is selected from cobalt, nickel and iron.

6. The composition according to any of the foregoing claims, further comprising complexing agents for gold ions.

7. The composition according to any of the foregoing claims, further comprising at least one brightening agent selected from pyridine and quinoline compounds.

8. The composition according to any of the foregoing claims, having a pH value between 1 - 6.

9. A method comprising:

(i) providing an electroplating composition according to claims 1 to 8;
(ii) contacting a substrate with the composition; and
(iii) applying an electrical current between the substrate and at least

one anode and thereby depositing a gold or gold alloy onto the substrate.

10. The method according to claim 9, wherein the substrate is iron, nickel, copper or an alloy thereof.

11. The method according to claims 9 or 10, wherein the substrate is an electrical connector.

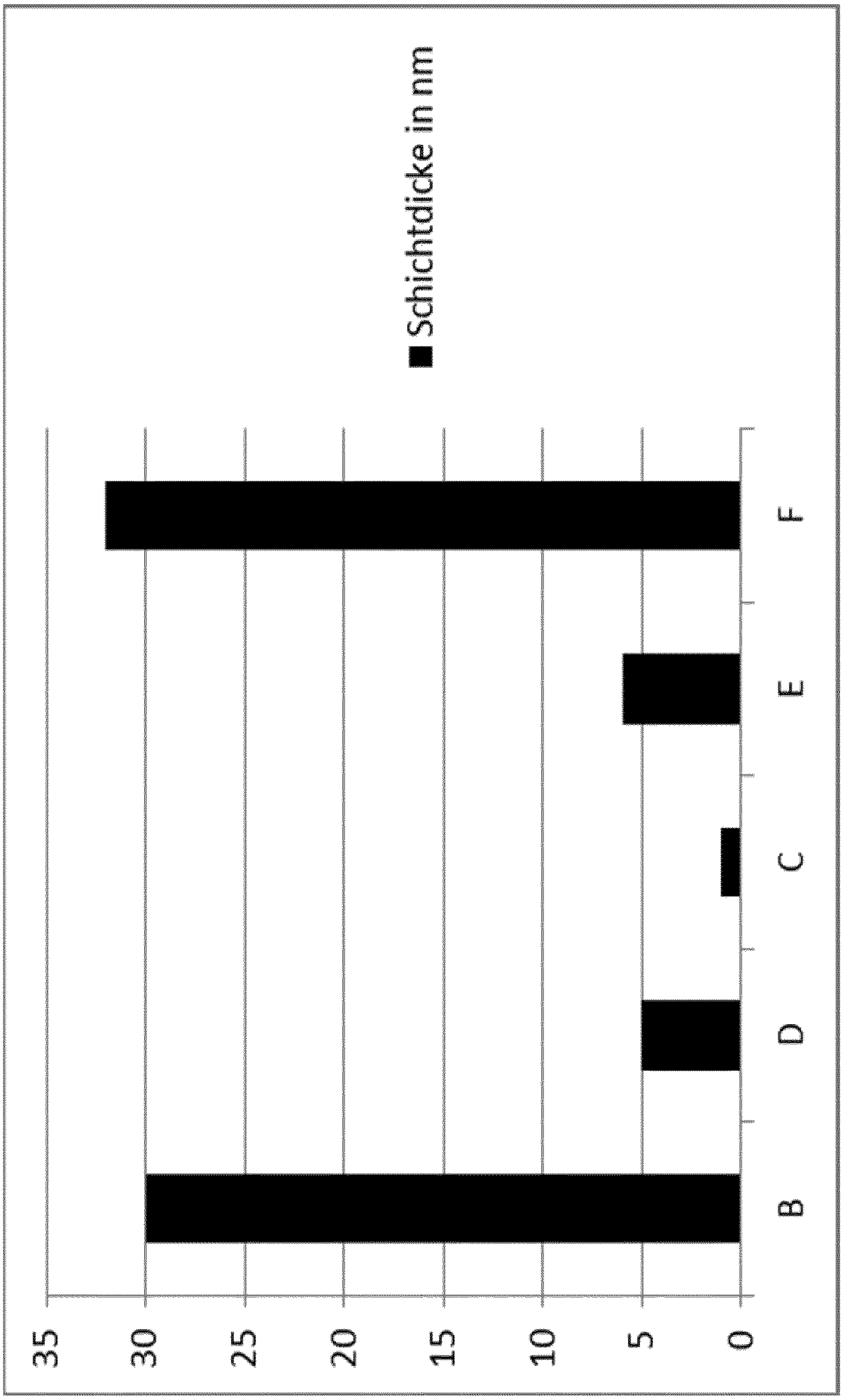
12. A method comprising:

(i) providing a used gold or gold alloy electroplating composition;
(ii) adding a mercapto-triazole to the used gold or gold alloy electroplating composition, and
(iii) contacting a substrate with the composition; and
(iv) applying an electrical current between the substrate and at least

one anode and thereby depositing a gold or gold alloy onto the substrate.

13. Use of mercapto-triazole, wherein the mercapto-triazole is as defined in claims 1 to 4, as anti-immersion additive in electrodeposition baths.

Figure 1



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EUROPEAN SEARCH REPORT

Application Number
EP 14 18 2083

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2004/069641 A1 (ABE MIWA [JP] ET AL) 15 April 2004 (2004-04-15) * abstract * * paragraph [0011] - paragraph [0012] * * example 4 * * claim 1 * -----	1-11	INV. C25D3/48 C25D21/18 C25D3/62
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A	CN 102 105 623 A (JAPAN PURE CHEMICAL CO LTD) 22 June 2011 (2011-06-22) * abstract * -----	1-11	TECHNICAL FIELDS SEARCHED (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
The Hague	29 April 2015	Picard, Sybille

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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Application Number
EP 14 18 2083

CLAIMS INCURRING FEES

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

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

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

LACK OF UNITY OF INVENTION

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

see sheet B

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

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

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

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

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

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LACK OF UNITY OF INVENTION SHEET B

Application Number
EP 14 18 2083

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

1. claims: 1-11

An electroplating composition comprising (i) at least one source of gold ions, and (ii) at least one mercapto-triazole or a salt thereof and method using such electroplating composition

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2. claims: 12, 13

2a: A method comprising:(i) providing a used gold or gold alloy electroplating composition; (ii) adding a mercapto-triazole to the used gold or gold alloy electroplating composition, and (iii) contacting a substrate with the composition; and (iv) applying an electrical current between the substrate and at least one anode and thereby depositing a gold or gold alloy onto the substrate
2b: Use of mercapto-triazole, wherein the mercapto-triazole is as defined in claims 1 to 4, as anti-immersion additive in electrodeposition baths.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 14 18 2083

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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