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ELECTROLESS COPPER PLATING

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ABSTRACT OF THE DISCLOSURE

An autocatalytic metal deposition solution is provided which comprises water; an ion of a metal to be deposited; a complexing agent for the ion to be deposited; a reducing agent for the ion to be deposited; an agent capable of adjusting pH; and a compound containing a cyanide radical (CN^-) complexed with a metal selected from Group VIII of the Periodic Table of Elements in an amount sufficient to effect acceleration of the deposition of the metal. The present invention relates to electroless or auto-catalytic plating of metals, and more particularly to accelerating the rate of deposition from autocatalytic metal plating baths.

Electroless or autocatalytic metal deposition solutions are characterized by a capacity to deposit metal on a wide variety of conducting and non-conducting or insulating surfaces without the assistance of an external supply of electrons. Typically, such solutions comprise a solvent, a supply of ions of a metal to be deposited, an agent capable of reducing the ions of the metal to be deposited, a complexing agent for the ions of the metal to be deposited and a pH regulator.

Such solutions are particularly suitable for metallizing insulating substrata on surfaces which have been suitably treated to make them sensitive to the reception of electroless metal deposition. Such sensitization techniques include the well known treatment with an acidic aqueous solution of stannous chloride ($SnCl_2$), followed by treatment with a dilute aqueous acidic solution of palladium chloride ($PdCl_2$). Alternately, sensitization may be achieved by treating the insuating substrata with an acidic solution containing a mixture of stannous chloride and precious metal chloride, such as palladium chloride, the stannous chloride being present in stoichiometric excess, based on the amount of precious metal chloride.

Alternate ways of achieving good sensitization of insulating substrata to the reception of electroless metal are disclosed in U.S. Patent 3,146,125 and U.S. Patent No. 3,226,256.

Commercial exploitation of electroless metal deposition solutions of the type described has been hampered by the fact that electroless metal deposition solutions which are stable over relatively long periods of time have a tendency to deposit copper at a relatively slow rate. As a result whenever thick deposits are required, a relatively long contact time is required.

Although techniques for speeding up the rate of deposition are known, in general it can be stated that such techniques tend either to render the solutions unstable, or to adversely affect the properties of the metal deposits.

One object of the present invention is to accelerate the deposition rate of autocatalytic or electroless metal baths.

A further object of the present invention is to enhance the deposition rate of electroless metal solutions without adversely affecting the stability or the physical properties of the electroless metal produced therefrom.

Another object of the present invention is to increase the rate of deposition for electroless metal solutions which contain relatively low concentrations of the basic ingredients described hereinabove.

Another object of this invention is to provide means for monitoring autocatalytic copper solutions so as to maintain an accelerated rate of deposition therefrom.

A further object of the invention is to provide autocatalytic metal deposition solutions which are capable of depositing bright, ductile electroless metal at enhanced rates over relatively long periods of time.

Still a further object of this invention is to provide new and useful addition agents for controlling the rate of deposition and stability of electroless copper solutions.

Other objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the steps, processes, compositions, instrumentalities and combinations pointed out in the appended claims.

Although for clarity of description, the invention will be particularly described with reference to electroless copper deposition, which is a preferred embodiment, it should be understood that the principles of the invention could be applied to the electroless deposition of other metals.

According to the present invention, it has been found that use of the accelerators described herein, in addition to improving deposition rate, also permits practical operation at lower concentrations of ingredients.

For example, use of these accelerators permits operation at a relatively low reducing agent concentration and/or results in lower reducing agent consumption. Since consumption of reducing agent represents a substantial cost factor in deposition solution operation, the reduction in consumption of this ingredient yields considerable cost savings and is a significant commercial advantage.

Another advantage occurring from the use of these accelerators is that they seem to act as bath stabilizers.

Electroless copper solutions are capable of depositing copper without the assistance of an external supply of electrons. Typically, such solutions comprise water, a small amount of copper ions, e.g. a water soluble copper salt, a reducing agent for copper ions, a complexing agent for copper ions, and a pH regulator.

The selection of the water soluble copper salt for such baths is chiefly a matter of economics. Copper sulfate is preferred for economic reasons, but the halides, nitrates, acetates and other organic and inorganic acid salts of copper may also be used.

Rochelle salts, the sodium mono-, di-, tri-, and tetrasodium) salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid and its alkali salts, gluconic acid, gluconates, and triethanolamine are preferred as copper ion complexing agents, but commercially available glucono-γ-lactone and modified ethylenediamineacetates are also useful, and in certain instances give even better results than the pure sodium ethylenediaminetetraacetates. One such material is N-hydroxyethylethylenediaminetriacetate. Other materials suitable for use as cupric complexing agents are disclosed in U.S. Patent Nos. 2,996,408, 3,075,856, 3,075,855 and 2,938,805.

Copper reducing agents which have been used in alkaline electroless metal baths include formaldehyde, and formaldehyde precursors or derivatives, such as paraformaldehyde, dimethyl hydantoin, glyoxal, and the like. Also suitable as reducing agents in alkaline baths are borohydrides, such as alkali metal borohydrides, e.g., sodium and potassium borohydride, as well as substituted borohydrides, e.g., sodium trimethoxyborohydride. As reducing agents in such baths may also be used boranes, such as amine borane, e.g., isopropylamine borane, morpholine borane, and the like.

Typical of the copper reducing agents for use in acid electroless copper solutions are hypophosphites, such as sodium and potassium hypophosphite and the like.

The pH adjustor or regulator may consist of any acid or base, and here again the selection will depend primarily on economics. For this reason, the pH adjustor on the alkaline side will ordinarily be sodium hydroxide. On the acid side, pH will usually be adjusted with an acid having a common anion with the copper salt. Since the preferred copper salt is the sulfate, the preferred pH adjustor on the acid side is sulfuric acid.

In operation of the bath, the copper salt serves as a source of copper ions, and the reducing agent reduces the copper ions to metallic form. The reducing agent is itself oxidized to provide electrons for the reduction of the copper ions. The complexing agent serves to complex the copper ion so that it will not be precipitated, e.g., by hydroxyl ions and the like, and at the same time makes the copper available as needed to the reducing action of the reducing agent. The pH adjustor serves chiefly to regulate the internal plating potential of the bath.

It should be understood, however, that every constituent in the electroless copper bath has an effect on plating potential, and therefore must be regulated in concentration to maintain the most desirable plating potential for the particular ingredients and conditions of operation. Other factors with affect internal plating voltage, deposition quality and rate include temperature and degree of agitation, in addition to type and concentration of the basic ingredients mentioned.

In electroless plating baths, the bath constituents are continuously being consumed, so that the bath is in a constant state of change. Control of such baths, so as to maintain a relatively high plating rate over relatively long periods of time is exceedingly difficult. As a result, such baths, and particularly those having a high plating potential, i.e., highly active baths, tend to become unstable and to spontaneously decompose with use. Heretofore, spontaneous decomposition of high plating potential baths has been an important factor in limiting the commercial acceptance of electroless copper solutions as a substitute for or a competitor of electroplating baths.

According to the present invention, it has been discovered that certain agents, when added to electroless copper plating solutions, serve to accelerate the rate of deposition over relatively long periods without adverse affect on either the stability of the solutions or the properties of the metal deposited.

The accelerating agents of this invention also appear to render electroless copper solutions less sensitive to changes of temperature and concentration, and therefore permit greater variation in operating conditions, ingredient concentration, temperature and types of ingredients than have heretofore been considered possible.

The present invention and the agents described herein although applicable to electroless metal deposition solutions generally, are particularly suitable for use in electroless copper deposition solutions which have high plating potential under the conditions of use.

The accelerating agents of this invention are water soluble complex cyano-metallo compounds in which the cyanide radical (CN^-) is complexed with certain metals of Group VIII of the Periodic Table of Elements, including mixtures of such compounds. Typical of such compounds are those in which the cyanide radical (CN^-) is complexed with iron, iridium and rhenium, including mixtures of such compounds.

Preferred for use are the water soluble complex cyano-iron compounds, i.e., hexacyanoferrate (II) and hexacyanoferrate (III) compounds, as well as mixtures of such compounds. Typical of such compounds are the ferricyanides and ferrocyanides of the metals of Groups IA (alkali metal) and IIA (alkaline earth metal) of the Periodic Table of Elements, and ammonium. Preferred for use are the sodium, potassium and ammonium ferricyanides and ferrocyanides. It will be appreciated that in alkaline solutions the ferricyanides will be reduced to ferrocyanides, so that in such solutions the ferrocyanides will function as the accelerator, even though the accelerator is added as a ferricyanide. The accelerators should be added in amounts of between about .0075 and 50 grams per liter, preferably between about 0.150 and 2.50 grams per liter. Ordinarily, the accelerator will be added in amounts of about 1 to 300 parts per million, preferably between 1 and 50 parts per million, based upon the metal which is complexed with the cyanide (CN^-) ion, e.g., iron (Fe).

A typical electroless metal deposition bath made according to the present invention will comprise:

Metal salt	0.01 to 1.0 moles.
Reducing agent	0.01 to 4 moles.
Electroless metal complexing agent	0.7 to 40 times the moles of metal salt.
Accelerating agent measured as metal complexed with cyanide	1 to 300 parts per million.
pH adjustor	Sufficient to give desired pH.
Water	Sufficient to make 1 liter.

In the preferred embodiments, the electroless metal salt will be a copper salt. Specific embodiments of a high plating potential electroless copper solution comprise:

Copper salt	0.01 to 1.0 moles.
Formaldehyde	0.01 to 4 moles.
Copper ion complexing agent	0.7 to 40 times the moles of metal salt.
Accelerating agent measured as metal complexed with cyanide	1 to 300 parts per million.
Alkali metal hydroxide	pH 10–14.
Water	Sufficient to make 1 liter.

Preferred embodiments of highly active solutions comprise:

A soluble cupric salt, preferably cupric sulfate	0.02 to 0.5 mole.
Alkali metal hydroxide, preferably soduim hydroxide, to give	pH 11–13.
Formaldehyde	0.4 to 1.0 mole.
Cupric ion complexing agent	0.001 to 0.60 moles and usually at least about 10% molar excess based on the amount of cupric salt employed.
Hexacyanoferrate (II)	1 to 50 parts per million calculated as Fe.
Water	Sufficient to make 1 liter.

In considering the general and specific working formulae set forth herein, it should be understood that as the baths are used up in plating, the ingredients will be replenished from time to time. Also, it is advisable to monitor the pH, and the concentration of the additive element described, and to adjust them to their optimum value as the bath is used.

According to the present invention, it has been also discovered that the performance of electroless metal baths of the type described herein is improved by the addition thereto of certain surfactants in an amount of less than about 5 grams per liter. Such surfactants include organic phosphate esters, and oxyethylated sodium salts, and mixtures thereof. Preferred surfactants are alkylphenoxy polyethoxy phosphate esters. Typical examples of such esters are nonylphenoxy polyethoxy phosphate esters having molecular weights of between about 800 and 1000, preferably about 900. Typical of the oxyethylated sodium salts is the product sold under the tradename Triton QS–15.

For best results, the electroless copper solutions will ordinarily contain small effective amounts of simple

water soluble organic and inorganic cyanide compounds, e.g., 0.00001 to 0.06 mole per liter.

Typical of such simple cyanides are the alkali metal, alkaline earth metal and ammonium cyanides, such as sodium, potassium, calcium and ammonium cyanide; and nitriles, preferably alpha-hydroxynitriles, e.g., glycolonitrile and lactonitrile.

The copper solutions may also contain small effective amounts, e.g., less than about 100 parts per million, of sulfur compounds capable of forming stable but dissociable chelates with cuprous ion.

Among the organic sulfur compounds may be mentioned the following: thio derivatives of alkyl glycols, such as 2,2'-thiodiethanol, dithiodiglycol, aliphatic sulfur-nitrogen compounds, such as thiocarbamates, e.g., thiourea; 5-membered heterocyclics containing S–N in the 5-membered ring, such as thiazoles and isothiazoles, and thioglycolic acid; e.g., thiazole, 2-mercaptobenzothiazole and the like; dithiols, e.g., 1,2-ethanedithiol and the like; 6-membered heterocyclics containing S–N in the ring, such as thiazones, e.g., 1,2-benzisothiazine, benzothiazine, and the like; thioamino acids, such as methionine, cystine, cysteine, and the like. Among the inorganic sulfur compounds may be mentioned: alkali sulfides, e.g., sodium sulfide, potassium sulfide, sodium polysulfide, potassium polysulfide; alkali thiocyanates, such as sodium-potassium thiocyanates.

Compounds which contain both sulfur and cyanide are known and may be used as the cuprous complexing agent. Typical of such compounds are 3,3'-thiodipropionitrile and homologs.

For most sulfur compounds 1 part per million will be too much, it will stop the bath. In general the amount will be less than 1 part per million and usually .01 to 0.2 part per million will be the preferable range.

The baths may be used at widely varying temperatures, e.g., between 15° and 100° C., although they will usually be used between about 20° and 80° C. As the temperature is increased it is usual to find that the rate of plating is increased, but the temperature is not highly critical and, within the usual operating range, excellent bright, ductile deposits of copper are obtained.

Performance data for baths made in accordance with the teachings contained herein are given in Table I.

	Grams/liter
$CuSO_4 \cdot 5H_2O$	25
Tetrasodiumethylenediamine tetraacetate	50
HCHO (37% solution)	12
Potassium ferrocyanide	0.25
Phenyl polyethylene ether phosphate	0.1
Lactonitrile	0.02
Water to make 1 liter.	

In room temperature solutions of the type described, it is preferred to use alpha-hydroxynitriles such as glycolonitrile as the simple cyanide compound.

Electroless metal solutions containing the accelerators of this invention are also characterized by an ability to deposit on surfaces of relatively low catalytic activity. This property is illustrated by the following example.

An electroless metal solution having the formula indicated below was prepared:

$CuSO_4 \cdot 5H_2O$	grams/liter	5
Rochelle salts	do	40
HCHO (37%)	ml./l.	6
NaCN	gram/liter	0.01
Potassium ferrocyanide	do	.45
Phenyl polyethylene ether phosphate	ml./l.	1
NaOH to give pH 12–12.2 at 25° C.		

As a control was used the identical bath without potassium ferrocyanide.

Two panels similarly sensitized and of equal cross-sectional area, were simultaneously immersed in an electroless copper solution corresponding substantially to solution No. 1, Table I, until a uniform deposit of electroless copper had formed on the sensitized surface of each panel.

One of the electroless copper coated panels was immersed in the solution identified above and containing potassium ferrocyanide, and the second panel was immersed at the same time in the control solution which was free of potassium ferrocyanide. Deposition of electroless copper from the potassium ferrocyanide containing solution onto the panel commenced immediately upon immersion of the panel. In comparison, no deposition occurred after 1½ hours on the panel which was immersed in the electroless copper solution which was free of ferrocyanide.

The solution containing the accelerators of this invention, because of their ability to deposit on surfaces which have a relatively low sensitivity to electroless metal deposition, are particularly useful for metallizing clear, readily available plastic impregnated laminates and plastic sheet stock, including those prepared from ABS (acrylonitrile-butadiene-styrene), acetal resins, acrylic resins, such as methyl methacrylate and methylmethacrylate styrene copolymers, allyl resins and monomers, such as diallyl phthalate, cellulosic resins, such as ethyl cellulose, cellulose acetate, cellulose acetate butyrate, cellulose propionate and the like, chlorinated polyethers, epoxy resins, fluoroplastics, furanes, melamine-formaldehyde resins, nylon, polyacrylic esters, phenol-formaldehyde and phenol-furfuryl resins, phenolic cast resins, aromatic polyimide resins, polyphenylene oxide resins, polyethylene, polypropylene, polystyrene, silicones, urea-formaldehyde, urethanes, vinyl polymers and copolymers and the like.

In using the autocatalytic or electroless copper solutions to plate metal, the surface to be plated must be free of grease and other contaminating material.

TABLE I

Soln. No.	$CuSO_4 \cdot 5H_2O$ (gm./l.)	Tetrasodium ethylenediamine tetraacetic acid (gm./l.)	HCHO 37% (m.l/l.)	NaCN (g./l.)	Potassium Ferrocyanide (p.p.m. as Fe)	Stability	Color	Rate (thickness deposit, hr. In./Hrx10^6)	Ductility (bends)
1	15	50	6	0.03	0	Stable	Bright	6	5.5
2	15	50	6	0.03	20	do	do	8	3
3	15	50	6	0.03	40	do	do	9	3
4	15	50	8	0.03	80	do	do	9	3
5	15	50	6	0.03	160	do	do	9	3
6	15	50	6	0.03	320	do	do	9	3.5

In Table I, the solutions were maintained at a pH of about 12 and at about 60° C. throughout use. In all instances about 1 ml./l. of the specific organic phosphate ester described above was used as a surfactant.

In Table I, ductility is measured by bending the copper deposit through 180°, in one direction, creasing, then returning it to its original position, with pressing along the crease to flatten it, this cycle constituting one bend.

Use of the accelerators of this invention in autocatalytic copper solutions improves deposition rate to a marked degree, as is brought out in Table I.

As also shown by Table I, the rate increase is achieved without sacrifice in brightness of the copper deposits.

Certain electroless metal solutions containing the accelerators described herein possess, as a further advantage, the ability to function at room temperature at practical rates of deposition. A solution capable of depositing metal at a relatively high rate at room temperature is given below:

Where a non-metallic surface is to be metallized, the surface area to receive the deposit must first be sensitized to render it catalytic to the reception of electroless copper, as has been brought out hereinabove.

Other ways of sensitizing non-metallic surfaces for reception of an electroless copper deposit from the baths described herein are disclosed in U.S. Patent No. 3,226,-256.

Where metal surface is to be plated, it should be degreased, and then treated with an acid, such as hydrochloric or phosphoric acid, to free the surface of oxides.

Following pre-treatment and/or sensitization, the surface to be metallized is immersed in the autocatalytic copper baths, and permitted to remain in the bath until a copper deposit of the desired thickness has been built up.

The solutions described herein are advantageous for use in the production of printed circuits. For example, portions of the surface of an insulating substratum in the form of a desired circuit pattern may be sensitized for the reception of electroless metal. Following sensitization, the substratum is immersed in or otherwise contacted with the electroless metal solution of the type described and permitted to remain therein until a metal deposit of the desired thickness has been built up. The circuit may be formed on one or more surfaces of the substratum. If desired, interconnections between the surfaces may be provided by drilling or punching holes and sensitizing the lateral walls thereof prior to exposure of the substratum to the electroless metal solution. In this embodiment, electroless metal builds up on the circuit pattern and on the walls surrounding the holes.

To further demonstrate the operation of the baths at room temperature, the following solution was prepared:

Copper sulfate ---------- mole--	0.10
Tetrasodium ethylenediamine tetraacetate ---------- do----	0.12
Formaldehyde ---------- do----	0.16
Phenyl polyethylene ether phosphate---percent--	0.01
Lactonitrile ---------- mole--	0.0003
pH (adjusted with NaOH) ----------	12.8
Water sufficient to make 1 liter.	
Temperature, °C. ----------	25

Room temperature rate of deposit from this bath with increasing quantities of potassium hexacyanoferrate (II) were as follows:

$K_4Fe(CN)_6.3H_2O$ addition (gram/liter)	Copper thickness in 5 hours (micron)
0	1.4
25	5.1
50	5.5

At elevated temperatures, the effect of potassium hexacyanoferrate (II) was tested in the following solution:

Copper sulfate ---------- mole--	0.06
Tetrasodium ethylenediamine tetraacetate-do----	0.13
Phenyl polyethylene ether phosphate--percent--	0.1
Formaldehyde ---------- mole--	0.08
Sodium cyanide ---------- do----	0.0005
pH (measured at 25° C.) ----------	11.9
Water sufficient to make 1 liter.	
Temperature, °C. ----------	60

The rates of deposit from this solution at 60° C. with increasing quantities of hexacyanoferrate were as follows:

$K_4Fe(CN)_6.3H_2O$ (gram/liter)	Copper thickness (microns/hour)
0	1.3
0.025	1.8
0.25	1.8

The accelerators described herein, in addition to improving deposition rate, also act as stabilizers and brighteners.

Practice of the invention with cyanoiridite compound is illustrated by the following example:

Solution ----------	1	2	3
Copper sulfate (moles/liter) ----------	0.1	0.1	0.1
E.D.T.A. (moles/liter) ----------	0.1	0.1	0.1
Formaldehyde (moles/liter) ----------	0.12	0.12	0.12
Surfactant [2] (percent) ----------	0.01	0.01	0.01
Lactonitrile (mg./liter) ----------	40	40	40
Potassium cyanoiridite _mg./liter) ----------	0	0.1	1.0
pH ----------	12.8	12.8	12.8
Operating temperature ----------	[1] R.T.	[1] R.T.	[1] R.T.
Copper deposited in 1 hr. (mg./cm.^{2}) ----------	0.68	0.75	0.79

[1] Room Temperature.
[2] Triton QS-15.

Practice of the invention with a cyanorhenate compound is illustrated by the following example:

Solution ----------	1	2	3	4
Copper sulfate (moles/liter) ----------	0.1	0.1	0.1	0.1
E.D.T.A. (moles/liter) ----------	0.1	0.1	0.1	0.1
Formaldehyde (moles/liter) ----------	0.12	0.12	0.12	0.12
Surfactant [2] (percent) ----------	0.01	0.01	0.01	0.01
Lactonitrile (mg./liter) ----------	40	40	40	40
Potassium cyanorhenate (mg./liter) --	0	1.8	18	180
pH ----------	12.8	12.8	12.8	12.8
Operating temp ----------	[1] R.T.	[1] R.T.	[1] R.T.	[1] R.T.
Copper deposit in 1 hr. (mg./cm.^{2}) ---	0.43	0.47	0.48	0.51

[1] Room Temperature.
[2] Triton QS-15.

The invention in its broader aspects is not limited to the specific steps, processes and compositions shown and described, but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed:

1. In an autocatalytic copper plating solution comprising water, copper ions, a complexing agent for the copper ions, a reducing agent for said copper ions and an agent capable of rendering the solution alkaline; the improvement in which the solution comprises a water-soluble compound containing a cyanide radical (CN^-) complexed with a metal selected from Group VIII of the Periodic Table of Elements, said compound being present in an amount which is sufficient to accelerate the deposition rate of the copper ions.

2. The solution of claim **1** wherein the compound contains a radical selected from the group consisting of hexacyanoferrate (II), hexacyanoferrate (III) and mixtures thereof.

3. The solution of claim **1** wherein the concentration of said compound is from about 1 to 300 parts per million, calculated as the metal with which the cyanide radical is complexed.

4. The solution of claim **3** wherein the metal is selected from the group consisting of iron, iridium and rhenium.

5. The solution of claim **1** wherein the copper ion reducing agent is formaldehyde.

6. In a process for depositing copper from an autocatalytic plating solution, the improvement which comprises contacting a substrate with the autocatalytic plating solution of claim **1.**

7. The process of claim **6** wherein the autocatalytic copper plating solution comprises a compound in which the cyanide radical is selected from the group consisting of hexacyanoferrate (II), hexacyanoferrate (III) and mixtures thereof.

8. The process of claim **7** wherein said compound is present in an amount of from about 1 to 300 parts per million, calculated as iron.

9. The process of claim **8** wherein said compound is present in an amount of from about 1 to 50 parts per million.

10. The process of claim **6**, wherein the autocatalytic plating solution comprises formaldehyde as a reducing agent for copper.

11. The solution of claim 1 comprising from about 0.002 to 1 mole per liter of a water soluble copper salt, a complexing agent for the copper ion in a concentration of from about 0.7 to 40 times the moles of the copper salt, from about 0.01 to 4 moles per liter of formaldehyde, a sufficient amount of an alkali metal hydroxide to render the pH of the solution from 10 to 14 and from 1 to 300 parts per million, based on iron, of a member selected from the group consisting of hexacyanoferrate (II), hexacyanoferrate (III) and mixtures thereof.

12. The solution of claim 11 wherein said member selected from the group consisting of hexacyanoferrate (II), hexacyanoferrate (III) and mixtures thereof are in the form of a salt of a member selected from the group consisting of alkali metal, alkaline earth metal and ammonium.

13. A method of accelerating the rate of deposition of an autocatalytic copper plating solution which comprises

maintaining in said solution a member selected from the group consisting of hexacyanoferrate (II), hexacyanoferrate (III) and mixtures thereof, in an amount which is sufficient to accelerate the deposition rate of copper ions.

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