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**(54) PLATING BATH COMPOSITION FOR ELECTROLESS PLATING OF GOLD**

GALVANISIERUNGSBADZUSAMMENSETZUNG ZUR STROMLOSEN GALVANISIERUNG VON GOLD

COMPOSITION DE BAIN DE PLACAGE POUR UN DÉPÔT AUTOCATALYTIQUE D'OR

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**US-A1- 2008 138 507**

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**Description****Field of the Invention**

5 [0001] The present invention relates to electroless aqueous gold plating bath compositions for electroless plating of gold layers onto a substrate. The plating bath is particularly suitable in the manufacture of printed circuit boards, IC substrates, semiconducting devices, interposers made of glass and the like.

**Background of the Invention**

10 [0002] Gold layers are of paramount interest in the manufacturing of electronic components and in the semiconductor industry. Gold layers are frequently used as solderable and/or wire bondable surfaces in the manufacture of printed circuit boards, IC substrates, semiconducting devices and the like. Typically, they are used as a final finish before soldering and wire bonding. In order to provide electrical connections of sufficient conductivity and robustness between the copper lines and wires that are bonded thereto while providing a good strength for wire bonding, there are various layer assemblies which are used conventionally in the art. Among others, there are electroless nickel electroless gold (ENIG), electroless nickel electroless palladium immersion gold (ENEPIG), direct immersion gold (DIG), electroless palladium immersion gold (EPIG) and electroless palladium autocatalytic gold (EPAG). Even though these techniques have been established some time ago, there are still many challenges unresolved. Such challenges are the corrosion of nickel layers which are placed between gold and copper lines (nickel corrosion) and insufficient stabilities of gold plating baths which is highly undesirable due to the cost of said baths. Also, it is highly desirable to deposit gold layers with sufficient plating rates to run manufacturing processes economically. Another desired property of the gold layer is the optical appearance that should be lemon yellow as a discolouration of the gold layer is not acceptable.

20 [0003] Due to the minuscule sizes of electrical components nowadays, it is not possible to use electrolytic processes which require electrical connections to the substrates. Therefore, electroless metal deposition processes (electroless plating) are used. Electroless plating generally describes methods without using external current sources for reduction of metal ions. Plating processes using external current sources are commonly described as electrolytic or galvanic plating methods. Non-metallic surfaces may be pretreated to make them receptive or catalytic for metal deposition. All or selected portions of a surface may suitably be pretreated. The main components of electroless metal baths are the metal salt, a reducing agent, and, as optional ingredients, a complexing agent, a pH adjuster, and additives, as for example stabilising agents. Complexing agents (also called chelating agents in the art) are used to chelate the metal being deposited and prevent the metal from being precipitated from solution (i.e. as the hydroxide and the like). Chelating metal renders the metal available to the reducing agent that converts the metal ions to metallic form.

25 [0004] A further form of metal deposition is immersion plating. Immersion plating is another deposition of metal using neither external current sources nor chemical reducing agents. The mechanism relies on the substitution of metals from an underlying substrate for metal ions present in the immersion plating solution. This is a distinct disadvantage of immersion plating because deposition of thicker layers is normally limited by the layer porosity.

30 [0005] In most cases, electroless gold plating baths use one or both types of electroless plating. Even if reducing agents have been added to the plating bath, immersion-type plating may occur albeit in a significantly reduced proportion.

35 [0006] In the context of the present invention electroless plating is to be understood (mainly) as autocatalytic deposition with the aid of a chemical reducing agent (referred to as "reducing agent" herein).

40 [0007] US 2012/0129005 A1 discloses an electroless gold plating bath comprising a water-soluble gold compound and an alkylene diamine, dialkylene triamines or the like. However, such gold plating solution lack sufficient stability and plating rate and are thus not applicable in industrial processes (see example 4).

45 [0008] US 2008/0138507 A1 reports electroless gold plating baths which use aldehyde compounds as reducing agents and N-substituted ethylene diamine derivatives such as *N*<sup>1</sup>,*N*<sup>2</sup>-dimethylethylenediamine and *N*<sup>1</sup>,*N*<sup>2</sup>-bis-(methylol)ethylenediamine. But again, the plating baths described therein lack plating rate and stability (see example 4). It is typically sufficient that gold plating bath have plating rates of 150 nm/h or more, preferably of 200 nm/h or more or ideally, of 250 nm/h or more to comply with today's industrial requirements.

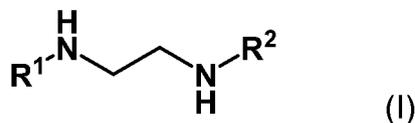
**Objective of the Invention**

50 [0009] It is the objective of the present invention to provide an aqueous electroless gold plating bath composition from which gold layers can be deposited with sufficient plating rate. It is another objective of the present invention to provide an electroless aqueous gold plating bath which has sufficient stability and which can be used for prolonged duration of time.

55 [0010] It is yet another objective that the gold layers which are formed show no discolouration.

Summary of the Invention

[0011] These objectives are solved by the electroless aqueous gold plating bath according to the invention, which comprises at least one source of gold ions and at least one reducing agent for gold ions, and is characterized in that it comprises at least one ethylenediamine derivative according to formula (I)



wherein the residues R<sup>1</sup> and R<sup>2</sup> comprise 2 to 12 carbon atoms and are selected from the group consisting of branched alkyl, unbranched alkyl, cycloalkyl or combinations thereof wherein the individual residues R<sup>1</sup> and R<sup>2</sup> are the same or different as plating enhancer compound.

[0012] These objectives can further be solved by using the method according to claim 13.

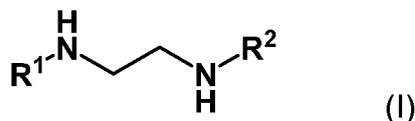
Description of Figures

[0013] Figure 1 shows a test substrate having a multitude of copper pads to be plated upon. Also depicted are the 10 different spots where the layer thickness is measured (circles labelled 1 to 10).

Detailed Description of the Invention

[0014] The ethylenediamine derivative according to formula (I) will be referred to herein as plating enhancer compound.

[0015] The plating enhancer compound according to formula (I)



bears the residues R<sup>1</sup> and R<sup>2</sup> which comprise 2 to 12 carbon atoms and are selected from the group consisting of branched alkyl, unbranched alkyl, cycloalkyl or combinations thereof wherein the individual residues R<sup>1</sup> and R<sup>2</sup> are the same or different.

[0016] The amine moieties in the plating enhancer compound of formula (I) are secondary amine moieties. It was found by the inventors that the respective diamine or a derivative thereof with methyl residues for R<sup>1</sup> and R<sup>2</sup> do neither allow for sufficient plating rates nor for sufficiently stable gold plating baths (see example 4).

[0017] In a preferred embodiment of the present invention the residues R<sup>1</sup> and R<sup>2</sup> of the plating enhancer compound of formula (I) comprise 2 to 8 carbon atoms, more preferred 2 to 6 carbon atoms, even more preferred 2 to 4 carbon atoms.

[0018] In another preferred embodiment of the present invention the residues R<sup>1</sup> and R<sup>2</sup> in formula (I) are the same. In yet another preferred embodiment of the present invention the alkyl residues R<sup>1</sup> and R<sup>2</sup> in formula (I) are free of terminal hydroxy moieties (-OH) as the inventors have found that terminal hydroxy moieties bound thereto are detrimental to stability of the plating bath (see example 4). In even another preferred embodiment of the present invention the residues R<sup>1</sup> and R<sup>2</sup> in formula (I) are free of terminal primary amino moieties as the inventors have found that said terminal amino moieties bound thereto are also detrimental to stability of the plating bath (see example 4). In another more preferred embodiment of the present invention, residues R<sup>1</sup> and R<sup>2</sup> are free of any further amino moieties and/or any hydroxy moieties. It is even more preferable that the alkyl residues are free of substituents and consist of carbon and hydrogen atoms only.

[0019] It is particularly preferred to select the plating enhancer compound from the following group consisting of N<sup>1</sup>,N<sup>2</sup>-diethylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-dipropylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-iso-propylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-dibutylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-iso-butylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-tert-butylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-dipentylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-iso-pentylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-sec-pentylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-tert-pentylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-neo-pentylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-dihexylethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-(1-methylpentyl)ethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-(2-methylpentyl)ethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-(3-methylpentyl)ethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-(4-methylpentyl)ethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-(1,1-dimethylbutyl)ethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-(1,2-dimethylbutyl)ethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-(1,3-dimethylbutyl)ethane-1,2-diamine, N<sup>1</sup>,N<sup>2</sup>-di-(2,2-

dimethylbutyl)ethane-1,2-diamine,  $N^1,N^2$ -di-(2,3-dimethylbutyl)ethane-1,2-diamine and  $N^1,N^2$ -di-(3,3-dimethylbutyl)ethane-1,2-diamine.

**[0020]** It is most preferred that  $R^1$  and  $R^2$  are branched alkyl residues having 3 to 6 carbon atoms. It was surprisingly found that high plating rate in conjunction with even more improved bath stability are obtained when using branched alkyl residues having 3 to 6 carbon atoms for  $R^1$  and  $R^2$  (see example 5).

**[0021]** The concentration of the at least one plating enhancer compound according to formula (I) in the electroless aqueous gold plating bath according to the invention preferably ranges from 0.001 - 1 mol/L, more preferably from 10 to 100 mmol/L, even more preferably from 25 to 75 mmol/L. If more than one plating enhancer compound is contained in the electroless aqueous gold plating bath according to the invention the concentration is based on the total amount of substance of all plating enhancer compounds.

**[0022]** The electroless aqueous gold plating bath according to the invention is an aqueous solution. The term "aqueous solution" means that the prevailing liquid medium, which is the solvent in the solution, is water. Further liquids, that are miscible with water, as for example alcohols and other polar organic liquids, that are miscible with water, may be added.

**[0023]** The electroless plating bath according to the invention may be prepared by dissolving all components in aqueous liquid medium, preferably in water.

**[0024]** The electroless aqueous gold plating bath according to the invention comprises at least one source of gold ions. Gold ions can be in either  $Au^+$ ,  $Au^{3+}$  or both oxidation states. The source of gold ions can be any water soluble gold salt having said oxidation states. Preferably, the source of gold ions is selected from the group consisting of gold cyanide, gold ammonium cyanide, gold (I) alkali cyanides including gold (I) potassium cyanide, gold (I) sodium cyanide, trisodium gold disulphite, tripotassium gold disulphite and triammonium gold disulphite, gold thiosulphate, gold thiocyanide, gold sulphate, gold chloride, and gold bromide. Preferably, the source of gold ions is a gold (I) alkali cyanide and may be added to the aqueous plating bath in the form of a solution containing this salt. The concentration of gold ions in the electroless aqueous gold plating bath according to the invention preferably ranges from 0.1 to 10 g/L, more preferably from 0.3 to 6 g/L.

**[0025]** The electroless aqueous gold plating bath further comprises at least one reducing agent for gold ions. The reducing agents for gold ions is preferably selected from the group consisting of aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, n-butylaldehyde,  $\alpha$ -methylvaleraldehyde,  $\beta$ -methylvaleraldehyde,  $\gamma$ -methylvaleraldehyde or the like; aliphatic dialdehydes such as glyoxal, succindialdehyde or the like; aliphatic unsaturated aldehydes such as croton aldehyde or the like; aromatic aldehydes such as benzaldehyde, o-nitrobenzaldehyde, m-nitrobenzaldehyde, p-nitrobenzaldehyde, o-tolaldehyde, m-tolaldehyde, p-tolaldehyde, o-hydroxybenzaldehyde, m-hydroxybenzaldehyde, p-hydroxybenzaldehyde, phenylacetaldehyde or the like; sugars having an aldehyde group (-CHO) such as glucose, galactose, mannose, ribose, maltose, lactose or the like; and precursors of formaldehyde such as urotropin, 1,3-bis(hydroxymethyl)-5,5-dimethylimidazolidine-2,4-dione (DMDM-hydantoin), paraformaldehyde, glyoxylic acid, sources of glyoxylic acid and glycolic acid. The term "source of glyoxylic acid" encompasses glyoxylic acid and all compounds that can be converted to glyoxylic acid in aqueous solution. In aqueous solution, the aldehyde containing acid is in equilibrium with its hydrate. A suitable source of glyoxylic acid is dihaloacetic acid, such as dichloroacetic acid, which will hydrolyse in an aqueous medium to the hydrate of glyoxylic acid. An alternative source of glyoxylic acid is the bisulphite adduct as is a hydrolysable ester or other acid derivative. The bisulphite adduct may be added to the electroless aqueous gold plating bath according to the invention or formed in situ. The bisulphite adduct may be made from glyoxylate and either bisulphite, sulphite or metabisulphite. Formaldehyde, sources of glyoxylic acid and glyoxylic acid are preferred, most preferred is formaldehyde.

**[0026]** The concentration of the at least one reducing agent for gold ions preferably ranges 0.0001 to 0.5 mol/L, more preferably 0.001 to 0.3 mol/L, even more preferably 0.005 to 0.12 mol/L.

**[0027]** Without being bound by theory, the inventors found with great inventive skill that reaction products of certain ethyleneamine derivatives such as triethylenetetraamine and reducing agents for gold ions such as formaldehyde (or its oxidised product formic acid) can be formed causing precipitation and reduced plating rates as a consequence. Typical reaction products are for example the respective aminal, enamine and amide derivatives. Therefore, it is preferable to limit the extent of reaction product formation by choosing a molar ratio of plating enhancer compound according to formula (I) to reducing agent for gold ions in the electroless aqueous gold plating bath according to the invention to range from 0.5 to 9, preferably from 0.8 to 3.0, more preferably from 1.0 to 2.0 (see Example 6). If more than one plating enhancer compound according to formula (I) and/or more than one reducing agent for gold ions are used in the electroless aqueous gold plating bath according to the invention this ratio is calculated based on the total mass of substance of all respective individual compounds.

**[0028]** The electroless aqueous gold plating bath according to the invention optionally further comprises at least one complexing agent. The optional at least one complexing agent present in the electroless aqueous gold plating bath according to the invention is preferably selected from the group consisting of carboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids, aminophosphonic acids or a salt of the aforementioned. The optional at least one complexing agent serves as a complexing agent for gold ions as well as for metal ions dissolved from the substrate during plating,

e.g., nickel ions or copper ions. A preferred carboxylic acid is for example oxalic acid or a salt thereof. Preferred hydroxycarboxylic acids are for example tartaric acid, citric acid, lactic acid, malic acid, gluconic acid and salts of the aforementioned. Preferred aminocarboxylic acids are for example glycine, cysteine, methionine and salts of the aforementioned. Preferred aminophosphonic acids are nitrilotri(methylphosphonic acid) (commonly abbreviated as ATMP), diethylenetriamine-pentakis(methylphosphonic acid) (commonly abbreviated as DTPMP) and ethylenediaminetetra(methylphosphonic acid) (commonly abbreviated as EDTMP). In all cases also the sodium, potassium and ammonium salts of said compounds are also suitable. The concentration of the optional at least one complexing agent preferably ranges from 0.1 to 50 g/L, more preferably from 0.5 to 30 g/L.

**[0029]** More preferably, the electroless aqueous gold plating bath according to the invention comprises two different complexing agents and/or salts thereof, such as a hydroxycarboxylic acid or a salt thereof and an aminocarboxylic acid or a salt thereof.

**[0030]** The electroless aqueous gold plating bath according to the invention optionally comprises a crystal adjuster which is selected from the group consisting of thallium ions, arsenic ions, selenium ions and lead ions. Such crystal adjuster is preferably added to the electroless aqueous gold plating bath according to the invention in a concentration range of 0.00001 to 0.1 g/L. Useful sources for said ions can be water-soluble salts thereof such as the respective nitrates, sulphates and halides.

**[0031]** The electroless aqueous gold plating bath according to the invention optionally comprises at least one stabilising agent selected from the group consisting of sources of cyanide ions, hydantoin and alkyl derivatives thereof such as alkylhydantoin and dialkylhydantoin wherein alkyl residues in this context comprise C<sub>1</sub> to C<sub>8</sub> alkyls, preferably methyl, which can be cyclic and/or alicyclic, branched or unbranched, sulphur compounds such as 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, mercaptoacetic acid, 3-(2-benzthiazolylthio)-1-propanesulphonic acid, mercaptosuccinic acid, thiosulphuric acid, thioglycol, thiourea, thiomalic acid and the like, and aromatic nitrogen compounds such as benzotriazole, 1,2,4-aminotriazole and the like. Suitable source of cyanide ions can be any soluble cyanide salts such as alkali cyanides including sodium cyanide, potassium cyanide.

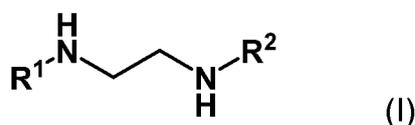
**[0032]** The concentration of the optional stabilising agent can be selected dependant on its chemical structure and can be determined in routine experiments by anyone known in the art. The concentration of the optional stabilising agent preferably ranges 0.0000001 to 0.2 mol/L, it ranges more preferably from 0.000001 to 0.1 mol/L. Such stabilising agents are conventionally added to electroless gold plating baths to improve their lifetime and to prevent plate-out.

**[0033]** In a preferred embodiment, two or more stabilising agents are used. More preferably, a source of cyanide ions in a concentration of 0.0003 to 5 mmol/L and one or more of hydantoin and alkyl derivatives thereof in a concentration of 10 to 100 mmol/L and/or sulphur compounds in a concentration of 0.000001 to 0.05 mol/L is selected.

**[0034]** In another preferred embodiment of the present invention, the electroless aqueous gold plating bath according to the invention is free of intentionally added second sources of reducible metal ions (disregarding trace of impurities commonly present in technical raw materials) allowing for pure gold deposits to be formed. Pure gold deposits are soft, malleable, and particularly suitable for wire bonding and soldering. Traces of impurities are understood as compounds present in a technical raw material of 1 wt.-% or less.

**[0035]** The pH of the electroless aqueous gold plating bath according to the invention preferably ranges from 5 to 9, more preferably from 6 to 8, even more preferably from 6.5 to 7.5. The target pH value is adjusted using for example acids such as phosphoric acid or bases such as sodium hydroxide or potassium hydroxide. It is advantageous and thus preferable to continuously control and adjust the pH value during plating as this also improves the plating bath lifetime.

**[0036]** The ethylenediamine derivative according to formula (I)



bearing the residues R<sup>1</sup> and R<sup>2</sup> which comprise 2 to 12 carbon atoms and which are selected from the group consisting of branched alkyl, unbranched alkyl, cycloalkyl or combinations thereof wherein the individual residues R<sup>1</sup> and R<sup>2</sup> are the same or different is used in aqueous gold plating baths to adjust the plating rate and improve their stability. Such aqueous gold plating baths can be electroless gold plating baths including immersion-type gold plating baths, autocatalytic gold plating baths and gold plating baths using a mixture of autocatalytic and immersion-type plating and electrolytic plating baths. Preferably, the plating enhancer compound is used in electroless plating baths.

**[0037]** The method for depositing a gold layer onto a substrate, comprising, in this order, the steps

- (i) providing a substrate;

(ii) contacting at least a portion of the surface of the substrate with the aqueous gold plating baths according to the invention;

and thereby depositing a gold layer onto at least a portion of the surface of the substrate.

**[0038]** The substrate to be plated with gold is contacted with the electroless aqueous gold plating bath according to the invention. This contact is preferably accomplished by dipping the substrate into the plating bath or by spraying the plating bath onto the substrate.

**[0039]** The substrate preferably has a surface area consisting of a metal or metal alloy and gold is then deposited onto the surface area consisting of a metal or metal alloy, selected from the group consisting of nickel, nickel alloys such as nickel phosphorous alloys, nickel boron alloys, cobalt, cobalt alloys such as cobalt phosphorous alloys, cobalt molybdenum phosphorous alloys, cobalt molybdenum boron alloys, cobalt molybdenum boron phosphorous alloys, cobalt tungsten phosphorous alloys, cobalt tungsten boron alloys, cobalt tungsten boron phosphorous alloys, palladium, palladium alloys such as palladium phosphorous alloys, palladium boron alloys, copper and copper alloys and gold or gold alloys. The electroless aqueous gold plating bath according to the invention can be used to deposit gold layers on gold substrates and may be utilised to thicken existing gold layers obtained for example from an immersion-type gold plating baths.

**[0040]** The substrates can be pretreated prior to plating as it is known in the art. Such pretreatment includes cleaning steps with solvents and/or surfactants to remove mostly organic contaminants, etching steps with acids and optionally, oxidising or reducing agents to remove oxides and activation steps. The latter are to deposit a noble metal on the surface or a part thereof to make it more receptive for plating. Such noble metal can be palladium which can be deposited as a salt before it is reduced to elementary palladium on the surface. Or it can be deposited in a colloidal form and - where appropriate - be subjected to an acceleration step with an acid such as hydrochloric acid to remove any protective colloids such as tin colloids. Such an activation layer normally is not a discrete layer but an aggregation of island structures of palladium. However, activation layers are considered as metal substrates in the context of the present invention.

**[0041]** The temperature of the electroless aqueous gold plating bath according to the invention is preferably in the range of 30 to 95 °C, more preferably from 70 to 90 °C, even more preferably from 75 to 85 °C, yet even more preferably from 77 to 84 °C during plating. The plating time is preferably in the range of 1 to 60 min, more preferably in the range of 5 to 30 min. However, if thinner or thicker deposits are desired, the plating time can be outside above-described ranges and adjusted accordingly.

**[0042]** It is preferable to continuously or in certain intervals replenish components which are being used during plating. Such components are *inter alia* the source of gold ions, the reducing agent for gold ions, the at least one stabilising agent and the plating enhancer compound. If necessary the pH value can be adjusted continuously or in intervals as well.

**[0043]** The electroless aqueous gold plating bath according to the invention may be used with horizontal, vertical and spray plating equipment.

**[0044]** It is an advantage of the present invention that the stability of the electroless aqueous gold plating baths according to the invention is improved compared to gold plating baths known in the art (see example 5). Stability herein is to be understood as the lifetime of the bath prior to precipitation of compounds from the bath ("plate-out") rendering it useless for plating purposes.

**[0045]** It is another advantage that the aqueous gold plating baths according to the invention allows for sufficient plating rates (deposited thickness of the plated metal layer over time) of 250 nm/h or more (see examples 1 to 3 and 5). Most plating baths known in the art which are somewhat stable do not allow for sufficient plating rates.

**[0046]** It is therefore a unique feature of the electroless aqueous gold plating bath according to the invention to provide highly stable gold plating baths with sufficient plating rates and thus allowing for more economically feasible gold plating processes.

**[0047]** The aqueous gold plating baths according to the invention form homogeneous gold deposits with little layer thickness diversion. The standard deviation of the gold layer thickness is below 10% or even below 8%. This little deviation is advantageously achievable even when plating on various substrates having different sizes.

**[0048]** The following non-limiting examples further illustrate the present invention.

## Examples

### General Procedures

**[0049]** Pallabond® CLN, Pallabond®ME, PallaBond® Pre Dip, PallaBond® Aktivator and PallaBond® ACT V3 STD are products available from Atotech Deutschland GmbH. The source of gold ions was in all cases  $K[Au(CN)_2]$ .

**[0050]** Printed circuit test boards having a multitude of copper pads of different sizes ranging from 0.25 to 49 mm<sup>2</sup> on both sides were used in all experiments as substrates. They were cleaned and etched prior to activation with palladium. Then, palladium was deposited on the copper surfaces before the gold layer was plated thereon. The different pads

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where the layer thickness was determined are shown in figure 1. The individual pads had the following areas 1: 0.25 mm<sup>2</sup>, 2: 0.52 mm<sup>2</sup>, 3: 0.68 mm<sup>2</sup>, 4: 0.97 mm<sup>2</sup>, 5: 1.33 mm<sup>2</sup>, 6: 1.35 mm<sup>2</sup>, 7: 3.3 mm<sup>2</sup>, 8: 6.7 mm<sup>2</sup>, 9: 25 mm<sup>2</sup>, 10: 49 mm<sup>2</sup>.

### Determination of thickness of the metal deposits and plating rate

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**[0051]** The deposit thickness was measured at 10 copper pads on each side of the test boards. The chosen copper pads had different sizes and are used to determine the layer thickness by XRF using the XRF instrument Fischerscope XDV-SDD (Helmut Fischer GmbH, Germany). By assuming a layered structure of the deposit the layer thickness can be calculated from such XRF data. The plating rate was calculated by dividing the obtained layer thickness by the time necessary to obtain said layer thickness.

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**[0052]** The layer thickness homogeneity was determined as the standard deviation from the average thickness value.

### Example 1 (inventive): *N*<sup>1</sup>,*N*<sup>2</sup>-di-iso-propylethane-1,2-diamine as plating enhancer compound

15 **[0053]** A gold plating baths containing the following components was prepared by dissolution of all components in water:

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	potassium hydroxide	to adjust pH to range from 7.9 to 8.1
	plating enhancer compound	50 mmol/L
	complexing agent	89 mmol/L
	5,5-dimethylhydantoin	47 mmol/L
	thallium ions	0.01 mmol/L
	potassium cyanide	0.6 mmol/L
	Formaldehyde	34.5 mmol/L
	gold ions	5.1 mmol/L

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**[0054]** A substrate was subjected to the following process steps (Table 1) by dipping the substrates into the respective solutions employing the given parameters:

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Table 1: Process sequence for gold plating.

#	Process step	Product	T[°C]	t [min]
1	Cleaner	Pallabond® CLN	40	5
2	Rinse	DI water	20	1
3	Etch Cleaner	Pallabond® ME	35	2
4	Rinse	DI water	20	1
5	PreDip	PallaBond® Pre Dip	20	1
6	Activation	PallaBond® Aktivator	35	1
7	Rinse	DI water	20	0.5
8	Rinse	DI water	20	0.5
9	Electroless Pd	PallaBond® ACT V3 STD	45	3.5
10	Rinse	DI water	20	2
11	Electroless Au	Gold plating bath	82	20
12	Rinse	DI water	20	2
13	Hot Rinse	DI water (< 2 μS/cm)	50	2
14	Drying	-	60	15

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**[0055]** After this process sequence the thicknesses of the individual metal layers were measured. The plating rate was calculated as described above.

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Table 2: Layer thickness and plating rate for a gold plating bath containing  $N^1, N^2$ -di-*iso*-propylethane-1,2-diamine.

	Layer thickness	Standard deviation	Plating rate
Palladium layer	74 nm		444 nm/h
Gold layer	103 nm	5.6%	309 nm/h

**[0056]** The gold layers were of lemon yellow colour. Also, the plating rate was very high and well above the desired minimum of 250 nm/h. The layer thickness distribution was very homogeneous, too, with only 5.6% deviation.

Example 2 (inventive):  $N^1, N^2$ -dipropylethane-1,2-diamine as plating enhancer compound

**[0057]** The process as described in Example 1 was repeated wherein the gold plating bath contained 50 mmol/L  $N^1, N^2$ -dipropylethane-1,2-diamine instead of 50 mmol/L  $N^1, N^2$ -di-*iso*-propylethane-1,2-diamine. The results are summarized in the following table:

Table 3: Layer thickness and plating rate for a gold plating bath containing  $N^1, N^2$ -dipropylethane-1,2-diamine.

	Layer thickness	Standard deviation	Plating rate
Palladium layer	82 nm		492 nm/h
Gold layer	101 nm	6.6%	303 nm/h

**[0058]** The gold layers were of lemon yellow colour. Also, the plating rate was very high and above the desired minimum of 250 nm/h. The layer thickness distribution was very homogeneous, too, with only 6.6% deviation.

Example 3 (inventive):  $N^1, N^2$ -diethylethane-1,2-diamine as plating enhancer compound

**[0059]** The process as described in Example 1 was repeated wherein the gold plating bath contained  $N^1, N^2$ -diethylethane-1,2-diamine instead of  $N^1, N^2$ -di-*iso*-propylethane-1,2-diamine but in the same concentration. The results are summarized in the following table:

Table 4: Layer thickness and plating rate for a gold plating bath containing  $N^1, N^2$ -diethylethane-1,2-diamine.

	Layer thickness	Standard deviation	Plating rate
Palladium layer	86 nm		516 nm/h
Gold layer	108 nm	6.4%	348 nm/h

**[0060]** The gold layers were of lemon yellow colour. Also, the plating rate was very high and clearly above the desired minimum of 250 nm/h. The layer thickness distribution was very homogeneous, too, with only 6.4% deviation.

Example 4 (comparative): Use of other amines

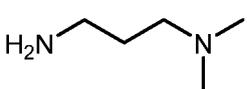
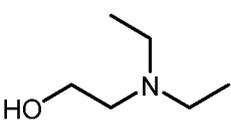
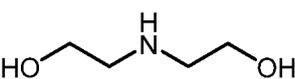
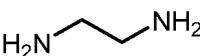
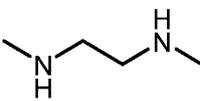
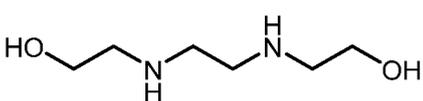
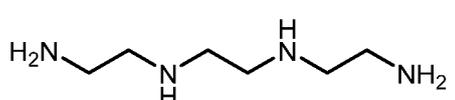
**[0061]** The process as described in Example 1 was repeated wherein the gold plating bath contained other compounds as listed in Table 5 instead of  $N^1, N^2$ -di-*iso*-propylethane-1,2-diamine. The results for 20 min gold plating are summarized in this table:

Table 5: Layer thickness and plating rate for comparative compounds in gold plating baths.

	Compound	Concentration	Layer thickness [nm]	Plating rate [nm/h]	Complete plate-out
A.		5.61 g/L	6	18	-

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(continued)

	Compound	Concentration	Layer thickness [nm]	Plating rate [nm/h]	Complete plate-out	
5	B.		5.11 g/L	10	30	-
10	C.		5.86 g/L	20	60	-
15	D.		5.26 g/L	28	84	-
20	E.		3.00 g/L	7	21	-
25	F.		4.40 g/L	50	150	~3d
30	G.		7.40 g/L	200	600	<1d
35	H.		7.30 g/L	140	420	3h

**[0062]** Various compounds containing amino moieties were tested. The stability tests were omitted in those cases where the respective plating rates were too low to meet today's industrial requirements of 250 nm/h plating rate.

**[0063]** Compound A comprised only tertiary amine moieties and did not bear any alkyl residues R<sup>1</sup> and R<sup>2</sup>. Hardly any gold plating took place when using this compound as substitute for a plating enhancer compound in a gold plating bath. The gold layers were also very inhomogeneous and the standard deviation of the layer thickness was 58%.

**[0064]** Compound B was an alkylene diamine derivative comprising only primary and tertiary amino moieties (with only methyl residues). The gold plating was very slow when using this compound as substitute for a plating enhancer compound in a gold plating bath. The gold layers were also very inhomogeneous and the standard deviation of the layer thickness was 53%.

**[0065]** Compounds C and D are alkanolamine with a tertiary amino moiety only or with only one secondary amino moieties. The gold plating was slow when using these compounds as substitutes for a plating enhancer compound in a gold plating bath. The gold layers were also very inhomogeneous and the standard deviation of the layer thickness was 24% for compound C and 33% for compound D.

**[0066]** Compounds E and F did not contain any alkyl residues of sufficient length and when using these compounds as substitutes for a plating enhancer compound in a gold plating bath the plating was slow. Compounds E and F are of similar structure as the plating enhancer compound according to formula (I) but they either have no alkyl residues at all or the alkyl residues are short. In case of compound E, the gold layer thicknesses were inhomogeneous having a standard deviation of 14.4% while for compound F the deviation was 6.4%.

**[0067]** Compound G bore two terminal hydroxy moieties. When using this compound as substitute for a plating enhancer compound in a gold plating bath the plating rate was high but the stability of the gold plating bath was insufficient. Within less than 1 day the gold plating bath was irrevocably degraded and could not be used for gold plating anymore. The standard deviation of the gold layer thickness was 6.3%.

**[0068]** Compound H bore two terminal primary amino moieties. When using this compound as substitute for a plating enhancer compound in a gold plating bath the plating rate was sufficiently high but the stability of the gold plating bath

was poor. Within 3 h the gold plating baths was irrevocably degraded. The standard deviation of the gold layer thicknesses was 8.5%.

[0069] In summary, comparative compounds A to F did not allow for sufficient plating rates of gold baths containing these compounds. The plating rates were always even below 200 nm/h and thus not sufficient for today's industrial demands. Comparative compounds G and H as additives gave sufficient plating rates but the stability of the respective gold plating baths were unsatisfactory.

#### Example 5 (inventive): Stability and life-time of gold plating baths

[0070] The gold plating baths of examples 1 to 3 were used to deposit gold on substrates for a prolonged time. The stability of the gold plating baths and the plating rate were monitored over time. If a plate-out occurred the solution was filtered and re-used. Every day during the experiment, the pH value was measured and adjusted to 7.1 with KOH and/or H<sub>3</sub>PO<sub>4</sub> if necessary. During plating, the source of gold ions, the source of cyanide ions and the plating enhancer compound were continuously replenished.

[0071] Table 6 provides information on the stability of gold plating baths containing different plating enhancer compounds. The plating baths were visually inspected directly after make-up (day 0) and for one week on a daily basis. The gold plating baths were also used to deposit gold on substrates every day during this test period. These results are summarized in

Table 7. The values given in said table are the deposit thickness in nanometres obtained after 20 min of plating.

Table 6: Visual inspection of gold plating baths over time while in usage.

Day	<i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -diethylethane-1,2-diamine	<i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -di- <i>iso</i> -propylethane-1,2-diamine	<i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -dipropylethane-1,2-diamine
0	Slightly yellow and clear solution	Colourless, clear solution	Intensively yellow, clear solution
1	No changes	No changes	No changes
2	No changes	No changes	No changes
3	No changes	No changes	Slight plate-out
4	Slight plate-out	No changes	Slight plate-out
5	Slight plate-out	No changes	Slight plate-out
6	Slight plate-out	No changes	Slight plate-out
7	Slight plate-out	No changes	Slight plate-out

Table 7: Gold layer thickness after 20 min deposition from gold plating bath containing plating enhancer compounds over various days.

Day	<i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -diethylethane-1,2-diamine	<i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -di- <i>iso</i> -propylethane-1,2-diamine	<i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -dipropylethane-1,2-diamine
1	116 nm	105 nm	147 nm
2	91 nm	89 nm	91 nm
3	110 nm	106 nm	108 nm
4	99 nm	98 nm	106 nm
5	112 nm	112 nm	116 nm
6	108 nm	103 nm	101 nm
7	99 nm	101 nm	111 nm

[0072] Although in the cases of the linear plating enhancer compounds, *N*<sup>1</sup>,*N*<sup>2</sup>-diethylethane-1,2-diamine and *N*<sup>1</sup>,*N*<sup>2</sup>-dipropylethane-1,2-diamine slight precipitates occurred, the plating baths were still able to deposit gold layers without any plating rate reduction. The branched plating enhancer compounds, *N*<sup>1</sup>,*N*<sup>2</sup>-di-*iso*-propylethane-1,2-diamine, showed no precipitates over 7 days and provided good plating rates over the entire tested period. It is thus deduced

that plating enhancer compounds having branched alkyl residues result in improved bath stability.

Example 6 (inventive): Ratio of plating enhancer compound to reducing agent for gold ions

5 **[0073]** A gold plating baths containing the following components was prepared by dissolving all components in water:

Water	100 mL
potassium hydroxide	12.4 g/L
<i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -di- <i>iso</i> -propylethane-1,2-diamine	see table 8
complexing agent	89 mmol/L
sulphur based stabilising agent	1.5 mg/L
thallium ions	4.4 mg/L
potassium cyanide	42 mg/L
formaldehyde	0.3 g/L
gold ion source	1.47 g/L

20 **[0074]** The gold plating bath was adjusted with KOH/H<sub>3</sub>PO<sub>4</sub> to a pH value of 7.1. A substrate was subjected to the process as described in table 1 wherein the electroless gold plating step was carried out for 10 min only.

**[0075]** The process was repeated several times with different gold plating baths containing increasing amounts of plating enhancer compounds whereby the amount of reducing agent for gold ions was kept at the same level. The results are provided by table 8.

Table 8: Ratio of plating enhancer compound and reducing agent for gold ions.

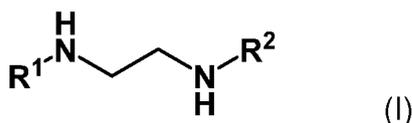
Molar ratio of <i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -di- <i>iso</i> -propylethane-1,2-diamine to formaldehyde	Plating rate [%]
1/1	100
2/1	100
4/1	71.4
8/1	71.4
10/1	62.8

35 **[0076]** It can be seen that the highest plating rates can be obtained if the molar ratio of plating enhancer compound and reducing agent for gold ions ranges between 1 or 2 to 1. The plating rate dropped upon further increasing the amount of plating enhancer compound.

40 **[0077]** Other embodiments of the present invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope of the invention being defined by the following claims only.

### Claims

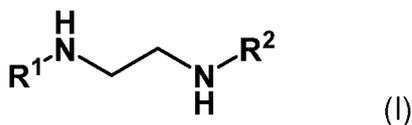
45 1. An electroless aqueous gold plating bath, comprising at least one source of gold ions and at least one reducing agent for gold ions, **characterized in that** it comprises at least one ethylenediamine derivative according to formula (I)



55 wherein the residues R<sup>1</sup> and R<sup>2</sup> comprise 2 to 12 carbon atoms and are selected from the group consisting of branched alkyl, unbranched alkyl, cycloalkyl or combinations thereof wherein the individual residues R<sup>1</sup> and R<sup>2</sup> are the same or different as plating enhancer compound.

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2. The electroless aqueous gold plating bath according to claim 1 **characterised in that** the residues R<sup>1</sup> and R<sup>2</sup> in formula (I) comprise 2 to 8 carbon atoms.
- 5 3. The electroless aqueous gold plating bath according to any of the preceding claims **characterised in that** the residues R<sup>1</sup> and R<sup>2</sup> in formula (I) are the same.
4. The electroless aqueous gold plating bath according to any of the preceding claims **characterised in that** the residues R<sup>1</sup> and R<sup>2</sup> in formula (I) are free of any further amino moieties and/or any hydroxy moieties.
- 10 5. The electroless aqueous gold plating bath according to any of the preceding claims **characterised in that** the residues R<sup>1</sup> and R<sup>2</sup> in formula (I) are branched alkyl residues having 3 to 6 carbon atoms.
6. The electroless aqueous gold plating bath according to any of the preceding claims **characterised in that** the concentration of the at least one plating enhancer compound according to formula (I) ranges from 0.001 - 1 mol/L.
- 15 7. The electroless aqueous gold plating bath according to claim 6 **characterised in that** the concentration of the at least one plating enhancer compound according to formula (I) ranges from 10 to 100 mmol/L.
8. The electroless aqueous gold plating bath according to any of the preceding claims **characterised in that** the at least one reducing agents for gold ions is selected from the group consisting of aliphatic aldehydes, aliphatic dialdehydes, aliphatic unsaturated aldehyde, aromatic aldehydes, sugars having an aldehyde group and precursors of formaldehyde.
- 20 9. The electroless aqueous gold plating bath according to any of the preceding claims **characterised in that** the molar ratio of reducing agent to plating enhancer compound according to formula (I) ranges from 0.8 to 3.
- 25 10. The electroless aqueous gold plating bath according to any of the preceding claims **characterised in that** the pH of the electroless aqueous gold plating bath ranges from 5 to 9.
- 30 11. The electroless aqueous gold plating bath according to any of the preceding claims **characterised in that** the concentration of gold ions ranges from 0.1 to 10 g/L.
- 35 12. The electroless aqueous gold plating bath according to any of the preceding claims **characterised in that** the electroless aqueous gold plating bath further comprises at least one complexing agent selected from the group consisting of carboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids, aminophosphonic acids or a salt of the aforementioned.
- 40 13. A method for depositing a gold layer onto a substrate, comprising, in this order, the steps
  - (i) providing a substrate
  - (ii) contacting at least a portion of the surface of the substrate with the electroless aqueous gold plating bath according to claims 1 to 12and thereby depositing a gold layer onto at least a portion of the surface of the substrate.
- 45 14. The method for depositing a gold layer onto a substrate according to claim 13 wherein the substrate has a surface area consisting of a metal or metal alloy and gold is then deposited onto the surface area consisting of a metal or metal alloy, selected from the group consisting of nickel, nickel alloys such as nickel phosphorous alloys, nickel boron alloys, cobalt, cobalt alloys such as cobalt phosphorous alloys, cobalt molybdenum phosphorous alloys, cobalt molybdenum boron alloys, cobalt molybdenum boron phosphorous alloys, cobalt tungsten phosphorous alloys, cobalt tungsten boron alloys, cobalt tungsten boron phosphorous alloys, palladium, palladium alloys such as palladium phosphorous alloys, palladium boron alloys, copper and copper alloys and gold or gold alloys.
- 50 15. Use of the ethylenediamine derivative according to formula (I)
- 55



5

bearing the residues R<sup>1</sup> and R<sup>2</sup> which comprise 2 to 12 carbon atoms and which are selected from the group consisting of branched alkyl, unbranched alkyl, cycloalkyl or combinations thereof wherein the individual residues R<sup>1</sup> and R<sup>2</sup> are the same or different in aqueous gold plating baths.

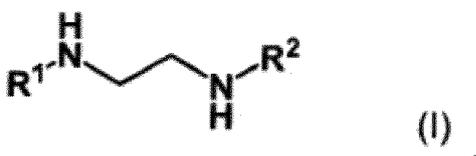
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### Patentansprüche

15

1. Wässriges Bad zur stromlosen Goldplattierung, umfassend wenigstens eine Quelle von Goldionen und wenigstens ein Reduktionsmittel für Goldionen, **dadurch gekennzeichnet, dass** es wenigstens ein Ethylendiaminderivat gemäß Formel (I) als Plattierungsverstärkerbindung umfasst,

20



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wobei die Reste R<sup>1</sup> und R<sup>2</sup> 2 bis 12 Kohlenstoffatome umfassen und ausgewählt sind aus der Gruppe bestehend aus verzweigtem Alkyl, unverzweigtem Alkyl, Cycloalkyl und Kombinationen davon, wobei die einzelnen Reste R<sup>1</sup> und R<sup>2</sup> gleich oder verschieden sind.

30

2. Wässriges Bad zur stromlosen Goldplattierung gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die Reste R<sup>1</sup> und R<sup>2</sup> in Formel (I) 2 bis 8 Kohlenstoffatome umfassen.

35

3. Wässriges Bad zur stromlosen Goldplattierung gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** die Reste R<sup>1</sup> und R<sup>2</sup> in Formel (I) gleich sind.

40

4. Wässriges Bad zur stromlosen Goldplattierung gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** die Reste R<sup>1</sup> und R<sup>2</sup> in Formel (I) frei von jeglichen weiteren Aminoeinheiten und/oder jeglichen Hydroxyeinheiten sind.
5. Wässriges Bad zur stromlosen Goldplattierung gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** die Reste R<sup>1</sup> und R<sup>2</sup> in Formel (I) verzweigte Alkylreste mit 3 bis 6 Kohlenstoffatomen sind.

45

6. Wässriges Bad zur stromlosen Goldplattierung gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** die Konzentration der wenigstens einen Plattierungsverstärkerbindung gemäß Formel (I) in dem Bereich von 0,001 bis 1 mol/l liegt.

50

7. Wässriges Bad zur stromlosen Goldplattierung gemäß Anspruch 6, **dadurch gekennzeichnet, dass** die Konzentration der wenigstens einen Plattierungsverstärkerbindung gemäß Formel (I) in dem Bereich von 10 bis 100 mmol/l liegt.

55

8. Wässriges Bad zur stromlosen Goldplattierung gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** das wenigstens eine Reduktionsmittel für Goldionen ausgewählt ist aus der Gruppe bestehend aus aliphatischen Aldehyden, aliphatischen Dialdehyden, aliphatischem ungesättigtem Aldehyd, aromatischen Aldehyden, Zuckern mit einer Aldehydgruppe und Vorläufern von Formaldehyd.
9. Wässriges Bad zur stromlosen Goldplattierung gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** das Molverhältnis von Reduktionsmittel zu Plattierungsverstärkerbindung gemäß Formel (I) in dem Bereich von 0,8 bis 3 liegt.

10. Wässriges Bad zur stromlosen Goldplattierung gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** der pH-Wert des wässrigen Bads zur stromlosen Goldplattierung in dem Bereich von 5 bis 9 liegt.

11. Wässriges Bad zur stromlosen Goldplattierung gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** die Konzentration von Goldionen in dem Bereich von 0,1 bis 10 g/l liegt.

12. Wässriges Bad zur stromlosen Goldplattierung gemäß einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** das wässrige Bad zur stromlosen Goldplattierung ferner wenigstens einen Komplexbildner ausgewählt aus der Gruppe bestehend aus Carbonsäuren, Hydroxycarbonsäuren, Aminocarbonsäuren, Aminophosphonsäuren oder einem Salz der Genannten umfasst.

13. Verfahren zum Abscheiden einer Goldschicht auf ein Substrat, umfassend die Schritte in dieser Reihenfolge:

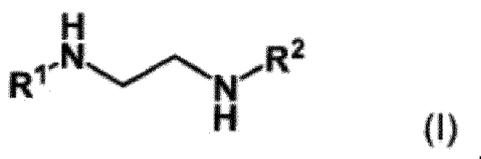
(i) Bereitstellen eines Substrats,

(ii) Inkontaktbringen wenigstens eines Teils der Oberfläche des Substrats mit einem wässrigen Bad zur stromlosen Goldplattierung gemäß Ansprüchen 1 bis 12,

und dadurch Abscheiden einer Goldschicht auf wenigstens einem Teil der Oberfläche des Substrats.

14. Verfahren zum Abscheiden einer Goldschicht auf ein Substrat gemäß Anspruch 13, wobei das Substrat einen Oberflächenbereich aufweist, der aus einem Metall oder einer Metalllegierung besteht und dann Gold auf den Oberflächenbereich, der aus einem Metall oder einer Metalllegierung besteht, abgeschieden wird, ausgewählt aus der Gruppe bestehend aus Nickel, Nickellegierungen, wie z. B. Nickel-Phosphor-Legierungen, Nickel-Bor-Legierungen, Cobalt, Cobaltlegierungen, wie z. B. Cobalt-Phosphor-Legierungen, Cobalt-Molybdän-Phosphor-Legierungen, Cobalt-Molybdän-Bor-Legierungen, Cobalt-Molybdän-Bor-Phosphor-Legierungen, Cobalt-Wolfram-Phosphor-Legierungen, Cobalt-Wolfram-Bor-Legierungen, Cobalt-Wolfram-Bor-Phosphor-Legierungen, Palladium, Palladiumlegierungen, wie z. B. Palladium-Phosphor-Legierungen, Palladium-Bor-Legierungen, Kupfer und Kupferlegierungen und Gold oder Goldlegierungen.

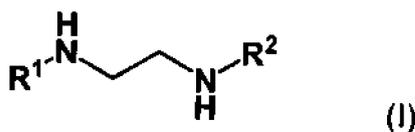
15. Verwendung des Ethylendiaminderivats gemäß Formel (I)



das die Reste R<sup>1</sup> und R<sup>2</sup> trägt, die 2 bis 12 Kohlenstoffatome umfassen und ausgewählt sind aus der Gruppe bestehend aus verzweigtem Alkyl, unverzweigtem Alkyl, Cycloalkyl und Kombinationen davon, wobei die einzelnen Reste R<sup>1</sup> und R<sup>2</sup> gleich oder verschieden sind, in wässrigen Goldplattierungsbädern.

### Revendications

1. Bain aqueux de placage d'or autocatalytique, comprenant au moins une source d'ions d'or et au moins un agent réducteur pour les ions d'or, **caractérisé en ce qu'il** comprend au moins un dérivé d'éthylènediamine selon la formule (I)



dans lequel les résidus R<sup>1</sup> et R<sup>2</sup> comprennent de 2 à 12 atomes de carbone et sont choisis dans le groupe constitué d'alkyle ramifié, alkyle non ramifié, cycloalkyle ou des combinaisons de ceux-ci dans lequel les résidus R<sup>1</sup> et R<sup>2</sup> individuels sont identiques ou différents en tant que composé d'adjuvant de placage.

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2. Bain aqueux de placage d'or autocatalytique selon la revendication 1 **caractérisé en ce que** les résidus R<sup>1</sup> et R<sup>2</sup> dans la formule (I) comprennent de 2 à 8 atomes de carbone.
- 5 3. Bain aqueux de placage d'or autocatalytique selon l'une quelconque des revendications précédentes **caractérisé en ce que** les résidus R<sup>1</sup> et R<sup>2</sup> dans la formule (I) sont identiques.
- 10 4. Bain aqueux de placage d'or autocatalytique selon l'une quelconque des revendications précédentes **caractérisé en ce que** les résidus R<sup>1</sup> et R<sup>2</sup> dans la formule (I) sont exempts de fragments amino et/ou fragments hydroxy supplémentaires.
- 15 5. Bain aqueux de placage d'or autocatalytique selon l'une quelconque des revendications précédentes **caractérisé en ce que** les résidus R<sup>1</sup> et R<sup>2</sup> dans la formule (I) sont des résidus alkyle ramifiés ayant 3 à 6 atomes de carbone.
- 20 6. Bain aqueux de placage d'or autocatalytique selon l'une quelconque des revendications précédentes **caractérisé en ce que** la concentration de l'au moins un composé d'adjuvant de placage selon la formule (I) est dans la plage de 0,001 à 1 mol/l.
- 25 7. Bain aqueux de placage d'or autocatalytique selon la revendication 6 **caractérisé en ce que** la concentration de l'au moins un composé d'adjuvant de placage selon la formule (I) est dans la plage de 10 à 100 mmol/l.
- 30 8. Bain aqueux de placage d'or autocatalytique selon l'une quelconque des revendications précédentes **caractérisé en ce que** l'au moins un agent réducteur pour les ions d'or est choisi dans le groupe constitué d'aldéhydes aliphatiques, de dialdéhydes aliphatiques, d'un aldéhyde insaturé aliphatique, d'aldéhydes aromatiques, de sucres comportant un groupe aldéhyde et de précurseurs de formaldéhyde.
- 35 9. Bain aqueux de placage d'or autocatalytique selon l'une quelconque des revendications précédentes **caractérisé en ce que** le rapport molaire de l'agent réducteur au composé d'adjuvant de placage selon la formule (I) est dans la plage de 0,8 à 3.
- 40 10. Bain aqueux de placage d'or autocatalytique selon l'une quelconque des revendications précédentes **caractérisé en ce que** le pH du bain aqueux de placage d'or autocatalytique est dans la plage de 5 à 9.
- 45 11. Bain aqueux de placage d'or autocatalytique selon l'une quelconque des revendications précédentes **caractérisé en ce que** la concentration d'ions d'or est dans la plage de 0,1 à 10 g/l.
- 50 12. Bain aqueux de placage d'or autocatalytique selon l'une quelconque des revendications précédentes **caractérisé en ce que** le bain aqueux de placage d'or autocatalytique comprend en outre au moins un agent complexant choisi dans le groupe constitué d'acides carboxyliques, acides hydroxycarboxyliques, acides aminocarboxyliques, acides aminophosphoniques et un sel des composés mentionnés ci-dessus.
- 55 13. Procédé de dépôt d'une couche d'or sur un substrat, comprenant, dans cet ordre, les étapes de
  - (i) fourniture d'un substrat
  - (ii) mise en contact d'au moins une portion de la surface du substrat avec le bain aqueux de placage d'or autocatalytique selon les revendications 1 à 12et déposer ainsi une couche d'or sur au moins une partie de la surface du substrat.
14. Procédé de dépôt d'une couche d'or sur un substrat selon la revendication 13 dans lequel le substrat comporte une surface constituée d'un métal ou un alliage métallique et de l'or est ensuite déposée sur la surface constituée d'un métal ou un alliage métallique, choisi dans le groupe constitué du nickel, d'alliages de nickel tels que des alliages phosphoreux de nickel, des alliages de bore-nickel, du cobalt, d'alliages de cobalt tels que des alliages phosphore-cobalt, des alliages phosphoreux de molybdène-cobalt, des alliages de bore-molybdène-cobalt, des alliages phosphoreux de bore-molybdène-cobalt, des alliages phosphoreux de tungstène-cobalt, des alliages de bore-tungstène-cobalt, des alliages phosphoreux de bore-tungstène-cobalt, du palladium, d'alliages de palladium tels que des alliages phosphoreux de palladium, des alliages de bore-palladium, du cuivre et d'alliages de cuivre et de l'or ou d'alliages d'or.

15. Utilisation du dérivé d'éthylènediamine selon la formule (I)



10 comportant les résidus R<sup>1</sup> et R<sup>2</sup> qui comprennent 2 à 12 atomes de carbone et qui sont choisis dans le groupe constitué d'alkyle ramifié, alkyle non ramifié, cycloalkyle ou des combinaisons de ceux-ci dans lequel les résidus individuels R<sup>1</sup> et R<sup>2</sup> sont identiques ou différents dans des bains aqueux de placage d'or.

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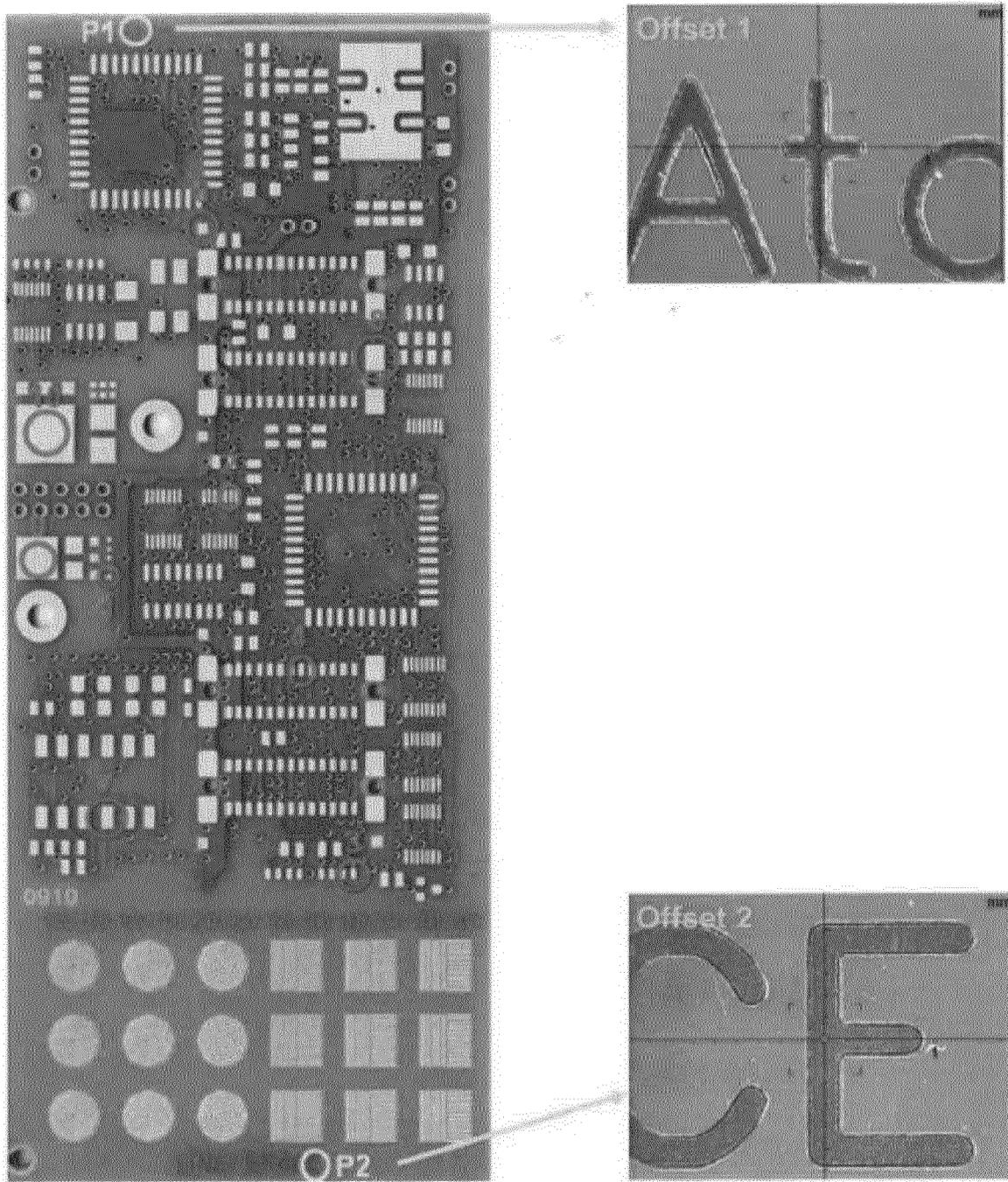
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Figure 1:



**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

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