
**COMPOSITION, USE THEREOF AND METHOD FOR
ELECTRODEPOSITING GOLD CONTAINING LAYERS**

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Field of the Invention

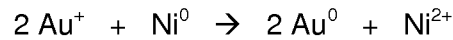
The present invention relates to a composition and method for electrodepositing gold containing layers using the inventive composition. The inventive composition contains a mercapto-triazole compound which acts as an anti-immersion additive.

10 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

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.

25 As gold is a noble metal which is to be plated onto connectors that are usually made of less noble metal, the problem of gold displacement arises. 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:



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.

- 5 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
10 without being electrically connected.

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.
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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.
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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.

- 25 Moreover, the problem of gold immersion increases with the age of the gold electrolyte.

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.

European patent EP 2 309 036 B1 discloses a hard gold plating bath which decreases the gold displacement reaction. The effect is due to mercapto-tetrazole 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.

Accordingly, there is still a need for inhibiting the gold immersion reaction in electro-deposition baths for functional pure gold and gold alloy layers.

Objective of the present Invention

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.

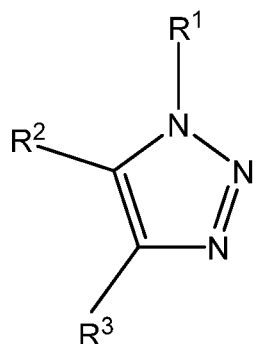
It is a further objective of the present invention to provide a method for reducing the increasing gold immersion reaction during the lifetime of the composition for gold electrodeposition.

Summary of the Invention

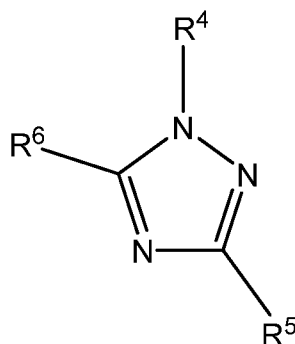
These objectives are achieved by the following compositions and methods.

An electroplating composition comprising

- (i) at least one source of gold ions, and
- (ii) at least one mercapto-triazole or a salt thereof, wherein the at least one mercapto-triazole has the following general formulae (I) or (II):



Formula (I)



Formula (II)

wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are as defined below.

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

A method comprising the steps:

- 5 (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.

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

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
- 15 (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.

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.

5 Brief Description of the Figures

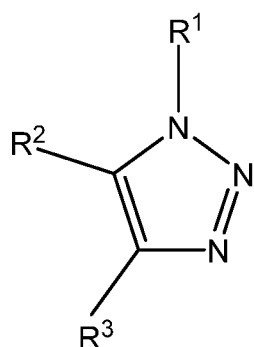
Figure 1 shows the thickness of gold alloy layers deposited from electroplating baths containing different mercapto azole compounds by immersion reaction.

Figure 2 shows the thickness of gold alloy layers deposited from electroplating baths containing different mercapto triazole compounds by immersion reaction.

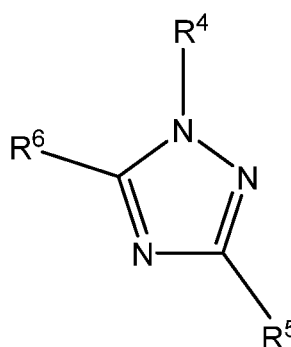
10 Detailed Description of the Invention

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, wherein the at least one mercapto-triazole has the following general formulae (I) or (II):



Formula (I)



Formula (II)

- 15 wherein R¹, R⁴ are independently of each other hydrogen, linear or branched, saturated or unsaturated (C₁-C₂₀) hydrocarbon chain, (C₈-C₂₀) aralkyl group; substituted or unsubstituted phenyl group, naphthyl group or carboxyl group; and R², R³, R⁵, R⁶ 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 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
- 5 at least one of R^2 and R^3 is $-S-X$, and at least one of R^5 and R^6 is $-S-X$.

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

10 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.

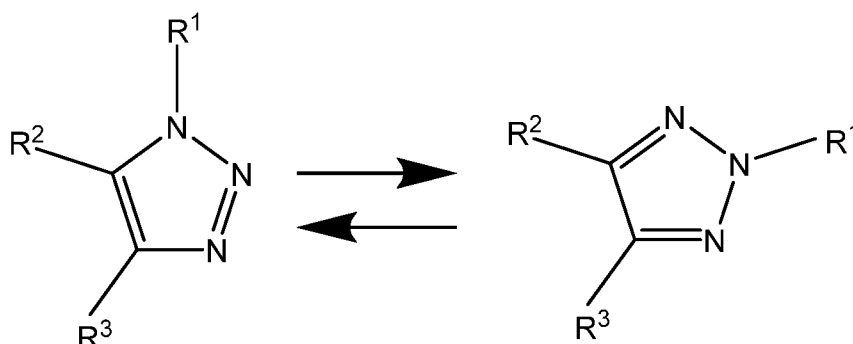
The mercapto-triazole or its salts according to (ii) significantly decrease or nearly inhibit the gold immersion reaction when electrodepositing gold containing layers.

- 15 In one embodiment, X is preferably a counter-ion selected from alkali metal ions, wherein the alkali metal ions are selected from sodium ion, potassium ion and lithium ion.

In another embodiment the substituent groups of the substituted phenyl or naphthyl group of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 are selected independently from branched or un-

20 branched (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.

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



Formula (I) therefore comprises both tautomeric forms. Tautomeric forms are relevant in particular when R^1 is an H atom.

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 (C₁ - C₄) alkyl group, and
 5 R^2 , R^3 , R^5 , R^6 are independently of each other -S-X, hydrogen or a linear (C₁ - C₄) alkyl group; and
 X is hydrogen, a methyl group, an ethyl group, or a counter-ion selected from sodium ion and potassium ion; and
 10 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.

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
 15 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.

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
 20 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.

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.

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; 3-mercapto-4-methyl-1,2,4-triazol; 5-phenyl-1H-1,2,4-triazol-3-thiol and salts thereof.

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.

In an even more preferred embodiment the at least one mercapto-triazole is selected from 5-mercapto-1,2,3-triazole; 3-mercapto-4-methyl-1,2,4-triazol; 5-phenyl-1H-1,2,4-triazol-3-thiol; 3-mercapto-1,2,4-triazol and salts thereof.

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.

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, even more preferably from 20 mg/l to 100 mg/l. If the concentration of the at least one mercapto-triazole is too high, the electrodeposition of gold containing layers is either prevented completely or the electrodeposited gold or gold alloy layer does not adhere sufficiently to the surface of the substrate.

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. Further, the advantageous functional property of high wear resistance of the gold or hard gold layers, particularly of hard gold layers, is also not compromised by adding one or more mercapto-triazoles according to the present invention to a gold or gold alloy electroplating composition.

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). Potassium gold cyanides have a better solubility than other gold compounds.

In one embodiment, in which the gold alloy layer deposited from the electroplating composition of the present invention is a hard gold layer, the source of gold ions is preferably a gold cyanide compound, more preferably an alkali gold cyanide such as potassium gold cyanide or sodium gold cyanide; or an ammonium gold cyanide. Electrodeposition of functional or hard gold alloy layers having high gold content is best possible if the source of gold ions is a gold cyanide compound. In this case

gold ions are contained in the electroplating composition in the form of gold-cyanide complexes, preferably as alkali ion-gold-cyanide complexes, more preferably as potassium ion-gold-cyanide complexes, which are particularly suited for electrodepositing hard gold alloy layers having high gold content. The same applies for electrodeposition of gold containing layers from electrolytes which are used with high current densities because gold compounds other than gold-cyanide complexes, alkali ion-gold-cyanide complexes or potassium ion-gold-cyanide complexes are less stable at high current densities.

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 50 g/l, more preferably ranging from 10 g/l to 50 g/l, even more preferably ranging from 5 g/l to 30 g/l, yet even more preferably ranging from 5 g/l to 20 g/l, yet even more preferably ranging from 10 g/l to 20 g/l. The tendency of the electroplating composition to deposit gold by immersion reaction increases with the gold concentration contained in the composition.

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 thereof such as sodium thiosulfate, potassium thiosulfate, and ammonium thiosulfate; sulfurous acid and salts thereof 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-diaminocyclohexane 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.

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
5 no alkali metal cyanide.

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.

In one embodiment the electroplating composition may further comprise at least one
10 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.

Hard gold alloy deposits have a gold content ranging from 99.00 mass % to less than 99.90 mass %. The content of the alloying metals cobalt, nickel and/or iron may
15 range from less than 0.03 mass % to greater than 0.3 mass % for hard gold alloys (ASTM B488-11, Section 7). The alloying metals impart highest hardness and highest wear resistance to the gold alloy which is required for industrial applications like contact material of electrical connectors for high reliability applications (ASTM B488-11, Appendix X1). Simultaneously, the hard gold alloys maintain high electrical con-
20 ductivity which is additionally important for their application within electrical connectors. In contrast, gold deposits having a gold content equal to or greater than 99.90 mass % have lower hardness (ASTM B488-11, Sections 4 and 7), lower wear resistance and are therefore not suited for applications in electrical connectors.

Alloying metal ions are selected from cobalt(II) ions, nickel(II) ions, iron(II) ions and
25 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.

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.

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 thereof 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.

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.

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 dicar-

boxylic 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.

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.

The brightening agents advantageously cause deposition of bright gold layers over a wide current density range of between 2 A/dm² to 100 A/dm².

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.

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

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
5 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.

In one embodiment the electroplating composition is an acidic electroplating composition. The electroplating composition may have a pH value below 7, more preferably below 5, even more preferably between 1 to 6, yet even more preferably between 3 to 6, yet even more preferably between 3.5 to 5.5, yet even more preferably between 3.5 to 4.5.
10

In one embodiment, in which the gold alloy layer deposited from the electroplating composition of the present invention is a hard gold layer, the electroplating composition is preferably an acidic electroplating composition. Electrodeposition of functional or hard gold alloy layers having a high gold content is best possible if the electrodeposition composition is acidic.
15

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

20 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.

25 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 increases the lifetime of the gold or gold alloy electroplating composition. The gold containing layers may be pure gold layers or gold alloy layers, preferably gold alloy layers, more preferably hard gold layers.

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
5 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.

Selective plating may be performed by known methods, like a masking method, a
10 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
15 metal plating solution.

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
20 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.

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 1 A/dm^2 to 40 A/dm^2 ,
25 even more preferably from 5 A/dm^2 to 40 A/dm^2 , yet even more preferably from 5 A/dm^2 to 20 A/dm^2 . Applying higher current densities during electrodeposition gold containing layers advantageously increases the deposition rate and thus the productivity of the electrodeposition method.

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 .

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

During plating the electroplating composition of the present invention may be un-moved or may be agitated. Agitation may be performed for example by mechanical movement of the aqueous plating bath like shaking, stirring or continuously pumping
10 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.

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
15 the substrate surface using typically acids or fluoride containing acids.

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
20 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.

25 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 al-

loy, copper, palladium, silver, cobalt and alloys thereof. Preferably the substrate is made from iron or copper and covered with a nickel layer.

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.

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.

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 60°C. The deposition rate increases with the lifetime of the electroplating bath. When the deposition rate arrives at 80 to 100 nm/5min metal at 60°C the gold or gold alloy electroplating bath usually needs to be replaced. Even when the deposition rate arrives at 20 to 40 nm/5min metal at 60°C the gold or gold alloy electroplating bath may be no more suited for industrial plating applications because then immersion reactions already cause high losses of gold. 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 regen-

erates an aged gold or gold alloy electroplating composition and significantly increases the lifetime of a gold or gold alloy electroplating composition.

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

- (i) providing an aged gold or gold alloy electroplating composition;
- 5 (ii) adding a mercapto-triazole as defined above to the aged 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 sub-
10 strate.

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 sam-
15 ple layer thicknesses can be calculated.

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 electro-
20 deposited 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
25 reaction when the composition is in operation again.

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

- (i) providing a gold or gold alloy electroplating composition that was temporarily out of operation;
- (ii) adding a mercapto-triazole as defined above to the gold or gold alloy

- electroplating composition that was temporarily out of operation, 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.

5

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

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.

10

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.

15

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.

20

Examples

Example 1

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

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
10 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/dm², a temperature of 60°, with agitation, for a time of 150 seconds.

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.

15

Example 2

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.

20 Copper panel B was contacted with an aged gold-cobalt alloy plating bath (Aurocor HSC, 15 g/l gold, pH 4.5, product of Atotech Deutschland GmbH) containing no mercapto triazole compound.

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
25 Deutschland GmbH) containing 500 mg/l each of a mercapto triazole compound or a mercapto tetraazole compound as outlined in Table 1.

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
 5 were held at a temperature of 60 °C and constantly agitated with 400 rpm (rounds per minute). Contacting each panel was performed for 5 minutes.

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.

10 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

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
 15 to 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 were deposited by immersion reaction. Moreover, comparative compound D caused unwanted precipitates 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 breakdown 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

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

An aged gold-cobalt alloy electroplating bath (Aurocor HSC, product of Atotech Deutschland GmbH) was first treated with active carbon for 30 min at 60 °C.

In step 1, the gold plating bath was held at 60 °C 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.

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.

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 increase the lifetime of a gold or gold alloy electroplating composition.

Example 4

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.

- 5 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.

- 10 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.

- 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.
- 15

Example 5

- Copper panels electroplated with nickel were used as substrates. The copper panels were electroplated with nickel and pre-treated as summarized in table 2 below. The copper panels were rinsed with water after each process step listed in table 2. Half of the area of the substrates was covered with tesa tapes in order to mask the area that is not to be plated.
- 20

- Copper panel G was contacted with an aged gold-cobalt alloy plating bath (Aurocor SC, 4 g/l gold, pH 4.5, product of Atotech Deutschland GmbH) containing no mercapto triazole compound.
- 25

Copper panels H to M were contacted with separate portions of the aged gold-cobalt alloy plating bath (Aurocor SC, 4 g/l gold, pH 4.5, product of Atotech Deutschland GmbH) containing 50 mg/l each of a mercapto triazole compound as outlined in Table 3.

- 5 While being in contact with the gold-cobalt alloy plating baths the nickel coated and pre-treated copper panels G to M 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 triazole compound were used for each panel. The gold-cobalt alloy plating baths were held at a temperature of 60 °C and constantly agitated with 400 rpm (rounds per minute). Contacting each panel was performed for 5 minutes.

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 3 and shown in Figure 2.

15 Table 2: Process steps of nickel electroplating and pre-treating of copper panels

Process step	Product *	Temperature / °C	current or potential	Agitation	Time
Cathodic Degreasing	Uniclean 260	45	7 V	MA	60 seconds
Activation	Uniclean 675	RT	---	MA	60 seconds
Nickel plating	Ni-Sulphamat HS	50	4 A/dm ²	MA	5 minutes
Oxydative Activation	Uniclean 675	RT	---	---	15 seconds

*Products of Atotech Deutschland GmbH; RT = room temperature (about 20 °C); MA = Mechanical Agitation; “---” = condition was not applied.

Table 3: Thickness of gold alloy layers deposited from electroplating baths containing different mercapto triazole compounds by immersion reaction

Panel	mercapto triazole	deposition thickness / nm/5min
G	None (comparative)	23
H	5-Mercapto-1,2,3-triazole (Na-salt) (according to invention)	16
I	3-Mercapto-4-methyl-1,2,4-triazol (according to invention)	11
K	5-Phenyl-1H-1,2,4-triazol-3-thiol (according to invention)	10
L	Mercapto-1,2,4-triazol (according to invention)	7
M	3-Amino-5-(methylmercapto)-1H-1,2,4- triazol (comparative)	23

The thickness of the gold-cobalt layer deposited from a plating bath containing no mercapto triazole compound (panel G) was lower than in Example 2 (panel B) because the gold concentration of the plating bath in Example 5 was significantly lower than in Example 2. The thickness of the gold-cobalt layer deposited from a plating bath containing 5-mercapto-1,2,3-triazole (panel H) was higher than in Example 2 (panel C) because the concentration of 5-mercapto-1,2,3-triazole within the plating bath in Example 5 was significantly lower than in Example 2.

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 minor thickness was deposited by immersion reaction. In contrast, from the gold alloy baths containing no mercapto triazole compound or a comparative amino modified mercapto triazole compound gold alloy layers of significant higher layer thickness were deposited by immersion reaction. Thus, the mercapto triazole compounds of the present invention significantly decrease the gold immersion reaction.

Example 6

Influence of mercapto-triazole compounds on deposition rate, hardness and adhesion of the deposited gold layer

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

At first, immersion reaction was measured of an aged gold-cobalt alloy plating bath (Aurocor HSC, 15 g/l gold, pH 4.5, product of Atotech Deutschland GmbH) as described in Example 5.

- 10 Copper panel N was plated by immersion reaction from a portion of the plating bath containing no mercapto triazole compound. Copper panel P was plated by immersion reaction from a portion of the plating bath containing 25 mg/l of the sodium salt of 5-mercapto-1,2,3-triazole. The gold-cobalt alloy layers deposited by immersion reaction on panel N had a thickness of 82 ± 6 nm and on panel P a thickness of $10 \pm$
15 4 nm.

Afterwards the same aged gold-cobalt alloy plating bath was used for electrodepositing gold-cobalt alloy layers on panels unless otherwise stated in the subsequent paragraphs. The deposition rate, hardness and adhesion of the deposited alloy layers were measured. Electrodeposition was performed as described in Example 1.

20

Deposition rate:

- Copper panels Q1 to Q4 were plated from separate portions of the aged plating bath containing no mercapto triazole compound. Copper panels R1 to R4 were plated from separate portions of the aged plating bath containing 25 mg/l of the sodium salt
25 of 5-mercapto-1,2,3-triazole. Current density was varied from 5 to 20 A/dm² as outlined in table 4. Thicknesses of the electrodeposited gold-cobalt alloy layers were measured by XRF. Results are summarized in table 4.

Table 4: Deposition rates in presence and absence of a mercapto-triazole at varying current densities

current density / A/dm ²	Panel	deposition rate / μm/min	Panel	deposition rate / μm/min
5	Q1	0.7 ± 0.1	R1	0.7 ± 0.1
10	Q2	1.5 ± 0.1	R2	1.3 ± 0.1
15	Q3	1.6 ± 0.1	R3	1.5 ± 0.1
20	Q4	1.6 ± 0.1	R4	1.6 ± 0.1

The deposition rate of gold-cobalt alloy from the aged plating bath in absence or presence of a mercapto-triazole was nearly the same. Thus, the presence of a mercapto-triazole according to the present invention within a gold electrodeposition bath did not influence the deposition rate.

Hardness:

Copper panel S was plated from a portion of the aged plating bath containing no mercapto triazole compound. Copper panel T was plated from a portion of the aged plating bath containing 25 mg/l of the sodium salt of 5-mercapto-1,2,3-triazole. Electroplating was performed at a current density of 15 A/dm² for 150 seconds to obtain gold-cobalt alloy layers of about 5 μm thickness. Hardness of the gold-cobalt alloy layers was determined by the Vickers hardness test using an XRF-SDD (X-ray Fluorescence - Silicon Drift Detector) instrument, model Fischerscope X-RAY XDRL from Fischer Technology, Inc. The gold-cobalt alloy layers electrodeposited on panel S had a hardness of 180 ± 10 HV 0.001 and on panel T a hardness of 178 ± 10 HV 0.001.

The hardness of gold-cobalt alloy layers deposited from the aged plating bath in absence or presence of a mercapto-triazole was nearly the same. Thus, the presence of a mercapto-triazole according to the present invention within a gold electrodeposition bath did not influence the hardness of the deposited gold containing layers.

Adhesion:

A newly made up gold-cobalt alloy plating bath (Aurocor HSC, 15 g/l gold, pH 4.5, product of Atotech Deutschland GmbH) was used for determining adhesion. A negative influence on adhesion of electrodeposited gold containing layers is best detectable when deposition is carried out using freshly made up gold or gold alloy plating baths because these plating baths have only low immersion reaction and the deposits usually have good adhesion.

Copper panels U1 to U2 were plated from separate portions of the newly made up plating bath containing no mercapto triazole compound. Copper panels V1 to V2 were plated from separate portions of the newly made up plating bath containing 50 mg/l of the sodium salt of 5-mercapto-1,2,3-triazole.

Copper panels U1 and V1 were firstly contacted with the respective plating baths for 5 minutes without being electrically connected. Thus, for panel V1 the mercapto-triazole was allowed to adhere to the nickel surface of the panel. Afterwards, copper panels U1 and V1 were electroplated from the respective plating baths at 5 A/dm² for 72 seconds, thereby electrodepositing gold-cobalt alloy layers onto the panels. The adhesion of the gold-cobalt alloy layers to the panel surface was determined by a bending test and by a tape test. The bending test was performed as follows: Part of a panel to be tested was bent once into an angle of 90°. When no bubbles were formed within the deposited gold layer or no flakes of the deposited gold layer were released from the bent region, adhesion was considered to be good. For the tape test, tesa tapes 4102 with adhesion strength of about 6 N/cm were adhered to the gold-cobalt plated panels and afterwards removed from the panel surface. If the tape did not remove a part or all of the gold-cobalt layer, adhesion was at least as good as 6 N/cm which was considered to be a good adhesion. In contrast, if the tape removes a part or the whole gold-cobalt layer, adhesion was insufficient.

The bending test as well as the tape test revealed that adhesion of the gold-cobalt alloy layer to the nickel surfaces of panels U1 and V1 was nearly identical and good.

Copper panels U2 and V2 were firstly contacted with the respective plating baths and thin gold-cobalt layers of thickness between 0.1 to 0.2 μm (first gold-cobalt layers) were electrodeposited. Afterwards, the plated copper panels were contacted with the respective plating baths for 10 seconds without being electrically connected.

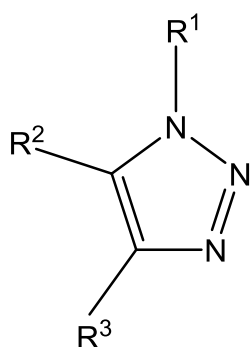
5 Thus, for panel V2 the mercapto-triazole was allowed to adhere to the surface of the gold-cobalt layer deposited. Then, copper panels U2 and V2 were electroplated from the respective plating baths at 5 A/dm^2 for 72 seconds, thereby electrodepositing a second gold-cobalt alloy layer onto the panels. The adhesion of the second gold-cobalt alloy layers to the surface of the first gold-cobalt layers was determined by
10 the bending test and by the tape test as described above.

The bending test as well as the tape test revealed that adhesion of the second gold-cobalt alloy layers to the surface of the first gold-cobalt layers of panels U2 and V2 was nearly identical and good.

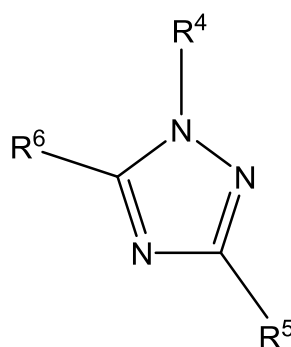
The adhesion of gold-cobalt alloy layers deposited from newly made up plating bath
15 in absence or presence of a mercapto-triazole was nearly identical. Thus, the presence of a mercapto-triazole according to the present invention within a gold electro-deposition bath did not influence the adhesion of the deposited gold containing layers.

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, 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 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 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 $-S-X$.

2. The composition according to claim 1, 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

5 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 claims 1 or 2, wherein the at least one mercapto-triazole has a concentration ranging from 1 mg/l to 1 g/l.
4. 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.
- 10 5. The composition according to any of the foregoing claims, further comprising complexing agents for gold ions.
6. The composition according to any of the foregoing claims, further comprising at least one brightening agent selected from pyridine and quinoline compounds.
- 15 7. The composition according to any of the foregoing claims, having a pH value between 1 – 6.
8. A method comprising:
 - (i) providing an electroplating composition according to claims 1 to 7;
 - 20 (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.
9. The method according to claim 8, wherein the substrate is iron, nickel, copper or an alloy thereof.
- 25 10. The method according to claims 8 or 9, wherein the substrate is an electrical connector.

11. 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 for regenerating, wherein the mercapto-triazole is as
5 defined in claims 1 to 2, 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.
- 10 12. Use of a mercapto-triazole, wherein the mercapto-triazole is as defined in claims 1 to 2, as anti-immersion additive in electrodeposition compositions for gold containing layers.