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3,475,186 10/1969 Dutkewych 106/1
 3,310,430 3/1967 Schneble et al..... 117/130

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[54] **ELECTROLESS COPPER PLATING**
19 Claims, No Drawings

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117/47, 117/130, 117/160
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 [50] Field of Search..... **106/1;**
117/130, 130 E, 47 R, 35 S, 213, 227, 160

[56] **References Cited**

UNITED STATES PATENTS

3,093,509 6/1963 Wein 117/213
 3,134,690 5/1964 Eriksson 117/213

ABSTRACT: An electroless copper plating solution comprising a source of cupric ions, hydroxyl radicals, formaldehyde or a formaldehyde precursor, preferably paraformaldehyde, and a complexing agent for copper; said solution characterized by the addition of a combination of additives comprising an organic silicon compound and a hydrogen inclusion retarding agent and preferably, the combination of the two with at least one member selected from the group consisting of a formaldehyde addition agent and a Group VIII metal salt of the Periodic Chart of the Elements. Copper plate deposited from a solution of this invention is distinguishable from prior art copper deposits by substantially improved bending or tensile properties and a smoother, more highly reflecting appearance. The electroless copper plating solution is capable of providing a rapid rate of copper deposition dependent upon the selection of the complexing agent and the stability of its chelate with copper without sacrifice in tensile or bending properties of the copper deposit.

ELECTROLESS COPPER PLATING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a metal depositing composition and more particularly, to an electroless copper plating solution capable of providing an electroless copper deposit of improved bending or tensile properties and having a highly reflective appearance.

2. Description of the Prior Art

Electroless copper deposition refers to the chemical plating of copper over active surfaces by chemical means in the absence of an external electric current. Such processes and compositions useful therefor are known and are in substantial commercial use. They are disclosed in a number of prior art patents, for example, U.S. Pat. Nos. 2,938,805; 3,011,920; 3,310,430; and 3,383,224.

Known electroless copper deposition solutions generally comprise four ingredients dissolved in water. They are (1) a source of cupric ions, usually a copper salt, such as copper sulfate (2) a reducing agent such as formaldehyde, or preferably, a formaldehyde precursor such as paraformaldehyde (3) hydroxide, generally an alkali metal hydroxide and usually sodium hydroxide, sufficient to provide the required alkaline solution in which said compositions are effective, and (4) a complexing agent for copper sufficient to prevent its precipitation in alkaline solution. A large number of suitable complexing agents are known and described in the above-cited patents, and also in U.S. Pat. Nos. 2,874,072; 3,075,856; 3,119,709; 3,075,855 and 3,329,512 all incorporated herein by reference. Known electroless copper solutions of the above type usually provide a plate which is mechanically dense and strong, is somewhat brittle such that it can withstand only limited bending or thermal stress without fracture. This is not a substantial disadvantage where the electroless plate is of the order of millionths of an inch of thickness and is overplated with ductile electrolytic copper. However, where the entire desired thickness, typically 1 to 3 mils in an electrical application, is provided by electroless plating, limited ductility is a serious limitation.

One means of improving bending or tensile characteristics of an electroless copper plate is described in U.S. Pat. No.

herein by reference. Improved properties are obtained by the addition of a silicon compound to an electroless copper solution where silicon is believed to be the active agent. A major advantage of this system is that the rate of copper deposition does not substantially affect tensile or bending properties. The manner in which a silicon compound improves tensile properties is not fully understood but is believed to be due, at least in part, to a surface effect resulting in deposition of a smoother deposit having fewer structural defects as will be explained in greater detail below.

A copper deposition solution capable of providing a copper plate having substantially improved tensile or bending properties is disclosed in copending U.S. Pat. application Ser. No. 752,250 filed concurrently herewith. Improved properties are obtained by the addition of a formaldehyde addition agent and/or a salt of a Group VIII metal of the Periodic Chart of the Elements, preferably a mixture of the two in combination with a silicon compound.

STATEMENT OF THE INVENTION

The subject invention is an improvement over that described in the above-noted U.S. Pat. Nos. 3,310,430 and 3,475,186 and provides an electroless copper solution capable of depositing an electroless copper plate of improved bending or tensile properties. The copper solution is characterized by the addition of the combination of a silicon compound and a hydrogen inclusion retarding agent, preferably a cyanide compound and preferably the combination of the two with at least one member selected from the group consisting of a formaldehyde addition agent and a salt of Group VIII metal of the Periodic Chart of the Elements. The addition of the hydrogen inclusion retarding agent to a solution containing an organic silicon compound produces a synergism resulting in substantially increased tensile or bending properties. The further addition of a formaldehyde addition agent or a salt of a Group VIII metal provides a further substantial improvement in properties, especially where a combination of the two are used. In addition to the above-noted improvement in ductility properties, electroless copper deposits from the solutions of this invention provide the further advantages of excellent laydown

		Preferred
Copper salt.....	0.002 mole to saturation.....	0.02 to 0.12 mole.
Formaldehyde.....	0.05 to 3.5 moles.....	0.1 to 1 mole.
Complexing agent.....	Minimum necessary to maintain copper in solution.....	About 1 to 3 times the moles of cupric.
Free hydroxide.....	Sufficient to provide pH 10 or greater.....	0.1 to 0.8 mole.
Hydrogen inclusion retarding agent.....	1 to 1,000 p.p.m.....	5 to 500 p.p.m.
Silicon compound.....	Greater than 1 p.p.m.....	5 to 250 p.p.m.
Formaldehyde addition agent.....	To that amount that restricts deposition.....	0.1 to 1 times the moles of formaldehyde.
Group VIII metal salt.....	5 to 2,500 p.p.m.....	30 to 1,000 p.p.m.
Water.....	To 1 liter of solution.....	To 1 liter of solution.

3,310,430 which discloses the addition to a copper plating solution of a water soluble compound of cyanide, vanadium, molybdenum, niobium, tungsten, arsenic, antimony, bismuth, rare earths of the actinium series and rare earths of the lanthanum series. Certain members of the above group, especially the vanadium compounds, provide significantly improved bending characteristics. The reason for this is not fully understood but is stated in the patent that the agents poison the catalytic surface so as to promote formation and release of hydrogen gas at the catalytic surface, thereby inhibiting the inclusion of hydrogen in the deposit as it forms. It has been found that where a complexing agent or bath formulation is used permitting rapid deposition of copper with rapid evolution of hydrogen gas at the surface, the improved ductility or bending characteristics are frequently sacrificed or lost.

An alternative means for improving the tensile properties of an electroless copper deposit while simultaneously improving brightness and other appearance properties as described in commonly assigned U.S. Pat. No. 3,475,186 incorporated

properties, excellent solderability, and improved smoothness, brightness, and overall appearance.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A typical electroless copper solution in accordance with the invention will have additives in the following concentration ranges:

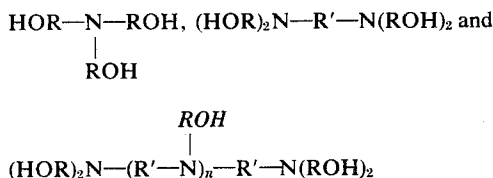
It should be understood that the above concentration ranges are preferred, but not critical. Variation in the ranges are possible without departing from the scope of the invention. In most cases, additives may be added in an amount up to that amount that poisons the solution.

In the above formulations, any water soluble copper salt heretofore used for preparing electroless copper deposition solutions may be used. For example, the halides, nitrate, acetate, sulfate and other organic and inorganic acid salts of

copper are generally suitable as is known in the art. Copper sulfate is preferred.

Suitable complexing agents for the copper ions include Rochelle salts, the sodium salts (mono, di, tri, and tetrasodium salts) of ethylenediaminetetraacetic acid, nitrilotriacetic acid and its alkali metal salts, triethanolamine, modified ethylenediaminetetraacetic acids such as N-hydroxyethylenediaminetriacetate, hydroxyalkyl substituted-dialkylene triamines such as pentahydroxypropyldiethylenetriamine, sodium salicylate, and sodium tartrate. Other complexing agent for copper ions are disclosed in U.S. Pat. Nos. 2,996,408; 3,075,855; 3,075,856; and 2,938,805.

The preferred class of complexing agents are those described in U.S. Pat. No. 3,329,512 noted above. They include hydroxyalkyl substituted tertiary amines corresponding to one of the following structures:



where R is an alkyl group having from two to four carbon atoms, R' is a lower alkylene radical and n is a positive integer. Examples of these complexing agents include tetrahydroxypropyl ethylene diamine, pentahydroxypropyl diethylene triamine, trihydroxypropylamine triisopropanolamine), trihydroxypropyl hydroxyethyl ethylene diamine, etc. As disclosed in said patent, the aforesaid amines are preferably used in small amounts in combination with other complexing agents and with certain polymers dispersed in solution such as cellulose ethers, hydroxyethyl starch, polyvinyl alcohol, polyvinylpyrrolidone, peptones, gelatin, polyamides and polyacrylamides.

The rate of copper deposition is, to some extent, dependent upon the selection of the complexing agent. Complexing agents such as pentahydroxypropyldiethylenetriamine provide a fast rate of copper deposition, usually in excess of 1.0 mils per hour. Though the copper solutions of this invention provide copper deposits from solutions containing any of the known complexing agents for copper ions, they are particularly well adapted for copper solutions having complexing agents that provide a rapid rate of copper deposition.

The silicon additive is one that is soluble in the copper solution and comprises the organic silicon compounds disclosed in the above-noted Pat. No. 3,475,186. It should be noted that many silicon compounds are not fully soluble in aqueous alkaline solutions and many are considered insoluble. However, the silicon, for purposes of the present invention, is required in solution in parts per million and silicon compounds termed insoluble in aqueous solution usually are soluble to the extent of a few parts per million and suitable for purposes of the present invention. For those silicon compounds considered insoluble in water, it is desirable to dissolve the compound in a solvent, such as alcohol, and add the solution to the electroless copper solution with agitation to form a dispersion or an emulsion. An excess of the silicon compound will be required to provide the necessary concentration of silicon compound in solution.

Exemplary of the silicon compound within the scope of the invention are the silanes, such as silane itself, disilane, tetramethylsilane, trimethylethylsilane, tetraethylsilane, tetraphenylsilane, dimethyldichlorosilane, etc., and low to intermediate molecular weight polysiloxanes such as silicone fluids, gums, and resins substituted with methyl, ethyl, vinyl, phenyl, chloro, bromo, methoxy, hydroxy, etc. Other suitable organic silicon compounds are disclosed in the above-noted U.S. Pat. No. 3,475,186.

The polysiloxanes are the least soluble silicon compounds in basic copper solution, but are preferred because they provide

the greatest increase in ductility and also enhance appearance by yielding a finer grained, more highly reflecting copper deposit. Of the polysiloxanes, the silicon fluids are most preferred. The solid polysiloxanes are preferably dissolved in a solvent such as alcohol and added to the copper solution.

The hydrogen inclusion retarding agent is of the same class disclosed in the above-noted U.S. Pat. No. 3,310,430 and includes simple and complex compounds which comprise one or more compounds or cyanide, vanadium, molybdenum, niobium, tungsten, rhenium, arsenic, antimony, bismuth, actinium, lanthanum, rare earths of both the lanthanum and actinium series and mixtures of the foregoing.

Preferred are those compounds which consist of or comprise elements of the type described which have at least two oxidation states. In this preferred group are compounds comprising vanadium, niobium, molybdenum, tungsten, rhenium, arsenic, antimony, bismuth, cerium, praseodymium, neodymium, samarium, europium, terbium, uranium, and mixtures of the foregoing. These elements are preferably added to the electroless copper plating baths in a form such that the element is at its most stable valence state. Vanadium and cyanide compound such as alkali metal cyanides exemplified by sodium cyanide and potassium cyanide as disclosed in the above-noted U.S. Pat. No. 3,310,430 are the most preferred hydrogen inclusion retarding agents. Where cyanide is selected as the hydrogen inclusion retarding agent, it may appear twice in the formulation dependent upon the selection of the remaining additives.

The hydrogen inclusion retarding agent is added to the bath, preferably as a soluble salt. For example, molybdenum may be supplied as molybdic trioxide as well as water soluble organic and inorganic acid salts of molybdenum, as for example alkali and alkaline earth metal, or ammonium molybdates. Suitable sources of tungsten, molybdenum, rhenium and arsenic are the oxides of such elements, as well as organic and inorganic acid water soluble salts of such elements, e.g., the tungstates, vanadates, arsenates, and rhenates of the metals of Groups I-A and II-A of the Periodic Chart of the Elements, and ammonium. Preferred for use are the sodium, potassium, and ammonium salts. Sources of antimony, bismuth, lanthanum, actinium, and rare earths are the oxides of such elements and water soluble organic and inorganic acid salts of such elements, including the sulfates, nitrates, halides, acetates, and the like. The function of the hydrogen inclusion retarding agent is not fully understood, but it is reported that it tends to poison the catalytic surface so as to promote the formation and release of hydrogen gas to the catalytic surface on which copper is depositing electrolessly, thereby inhibiting the inclusion of hydrogen in the deposit as it forms.

The formaldehyde addition agent for purposes of this invention is one that may be added to solution in amounts sufficient to undergo reaction with formaldehyde to form a relatively unstable formaldehyde adduct. Reactions of this nature and formaldehyde, addition agents are well known in the art and described in various publications, such as *Formaldehyde* J. Frederick Walker, Reinhold Publishing Company, Third Edition 1964, pages 219 to 221, included herein by reference. Preferred addition agents are sulfites, bisulfites, and phosphites of a metal cation that does not codeposit with copper and preferably an alkali metal cation. Preferred formaldehyde addition agents are sodium sulfite, potassium bisulfite and sodium phosphite.

The formaldehyde addition agent and formaldehyde or preferably, paraformaldehyde are reacted with each other to form the adduct prior to addition to the remaining components of the copper solution.

The Group VIII metal salts include water-soluble inorganic salts of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum, salts of iron, nickel and platinum being most preferred and salts of palladium being least preferred due to solution stability problems caused by palladium. Suitable salts include phosphates, nitrates, halides,

and acetates of the above metals. A wetting agent may be added to solution in accordance with art recognized procedures.

The baths may be used at widely varying temperatures, e.g., at least room temperature and preferably up to 140° F. As temperature is increased, it is customary to find an increase in the rate of plating. Temperature is not highly critical, and within the usual operating ranges, excellent, bright deposits of electroless copper having excellent tensile or bending properties are obtained. Preferably, the bath is used without agitation.

In using the electroless copper solution to plate metal, the surface to be plated should be catalytically active and free of grease and contaminating material. Where a nonmetallic surface is to be plated, the surface area to receive the deposit must first be sensitized to render it catalytically active as by the well-known treatment with an acidic aqueous solution of stannous chloride followed by treatment with a dilute aqueous acidic solution of palladium chloride. Alternatively, extremely good sensitization of nonmetallic surfaces is achieved by contact with an acidic colloidal formulation formed by the admixture of stannous chloride and a precious metal chloride, preferably palladium chloride, the stannous chloride being present in stoichiometric excess based upon the amount of precious metal chloride.

The invention will be better understood by reference to the following examples where all parts were plated using the following procedure:

- Cut a phenolic substrate to a size of 2 inches × 2 inches.
- Scrub part clean using an abrasive cleaner.
- Rinse in cold water.
- Immerse in a solution of a wetting agent identified as Shipley Conditioner 1159 at room temperature for 1 to 3 minutes.
- Rinse in cold water.
- Immerse in a colloidal stannic acid-palladium catalyst (identified as Cuposit Catalyst 6F) maintained at room temperature for 1 to 5 minutes.
- Rinse in cold water.
- Immerse in Cuposit Accelerator 19 or a mild perchloric acid solution maintained at room temperature for 3 to 10 minutes.
- Rinse in cold water.
- Immerse in electroless copper solution maintained at between 110 and 130° F. for a period sufficient to provide a deposit of desired thickness not to exceed 3 hours.
- Dry parts and examine deposit for appearance and ductility. Ductility is determined by peeling a copper deposit from the substrate and bending through 180° in one direction, creasing at the fold, then returning it to its original position with pressing along the crease to flatten it. This cycle constitutes one bend. The procedure is repeated until the sample breaks at the crease. A sample unable to withstand at least ½ bend is considered brittle.

EXAMPLES 1-20

CuSO ₄ ·5H ₂ O	8.0 g.
Paraformaldehyde	7.5 g.
NaOH(25% solution by wt.)	50.0 ml.
tetrahydroxypropylene diamine	12.0 g.
triisopropanolamine	2.0 g.
Water	to 1 liter of solution

The above formulation, with various additives was used to deposit electroless copper. Additive composition and deposit properties are set forth in the following table:

Ex. No.	Additives	Additive concentration	Deposit appearance	Deposit thickness (in. × 10 ⁻³)	Ductility (bends)
1	Control		Poor	0.50	Brittle.
2	NaCN	7 p.p.m.	do	0.29	Do.
3	V ₂ O ₅	20 p.p.m.	Poor	0.37	~½.
4	As ₂ O ₃	10 p.p.m.		0.36	Brittle.
5	Methylvinylsilane.	250 p.p.m.	Fair	0.87	~½.
6	F-1-3514 ¹	200 p.p.m.	do	0.34	~½.
7	SF-1138 ²	200 p.p.m.	do	0.46	~½.
8	NaHSO ₃	20 g./l.	Poor	0.43	Brittle.
9	Na ₂ SO ₃	8 g./l.	do	0.46	Do.
10	NiSO ₄	300 p.p.m.	do	0.09	Do.
11	CoSO ₄	300 p.p.m.	do	0.36	Do.
12	Fe ₂ (SO ₄) ₃	300 p.p.m.	do	0.25	Do.
13	NaCN	7 p.p.m.	Poor	0.32	~½.
	Fe ₂ (SO ₄) ₃	300 p.p.m.			
14	As ₂ O ₃	10 p.p.m.	Poor	0.46	~½.
	CoSO ₄	300 p.p.m.			
15	NaCN	7 p.p.m.	Poor	0.44	~½.
	NaHSO ₃	30 g./l.			
16	V ₂ O ₅	20 p.p.m.	Poor	0.50	~½.
	NiSO ₄	300 p.p.m.			
17	NaCN	7 p.p.m.	Poor	0.43	~½.
	Fe ₂ (SO ₄) ₃	300 p.p.m.			
18	F-1-3514 ¹	200 p.p.m.	Good	0.40	1.
	NaCN	7 p.p.m.			
19	SF-1138 ²	200 p.p.m.	Good	0.32	1½.
	NaCN	7 p.p.m.			
20	NiSO ₄	300 p.p.m.	Good	0.43	2.
	SF-1138 ²	200 p.p.m.			
	NaHSO ₃	20 g./l.			
	NaCN	7 p.p.m.			

(1) F-1-3514 A silicone fluid believed to be a dimethylpolysiloxane-ethylene glycol copolymer available from the General Electric Company. X

(2) SF-1138 A silicone fluid believed to be a dimethylpolysiloxane-polyalkyleneoxide copolymer available from the General Electric Company.

In the above examples, a deposit was considered poor if it was dark in color and powdery. A fair deposit was one lighter in color, though powdery in appearance. A good deposit was one having a fine grained metallic copper appearance.

The improvements in tensile or bending properties using the preferred electroless copper solutions of the present invention are readily apparent by reference to the above examples. Examples 2 to 12 illustrate the use of a single additive. The only single additives showing observable improvement in properties are the silicon and vanadium compounds. Combination of a silicon compound with a cyanide gives greater improvement. Significantly greater improvements are obtained by the combination of a silicon compound, a cyanide compound, and a member selected from the group of a formaldehyde addition agent and a metal salt of a Group VIII metal (Examples 19 to 20).

EXAMPLES 21 to 25

CuSO ₄ ·5H ₂ O	8.0 g.
Formaldehyde	7.5 g.
NaOH(25% solution)	50.0 ml.
Sodium/potassium tartrate	40.0 g.
Water	to 1 liter of solution

The above formulation, with various additives, is used to deposit electroless copper. Additive compositions and deposit properties are set forth in the following table:

Ex. No.	Additive	Additive concentration	Deposit appearance	Ductility (bends)
21	Control		Fair	1
22	F-1-3514 ¹	200 p.p.m.	Good	2
23	NaCN	7 p.p.m.	Fair	1½
24	F-1-3514 ¹	200 p.p.m.	Good	5
	NaCN	7 p.p.m.		
25	NiSO ₄	300 p.p.m.	Good	5+
	F-1-3514 ¹	200 p.p.m.		
	NaCN	7 p.p.m.		
	NiSO ₄	300 p.p.m.		
	NaHSO ₃	20 g./l.		

Copper solutions of this invention find utility for all purposes for which electroless copper solutions have heretofore

been used including both decorative and industrial applications. They are especially useful for the formation of printed circuit boards where the deposits act as a ductile conductor and as a ductile connector plated onto the walls of through-holes. The formation of a printed circuit board having through-holes is illustrated in the following example.

EXAMPLE 26

- a. Sandblast one side of a phenolic substrate leaving the second surface smooth.
- b. Drill through-holes at desired locations.
- c. Silk screen a reverse image of a printed circuit pattern onto the roughened surface of the phenolic substrate using an epoxy resin.
- d. Immerse in a colloidal palladium sensitizing solution maintained at room temperature for a period of five minutes.
- e. Immerse in a stripping solution comprising 10 grams of copper chloride, 100 grams of 37 percent hydrochloric acid, and water to one liter. Maintain solution at room temperature and immerse for 6 minutes.
- f. Deposit electroless copper of example 25 with copper deposition taking place on the walls of the through-holes and on the roughened surfaces in the image pattern. No copper deposition takes place on the epoxy resist nor on the smooth surfaces of the plastic laminate.

The mechanism by which copper deposits from the solution of this invention differs from that of the above-referenced U.S. Pat. No. 3,310,430 where hydrogen inclusion retarding agents alone are used to improve ductility. Though neither mechanism is fully understood, a different mechanism is suggested by the observation that the Group VIII metal cation codeposits with copper, to some extent, in the absence of a hydrogen inclusion retarding agent but codeposition is lessened when a hydrogen inclusion retarding agent is in solution. This is shown by the following examples:

Examples 27 and 28

	27	28
CuSO ₄ ·5H ₂ O (g.)	8.0	8.0
Paraformaldehyde (g.)	7.5	7.5
NaOH (25% solution by wt.) (ml.)	50.0	50.0
Tetrahydroxypropyl ethylene diamine (g.)	15.0	15.0
NaHSO ₃ (g.)	20.0	20.0
V ₂ O ₅ (p.p.m.)	20	
NiSO ₄ (p.p.m.)	300	300

The copper deposits of the above examples were analyzed. In example 27 containing both vanadium and nickel compounds in solution, only 0.00088 percent nickel was found in the deposit. Omission of the vanadium compound in example 28 results in a copper deposit containing 0.100 percent nickel. This indicates that the vanadium somehow retarded the codeposition of nickel.

It should be understood that various changes may be made in the embodiments described above without departing from the spirit and scope of the invention as defined by the following claims:

1. In an aqueous electroless copper plating solution comprising a source of cupric ions, hydroxyl radicals, a source of formaldehyde and sufficient complexing agent to render said cupric ions soluble in alkaline solution, the improvement comprising an additive in the solution of a combination of an organic silicon compound and a hydrogen inclusion retarding agent, said organic silicon compound and said hydrogen inclusion retarding agent being present in combined amounts insufficient to prevent copper deposition and each of said organic silicon compound and said hydrogen inclusion retarding agent being present in solution in an amount of at least one part per million parts of solution.

2. The copper plating solution of claim 1 containing as an additional additive at least one member selected from the group consisting of a formaldehyde addition agent in an amount of at least 0.1 moles per mole of formaldehyde in solution to that amount that prevents deposition of copper and a salt of a Group VIII metal of the Periodic Chart of the Elements in an amount of at least five parts per million parts of solution, said Group VIII metal salt having an anion noninterfering with said solution.

3. In an aqueous electroless copper plating solution comprising a source of cupric ions, hydroxyl radicals, formaldehyde and sufficient complexing agent to render said cupric ions soluble in alkaline solution, the improvement comprising an additive in the solution of an organic silicon compound, a solution-soluble alkali metal cyanide compound, and at least one of a formaldehyde addition agent selected from the group of alkali metal sulfites, bisulfites and phosphites and solution soluble salts of a Group VIII metal selected from the group of iron, nickel and platinum, said salts of a Group VIII metal having an anion noninterfering with said electroless copper solution, said organic silicon compound and said alkali metal cyanide being present in solution in combined amount insufficient to prevent copper deposition, each of said organic silicon compound and said alkali metal cyanide being present in solution in an amount of at least one part per million parts of solution, said formaldehyde addition agent being in an amount of about 0.1 moles per mole of formaldehyde to that amount that prevents copper deposition and said Group VIII metal salt being present in an amount of at least five parts per million parts of solution.

4. The copper plating solution of claim 3 having as additives the silicon compound, the cyanide compound, the formaldehyde addition agent and the Group VIII metal salt.

5. The copper solution of claim 4 where the silicon compound is a silicone fluid.

6. The copper solution of claim 5 where the Group VIII metal salt is selected from the group consisting of NiSO₄, Fe₂(SO₄)₃ and H₂PtCl₆.

7. The copper solution of claim 3 where the formaldehyde addition agent is selected from the group consisting of Na₂SO₃, NaHSO₃ and Na₂HPO₃·5H₂O.

8. The copper solution of claim 5 where the cyanide compound is sodium cyanide.

9. In an aqueous electroless copper plating solution comprising a source of cupric ions, hydroxyl radicals, a source of formaldehyde and sufficient complexing agent to render said cupric ions soluble in alkaline solution, the improvement comprising an additive in the solution of a combination of an organic silicon compound and a hydrogen inclusion retarding agent selected from the group consisting of a water soluble cyanide compound, vanadium, molybdenum, niobium, tungsten, rhenium, arsenic, antimony, bismuth, rare earths of the actinium series, rare earths of the lanthanum series and mixtures of the foregoing, said organic silicon compound and said hydrogen inclusion retarding agent being present in a combined amount insufficient to prevent copper deposition and said organic silicon compound and said hydrogen inclusion retarding agent being present in solution in an amount of at least 1 part per million parts of solution.

10. The copper plating solution of claim 9 containing as an additional additive at least one member selected from the group consisting of a formaldehyde addition agent in an amount of at least 0.1 moles per mole of formaldehyde in solution to that amount that prevents copper deposition and a salt of a Group VIII metal of the Periodic Chart of the Elements in an amount of at least five parts per million parts of solution, said formaldehyde addition agent being selected from the group consisting of metal salts of a member selected from the group consisting of sulfites, bisulfites and phosphites, and said salt of a Group VIII metal being selected from the group consisting of salts of platinum, iron and nickel and having an anion noninterfering with said electroless copper plating solution.

11. The copper solution of claim 10 having as additives, the

silicon compound, the hydrogen inclusion retarding agent and the formaldehyde addition agent.

12. The copper solution of claim 10 having as additives, the silicon compound, the hydrogen inclusion retarding agent and the Group VIII metal salt.

13. The copper solution of claim 10 having as additives, the silicon compound, the hydrogen inclusion retarding agent, the formaldehyde addition agent and the Group VIII metal salt.

14. The copper solution of claim 13 having the following formulation:

copper salt	0.02 to 0.12 moles
formaldehyde	0.1 to 1 moles
complexing agent	1 to 3 times the moles of cupric ion
free hydroxide	0.1 to 0.8 moles
hydrogen inclusion retarding agent	5 to 250 p.p.m.
silicon compound	5 to 250 p.p.m.

formaldehyde addition

agent
Group VIII metal salt
Water

0.1 to 1 times the moles of formaldehyde
30 to 1,000 p.p.m. to 1 liter of solution

- 5 15. The copper solution of claim 10 where the organic-silicon compound is selected from the group consisting of silanes and polysiloxanes.
- 10 16. The copper solution of claim 15 where the silicon compound is a polysiloxane.
- 15 17. The copper solution of claim 10 where the silicon compound is added to the copper solution by dissolution in a solvent and addition of the solution to the copper solution.
- 15 18. The copper solution of claim 9 where the hydrogen inclusion retarding agent is an alkali metal cyanide.
- 15 19. The copper solution of claim 18 where the alkali metal cyanide compound is sodium cyanide.

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