United States Patent

[11] 3,615,732

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[21] Appl. No. **752,165**
[22] Filed **Aug. 13, 1968**
[45] Patented **Oct. 26, 1971**
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[54] **ELECTROLESS COPPER PLATING**
16 Claims, No Drawings

[52] **U.S. Cl.** **106/1,** 117/47, 117/130, 117/160
[51] **Int. Cl.** **C23c 3/02**
[50] **Field of Search** ..... 106/1; 117/130 E, 130, 47 R, 35 S, 213, 227

[56] **References Cited**

UNITED STATES PATENTS

3,093,509	6/1963	Wein	117/35 X
3,134,690	5/1964	Eriksson	117/47 X
3,310,430	3/1967	Schneble et al.	106/1 X
3,329,512	7/1967	Shipley et al.	106/1

FOREIGN PATENTS

401,083	1/1965	Japan	106/1

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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 hydrogen inclusion retarding agent and at least one member selected from the group consisting of a formaldehyde addition agent and a salt of a Group VIII metal of the Periodic Chart of the Elements. The electroless copper plating solution is capable of providing a rapid rate of copper deposition dependent upon the selection of the complexing agent without sacrifice in tensile properties of the copper deposit. The copper plate deposited from the electroless solution of this invention is distinguishable from prior art electroless copper deposits by substantially improved bending or ductility properties.

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 electroless copper deposit of improved bending or ductility properties.

2. Description of the Prior Art

Electroless copper deposition refers to the chemical plating of copper over clean catalytically active surfaces by chemical reduction 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) free 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 on 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 plating solutions of the above type usually provide a plate which, if 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 in 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 for improving the tensile properties of an electroless copper deposit while simultaneously improving brightness and other appearance properties is described in U.S. Pat. 3,475,186 filed Jan. 5, 1968, and incorporated herein by reference. Improved properties are obtained by the addition of an organic silicon compound to be 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 properties. The manner in which the silicon compound improves tensile properties is not fully understood but it is believed to be due, at least in part, to a surface effect resulting in deposition of a smoother deposit having fewer structural defects.

An improved method for improving tensile properties is set forth in copending U.S. Pat. application Ser. No. 752,250 filed concurrently herewith. In a preferred embodiment, a combination of additives comprising a silicon compound, a formaldehyde addition agent, and a salt of a Group VIII metal of the Periodic Chart of the Elements is added to the electroless copper bath. Electroless copper deposited from said bath is characterized by substantially improved tensile properties resulting from a synergistic reaction between the additives and possesses increased tensile properties, improved brightness and substantially improved solderability.

An additional method for improving the bending or tensile properties of an electroless copper plate using a different mechanism is described in U.S. Pat. No. 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 group, especially the vanadium compounds, provide significantly improved bending characteristics. The reason for this is not fully understood but it is stated in the patent that the agents poison the catalytic surface so as to promote formation and release of hydrogen at the catalytic surface, thereby inhibiting the inclusion in the deposit as it forms. It has been found that where a complexing agent or a 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.

STATEMENT OF THE INVENTION

The subject invention is an improvement over that described in the above-noted U.S. Pat. No. 3,310,430 in that it avoids the disadvantages noted above and provides an electroless copper solution capable of depositing an electroless copper plate having substantially improved bending or tensile properties regardless of the rate of copper deposition and the complexing agent used. The copper solution is characterized by the addition of a hydrogen inclusion retarding agent and at least one member selected from the group consisting of a formaldehyde addition agent, and a salt of a Group VIII metal of the Periodic Chart of the Elements. In addition to an improvement in bending or tensile properties, electroless copper deposits from the solutions of this invention provide the further advantages of excellent laydown properties, and excellent solderability along with improvement in 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:

		Preferred
Copper salt	0.002 moles to saturation	0.02 to 0.12 moles
Formaldehyde	0.05 to 3.5 moles	0.1 to 1 moles
Complexing agent	minimum necessary to maintain copper in solution	1 to 3 times the moles of cupric ion
Free hydroxide	Sufficient to provide pH 10 or greater	0.1 to 0.8 moles
Hydrogen inclusion retarding agent	1 to 1000 p.p.m.	5 to 250 p.p.m.
Formaldehyde addition agent	up to that amount that restricts deposition	0.1 to 1 times the moles of formaldehyde
Group VIII metal salt	5 to 2500 p.p.m.	30 to 1000 p.p.m.
Water	to 1 liter of solution	

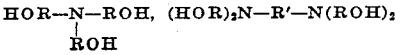
It should be understood that the above concentration ranges are preferred but not critical. Variations in the ranges are possible without varying from the scope of the invention. In most cases, additives may be added in any amount up to that amount that poisons the solution and prevents deposition.

In the above formulations, any water soluble copper salt heretofore used for preparing electroless copper deposition solutions may be used. For example, certain of 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 are well known in the art and 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 agents 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:



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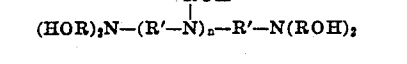

where R is an alkyl group having from two to four carbon atoms, R' is a lower alkylene radical and n is a positive integer. Examples of these complexing agents include tetrahydroxypropyl ethylene diamine, pentahydroxypropyl diethylene triamine, trihydroxypropylamine (tripropanolamine), trihydroxypropyl 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 rapid 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 solution having complexing agents that provide a rapid rate of copper deposition.

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 of 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 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 at 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 without poisoning the solution. 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 formaldehyde addition agents include alkali and alkaline earth metal 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, sodium bisulfite, potassium sulfite 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 are preferably water soluble inorganic salts of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum; salts of nickel, iron 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.

The cyanide compound is a water soluble compound such as an alkali metal cyanide, such as sodium cyanide, potassium cyanide, sodium nitrile, potassium nitrile, organic nitriles such as alphahydroxynitrile, e.g., glycolnitrile and lactonitrile, and dinitriles, such as iminodiacetonitrile and 3,3'-iminodipropionitrile.

A wetting agent may be added to solution in accordance with art recognized procedure.

The bath 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 ductility 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:

a. Cut a phenolic substrate to a size of 2" ×2."

b. Scrub part clean using an abrasive cleaner.

c. Rinse in cold water.

d. Immerse in a solution of a wetting agent identified as Shipley Conditioner 1159 at room temperature for 1 to 3 minutes.

e. Rinse in cold water.

f. Immerse in a colloidal stannic acid-palladium catalyst (identified as Cuposit Catalyst 6F) maintained at room temperature for 1 to 5 minutes.

g. Rinse in cold water.

h. Immerse in a Cuposit Accelerator 19 or a mild perchloric acid solution maintained at room temperature for 3 to 10 minutes.

i. Rinse in cold water.

j. 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.

k. Dry parts and analyze the deposit for appearance and ductility. Ductility is determined by peeling a copper deposit from the substrate and bending it through 180° F. 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 one-half bend is considered brittle.

EXAMPLES 1–20

$CuSO_4 \cdot H_2O$	8.0 g.
Paraformaldehyde	7.5 g.
NaOH (25% solution by wt.)	50.0 ml.
Tetrahydroxypropylethylene amine	12.0 g.
Triisopropanoldiamine	2.0 g.
Water	to 1 l. 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:

Example number	Additive	Additive concentration	Deposit appearance	Deposit thickness, in.$\times 10^{-3}$	Ductility (bends)
1	Control		Poor	0.50	Brittle.
2	V_2O_5	20 p.p.m.	Poor	0.37	~½.
3	AS_2O_3	10 p.p.m.	Poor	0.36	Brittle.
4	NaCN	7 p.p.m.	Poor	0.29	Do.
5	$NiSO_4$	300 p.p.m.	Poor	0.09	Do.
6	$CoSO_4$	300 p.p.m.	Poor	0.36	Do.
7	$Fe_2(SO_4)_3$	300 p.p.m.	Poor	0.25	Do.
8	H_2PtCl_6	150 p.p.m.	Good	0.10	N.m.
9	O_8O_4	100 p.p.m.	Poor	0.14	Brittle.
10	$NaHSO_3$	20 g./l.	Poor	0.43	Do.
11	Na_2SO_3	8 g./l.	Poor	0.46	Do.
12	$Na_2HPO_3 \cdot 5H_2O$	20 g./l.	Fair	0.45	Do.
13	V_2O_5 + $NiSO_4$	20 g./l. + 300 p.p.m.	Poor	0.50	~½.
14	As_2O_3 + $CoSO_4$	10 p.p.m. + 300 p.p.m.	Poor	0.46	~½.
15	V_2O_5 + $NaHSO_3$	20 p.p.m. + 20 g./l.	Poor	0.45	~½.
16	NaCN + $Fe(SO_4)_3$	7 p.p.m. + 300 p.p.m.	Poor	0.32	~½.
17	NaCN + $NaHSO_3$	7 p.p.m. + 20 g./l.	Poor	0.44	~½.
18	NaCN + $Fe_2(SO_4)_3$ + $NaHSO_3$	7 p.p.m. + 300 p.p.m. + 20 g./l.	Poor	0.43	1½.
19	V_2O_5 + $NiSO_4$ + $NaHSO_3$	20 p.p.m. + 300 p.p.m. + 20 g./l.	Poor	0.50	1½.
20	As_2O_3 + $CoSO_4$ + Na_2SO_3	10 p.p.m. + 300 p.p.m. + 8 g./l.	Poor	02.9	1½.

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 properties using the electroless copper solutions of the present invention are readily apparent by reference by the above examples. Examples 2 to 4 illustrate copper solutions containing only a hydrogen inclusion retarding agent. Examples 5 to 9 illustrate copper solutions containing only a Group VIII metal salt. Examples 10 to 12 illustrate copper solutions containing only a formaldehyde addition agent. Using any of these single additives alone, little or no improvement in tensile properties is obtained. In examples 13 to 17, there is represented combinations of two additives resulting in minor improvements in tensile properties. Examples 18 to 20 represent deposits formed from solutions of the subject invention and illustrate a minimum of a 300 percent increase in ductility as measured by bending. It should be noted that the base formulation is one typically providing brittle deposits. Greater increases in tensile properties are possible with other copper solutions as will be illustrated below.

EXAMPLES 21-25

$CuSO_4 \cdot 5H_2O$	8.0 gm.
Paraformaldehyde	7.5 gm.
NaOH (25% solution)	50.0 ml.
Ethylenediaminetetraacetic acid	30.0 gm.
Water	To 1 liter of solution.

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

Ex. No.	Additive	Additive concentration	Deposit appearance	Deposit thickness in.$\times 10^{-3}$	Ductility (bends)
21	Control		Fair	0.19	Brittle.
22	As_2O_3	10 p.p.m.	Fair	0.29	Do.
23	As_2O_3 + $NiSO_4$	10 p.p.m. + 300 p.p.m.	Poor	0.32	~½.
24	As_2O_3 + $NaHSO_3$	10 p.p.m. + 20 g./l.	Poor	0.31	~½.
25	As_2O_3 + $NiSO_4$ + $NaHSO_3$	10 p.p.m. + 300 p.p.m. + 8 g./l.	Fair	0.30	2.

Example 25 of the above represents a substantial improvement in tensile properties.

EXAMPLES 26-29

$CuSO_4 \cdot 5H_2O$	8.0 gm.
Formaldehyde	7.5 gm.
NaOH (25% solution)	50.0 ml.
Sodium/potassium tartrate	40.0 gm.
As_2O_3	10 p.p.m.
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	Additive thickness in.$\times 10^{-3}$	Additive appearance	Ductility (bends)
26	Control		0.06	Fair	~½
27	NaCN	7 p.p.m.	0.30	Good	1
28	NaCN + $NiSO_4$	7 p.p.m. + 300 p.p.m.	0.17	Good	3
29	NaCN + $NiSO_4$ + $NaHSO_3$	7 p.p.m. + 300 p.p.m. + 8 g./l.	0.23	Good	5+

In the above, example 26 represents a poor control sample because of the thinness of the deposit. A thicker deposit would probably be brittle. However, the combination of the hydrogen inclusion retarding agent, Group VIII metal salt and formaldehyde addition agent provides deposits substantially improved over that of the control capable of withstanding in excess of five bends without fracturing.

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 deposit acts as a ductile conductor both in a circuit pattern and on the walls of through-holes. The formation of a printed circuit board having conductive through-holes is illustrated in the following example:

EXAMPLE 30

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 resist.

d. Immerse in a colloidal palladium sensitizing solution maintained at room temperature for a period of 5 minutes.

e. Immerse in a stripping solution comprising 10 grams of copper chloride, 100 grams of 37 percent hydrochloric acid, and water to 1 liter. Maintain stripping solution at room temperature and immerse part in solution 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 an image pattern. No copper deposition takes place on the epoxy resist or on the smooth side 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 31–32

	31	32
$CuSO_4 \cdot 5H_2O$	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_2O_5 (p.p.m.)	20	
$NiSO_4$ (p.p.m.)	300	300

The copper deposits of the above examples were analyzed. In example 31 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 32 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:

We claim:

1. In an 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 solution of at least one hydrogen inclusion retarding agent in an amount of from 1 to 1,000 parts per million parts of solution, said hydrogen inclusion retarding agent being selected from the group consisting of solution soluble compounds of alkali and alkaline earth metal cyanides and nitriles, vanadium, molybdenum, niobium, tungsten, rhodium, arsenic, antimony, bismuth, rare earths of the actinium series, rare earths of the lanthanum series and mixtures thereof; and at least one solution soluble member selected from the group consisting of a formaldehyde addition agent in an amount of from 0.1 moles times the moles of formaldehyde to 1 times the moles of formaldehyde, said agent being selected from the group consisting of alkali metal sulfites, bisulfites, and phosphites; and a salt of a member selected from the group of iron, nickel, and platinum in an amount of from 5 to 2500 parts per million parts of solution, said salt having an anion noninterfering with said electroless copper solution.

2. The copper plating solution of claim 1 having as additive at least one hydrogen inclusion retarding agent and a salt of Group VIII metal.

3. The copper plating solution of claim 1 having as additive at least one hydrogen inclusion retarding agent and a formaldehyde addition agent.

4. The copper plating solution of claim 1 having as additive at least one hydrogen inclusion retarding agent, a salt of a Group VIII metal and a formaldehyde addition agent.

5. The copper plating solution of claim 1 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.
formaldehyde addition agent	0.1 to 1 times the moles of formaldehyde
Group VIII metal salt	30 to 1000 p.p.m.
Water	to 1 liter of solution

6. The copper plating solution of claim 1 where the cyanide compound is sodium cyanide.

7. The copper plating solution of claim 1 where the hydrogen inclusion retarding agent is As_2O_3.

8. The copper plating solution of claim 1 where the hydrogen inclusion retarding agent is V_2O_5.

9. In an electroless copper 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 comprising at least one hydrogen inclusion retarding agent and at least one solution soluble member selected from the group consisting of a formaldehyde addition agent and a salt of a Group VIII metal of the Periodic Chart of the Elements; said hydrogen inclusion retarding agent, and Group VIII metal salt being present in solution in minor amounts sufficient to improve ductility of a copper deposit and said formaldehyde addition agent being present in an amount of from 0.1 moles per mole of formaldehyde to that amount that restricts copper deposition.

10. The copper plating solution of claim 9 having as additive at least one hydrogen inclusion retarding agent, and the Group VIII metal salt.

11. The copper plating solution of claim 9 having as additive at least one hydrogen inclusion retarding agent and the formaldehyde addition agent.

12. The copper plating solution of claim 9 having as additive the hydrogen inclusion retarding agent, the formaldehyde addition agent and the salt of the Group VIII metal.

13. The copper plating solution of claim 9 where the salt of the Group VIII metal is selected from the group consisting of $NiSO_4$, $Fe_2(SO_4)_3$ and H_2PtCl_6.

14. The copper solution of claim 9 where the formaldehyde addition agent is selected from the group consisting of Na_2SO_3, $NaHSO_3$, and $Na_2HPO_3 \cdot 5H_2O$.

15. The copper plating solution of claim 9 where the hydrogen inclusion retarding agent is NaCN.

16. The copper plating solution of claim 9 where the hydrogen inclusion retarding agent is selected from the group consisting of V_2O_5 and As_2O_3.