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[54] ELECTROLESS COPPER PLATING

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[51] **Int. Cl.** **C23c 3/02**

[58] **Field of Search** ..... 106/1; 117/130 R, 130 E, 130 B, 117/47 A

[56] **References Cited**

UNITED STATES PATENTS

3,310,430	3/1967	Schneble et al.	106/1 X
3,515,563	6/1970	Hodoley et al.	106/1

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[57] **ABSTRACT**

An improved aqueous autocatalytic copper deposition solution is provided which comprises maintaining in a solution, containing complexing and reducing agents for the copper ion and a pH adjuster, a small effective amount of a compound providing a metal value selected from the group consisting of molybdenum, niobium, tungsten, rhenium, rare earths of the actinide series, rare earths of the lanthanide series, and mixtures of the foregoing. Additionally, an improved method of depositing electroless copper is provided which comprises employing the solution hereinabove defined.

13 Claims, No Drawings

ELECTROLESS COPPER PLATING

REFERENCE TO COPENDING APPLICATIONS

This application is a continuation-in-part of copending application, Ser. No. 9,062, filed Feb. 5, 1970, which, in turn, is a continuation-in-part of copending application Ser. No. 772,061, filed Oct. 18, 1968, which, in turn is a streamlined continuation of application Ser. No. 451,335, filed Apr. 27, 1965, all now abandoned.

The present invention relates to electroless or autocatalytic plating of copper, and more particularly to controlling the stability of autocatalytic copper plating baths and enhancing the physical properties of the electroless copper deposits produced therefrom.

One object of the present invention is to improve the stability of autocatalytic copper baths without adversely affecting the deposition rate or the physical properties of the electroless copper produced therefrom.

Another object of this invention is to provide means for monitoring autocatalytic copper solutions so as to maintain them in a state of dynamic equilibrium.

A further object of the invention is to provide autocatalytic copper deposition solutions which are capable of producing electroless copper having enhanced physical properties including improved ductility, brightness, and the like.

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

Other objects of this invention will in part be obvious and will in part be made clear herefrom.

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.

The selection of complexing agents is well within the ability of those skilled in the art. Illustrative copper ion complexing agents include ammonia and organic complex-forming agents containing one or more of the following functional groups: primary amino group ($-NH_2$), secondary amino group (>NH), tertiary amino group (>N—), amino group (=NH), carboxy group (—COOH), and hydroxy group (—OH). Cahill, U.S. Pat. No. 2,874,072, for example, describes complexing agents which are tartrates and salicylates used in the presence of stabilizing amounts of carbonates. In U.S. Pat. No. 3,075,856 there are described complexing agents which are ethyleneaminoacetic acids which are selected from the class consisting of ethylene diaminetetracetic acid, diethylenetriaminepentacetic acid and 1,2-cyclohexylenediaminetetraacetic acid. In U.S. Pat. No. 2,938,805 there are described a family of complexing agents including triethanolamine, ethylenediaminetetraacetic acid, sodium potassium tartrate, ammonium hydroxide, and others. Complete details concerning the use of such complexing agents are shown in the examples of these patents. Still more details concerning copper ion complexing agents and their use may readily be found by those skilled in the art by reference to standard works, for example, William Goldie, METALLIC COATING OF PLASTICS, Volume 1, Electrochemical Publications, Limited, Middlesex, England, 1968, the disclosure of which is incorporated herein by reference.

In this invention, Rochelle salts, the sodium salts (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-Δ-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. Pat. Nos. 2,996,408 and 3,075,855.

Copper reducing agents which have been used in alkaline electroless metal baths include formaldehyde, and formaldehyde precursors or derivatives, such as paraformaldehyde, trioxane, 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 borohydrides, 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 adjuster or regulator may consist of any acid or base, and here again the selection will depend primarily on economics. For this reason, the pH adjuster 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 adjuster on the acid side in 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 adjuster 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 which 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 maintain the baths in a dynamic state of equilibrium for long periods of time and to prevent or substantially retard spontaneous decomposition.

The addition agents of this invention 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 then have heretofore been considered possible.

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

The stabilizing agents of this invention are simple or complex compounds, hereinafter called "metal values," comprising one or more of the elements, molybdenum, niobium, tungsten, rhenium, rare earths of the actinide series, e.g., actinium,

uranium, and the like, rare earths of the lanthanide series, e.g., lanthanum, neodymium, ytterbium, and the like, as well as mixtures of compounds containing one or more of such metal values.

Preferred for use are those compounds which comprise elements of the type described which have at least two oxidation states. In this preferred group are compounds comprising molybdenum, tungsten and uranium, including mixtures of the foregoing. Such compounds are preferably added to the electroless copper plating baths in a form such that the stabilizing element is at its most stable valence state.

Any compound containing the stabilizing element which is soluble in the electroless copper solution may be used.

For example, molybdenum may be supplied as molybdic trioxide, molybdenum pentachloride, $MoCl_5$, as well as water soluble organic and inorganic acid salts of molybdenum, as for example, alkali and alkaline earth metal, or ammonium molybdate: Suitable sources of tungsten and rhenium are the oxides of such elements, as well as organic and inorganic acid-water soluble salts of such elements, e.g., the tungstates, and rhenates of the metal Groups IA and IIA of the Periodic Table of Elements, and ammonia. Preferred for use are the sodium, potassium and ammonium salts. Sources of lanthanum, actinium and other rare earths, e.g., uranium, neodymium, ytterbium, and the like, 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 foregoing compounds are merely typical of those which are capable of providing stabilizing elements of the type and form described.

The amount of the stabilizing element maintained in the baths will be a small effective amount. Ordinarily, its concentration will average between about 0.1 and 3,000 microgram atoms of the element per liter of solution, preferably between about 1 and 300 microgram atoms per liter. As used herein, a microgram atom is 1×10^{-6} gram atom.

It should be emphasized however that the small effective amount of stabilizing element will vary with the nature and activity of the element, and with makeup of the solution and the conditions, e.g., temperature, under which it is used. The upper limit of the stabilizing element is an amount which will stop the bath, i.e., prevent autocatalytic deposition of copper under conditions of use. The lower limit is the least amount of stabilizing element which will be effective in manifesting the result described herein, again under the particular conditions of use.

Here it should be noted that excess amounts of compounds comprising the elements described may stop the bath completely under certain conditions of use. So sensitive is the concentration on some of the elements that amounts measured in parts per million may stop the bath completely and practically instantaneously at a given activity level, as controlled by a given temperature and given reactant concentrations and types.

Preferred solutions according to this invention will include a soluble cyanide compound. Due to some type of cooperative effect, the reason for which is not clearly understood at this time, cyanide ion and the specified metal values provide unusually high stability. Typical of such water soluble cyanide compounds are alkali metal cyanides, such as sodium and potassium cyanide, and nitriles, such as alpha-hydroxynitriles, e.g., glycolonitrile and lactonitrile, and dinitriles, e.g., iminodiacetonitrile and 3,3'-iminodipropionitrile. Such water soluble cyanide compounds may be present in amounts of between about 0.00002 and 0.06 moles per liter.

In addition to stabilizing the bath, certain of the metal values described and particularly the tungstates, molybdates and uranates, enhance the physical properties of the electroless copper deposits, particularly brightness and ductility. This is a completely surprising result and contributes materially to the value of the baths utilizing the instant invention.

Typical electroless copper deposition bath made according to the present invention will comprise:

Copper salt	0.002 to 0.60 moles
Reducing agent	0.03 to 1.3 moles
Copper ion complexing agent	0.7 to 2.5 times the moles of copper
Stabilizing element	0.1 to 3,000 microgram atoms
pH adjustor	sufficient to give desired pH
Water	sufficient to make 1 liter.

A water soluble cyanide, 0.00002 to 0.06 moles per liter, is preferably included.

Specific embodiments of a high plating potential solution comprises:

Copper salt	0.002 to 0.60 moles
Formaldehyde	0.03 to 1.3 moles
Copper ion complexing agent	0.7 to 2.5 times the moles of copper
Stabilizing element	0.1 to 3,000 microgram atoms
Alkali metal hydroxide	sufficient to give a pH of 10–14
Water	sufficient to make 1 liter.

Preferred embodiments of highly active solutions comprise:

A soluble cupric salt, preferably cupric sulfate	0.002 to 0.2 moles
Alkali metal hydroxide preferably sodium hydroxide to give	pH of 10–13
Formaldehyde	0.06 to 0.50
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)
Stabilizing agent	1 to 300 microgram atoms
Water	sufficient to make 1 liter.

An alkali metal cyanide, 0.00005 to 0.01 moles per liter, is preferably included.

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.

For best results, surfactants in an amount of less than about 5 grams per liter may be added to the baths. Typical of suitable surfactants are organic phosphate esters, and oxyethylated sodium salts.

The baths may be used at widely varying temperatures, e.g., between 15°C. and 100°C., although they will usually be used between about 20°C. 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 the following examples:

EXAMPLE 1

A solution is prepared which contains:

$CuSO_4 \cdot 5H_2O$	15 g./l.
Tetrasodium ethylenediaminetetracetic acid	40 g./l.
Formaldehyde (37% in water)	6 ml./l.
$MoCl_5$	2.0 g./l.
Potassium hydroxide	to pH 12
Water (to make)	1,000 ml.

It is heated to 60° C. and a clean sensitized nonmetallic surface is placed in the solution. After 18 hours of plating, bright, ductile (two to two and one-half bends) copper has been electrolessly deposited to a thickness of 0.00046 inches. The solution is stable—no copper has precipitated from it.

In contrast, a control bath identical to that described, except that no molybdenum compound had been added is not stable and at the end of 18 hours, there is a heavy copper

deposit on the bottom of the container. The plating of electroless copper on the article has lower ductility (one to one and one-half bends).

The addition of 0.03 grams per liter of sodium cyanide to the first bath provides a stable bath and enhances the ductility of the copper deposit three and one-half bends). This level of cyanide permits the $MoCl_5$ in such a bath to be reduced stepwise from 2.0 g./l. to 1.0, 0.2, 0.01, 0.005 and 0.001 g./l., with no loss in stability and with retention of ductility (2 to 4 bends).

EXAMPLE 2

The procedure of Example 1 is repeated, substituting for the $MoCl_5$, the tungsten compound K_2WO_4. In the absence of added cyanide, ductility is improved (two bends) in comparison with the control; some copper precipitates from the bath on long standing.

The addition of 0.030 g./l. of sodium cyanide provides a completely stable solution and the copper deposited is significantly more ductile (three to five bends) than that seen in the combination with the molybdenum values (Example 1).

EXAMPLE 3

The procedure of Example 1 is repeated, substituting for the $MoCl_5$, the uranium compound $UO_2(NO_3)_2 \cdot 6H_2O$. Instead of 2 g./l., 0.002 g./l. is sufficient to provide a stable bath and enhanced ductility (two bends).

The addition of 0.030 g./l. of sodium cyanide to this bath enhances ductility (four to four and one-half bends) and permits the uranium compound to be reduced stepwise from 0.002 to 0.001 to 0.0005 to 0.0002 g./l. with no loss in stability.

EXAMPLE 4

The procedure of Example 1 is repeated, substituting for the $MoCl_5$, the lanthanum compound $LaCl_3 \cdot 6H_2O$. This bath also contains 0.030 g./l. of sodium cyanide. The bath is stable with 0.020 and 0.200 g./l. of the lanthanum compound and the copper deposit is highly ductile (four to five bends).

EXAMPLE 5

The procedure of Example 1 is repeated, substituting for the $MoCl_5$, the neodymium compound, $NdCl_3$. This bath also contains 0.030 g./l. of sodium cyanide. The bath is stable with 0.002, 0.01, 0.02, 1.0 and 3.0 g./l. of the neodymium compound. The copper deposit is highly ductile (four to four and one-half bends).

EXAMPLE 6

The procedure of Example 1 is repeated, substituting for the $MoCl_5$, the ytterbium compound, $YbCl_3 \cdot 6H_2O$. This bath also contains 0.030 g./l. of sodium cyanide. The bath is stable with 0.002, 0.20 and 1.0 g./l. of the ytterbium compound. The copper deposit is highly ductile (four to four and one-half bends).

In the examples, the solutions were maintained at a pH of about 12 and at elevated temperature of about 60° C. throughout use. In all instances about 1 ml./l. of an organic phosphate ester was used as a surfactant.

In the examples, ductility is reported after measurement 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 metal values described herein in autocatalytic copper solutions improves stability to a marked degree, as is brought out in the examples. Similar results are also obtained if, instead of $MoCl_5$, there is used niobium (columbium) pentachloride, $CbCl_5$; and rhenium hexafluoride, ReF_6.

Also shown by the examples, the presence of these metal values also enhances the ductility of the copper deposits.

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.

Where a nonmetallic surface is to be plated, the surface area to receive the deposit must first be sensitized to render it catalytic to the reception of electroless copper, as by 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 ($PdCl_2$).

Alternatively, extremely good sensitization of nonmetallic surfaces is achieved by contact 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.

Other ways of sensitizing nonmetallic surfaces for reception of an electroless copper deposit from the baths described herein are disclosed in copending application Ser. No. 785,703, filed Jan. 8, 1959, now abandoned.

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 pretreatment and/or sensitization, the surface to be plated 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 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.

We claim:

1. In an autocatalytic copper deposition solution which consists essentially of:
   - water;
   - a water soluble copper salt, in an amount of 0.002 to 0.60 moles per liter;
   - a complexing agent for copper ion which is selected from the group consisting of ammonia and compounds containing at least one of an amine group, carboxy group and hydroxy group, in an amount of 0.7 to 2.5 times the moles of copper;
   - a reducing agent for copper ion which is selected from the group consisting of formaldehyde, paraformaldehyde, trioxane, dimethyl hydantoin, glyoxal, alkali metal borohydrides, amine boranes, and alkali metal hypophosphites, in an amount of 0.03 to 1.3 moles per liter; and
   - an acid or base capable of adjusting pH; the improvement which comprises maintaining in the solution a compound soluble in the solution and providing a small effective amount of at least 0.1 microgram atoms per liter of a metal value selected from the group consisting of molybdenum, niobium, tungsten, rhenium, rare earths of the actinide series, rare earths of the lanthanide series, and mixtures of the foregoing.

2. The solution of claim 1 which includes a water soluble cyanide compound in an amount of 0.00002 to 0.06 moles per liter.

3. The solution of claim 1 wherein said metal value is present in amount of between about 0.1 and 3,000 microgram atoms per liter, said amount being insufficient to prevent autocatalytic deposition of copper from the solution at the conditions of use, but sufficient to enhance the stability of the solution at said conditions.

4. The solution of claim 3 wherein said metal value is present in an amount of between 1 and 300 microgram atoms per liter.

5. The autocatalytic copper deposition solution of claim 1 wherein the pH adjuster maintains the pH in the alkaline range.

6. The solution of claim 5 wherein the reducing agent for copper ion is formaldehyde.

7. In a process for depositing copper on a surface catalytic to the reception of electroless copper by contacting said surface with an electroless copper solution consisting essentially of:
   - water;
   - a water soluble copper salt, in an amount of 0.002 to 0.60 moles per liter;
   - a complexing agent for copper ion which is selected from the group consisting of ammonia and compounds containing at least one of an amine group, carboxy group and

hydroxy group, in an amount of 0.7 to 2.5 times the moles of copper;

a reducing agent for copper ion which is selected from the group consisting of formaldehyde, paraformaldehyde, trioxane, dimethyl hydantoin, glyoxal, alkali metal borohydrides, amine boranes, and alkali metal hypophosphites, in an amount of 0.03 to 1.3 moles per liter; and

an acid or base adjuster for pH; the improvement which comprises maintaining in the solution a compound soluble in the solution and providing a small effective amount of at least about 0.1 microgram atoms per liter of a metal value selected from the group consisting of molybdenum, niobium, tungsten, rhenium, rare earths of the actinide series, rare earths of the lanthanide series, and mixtures of the foregoing.

8. The process of claim **7** wherein said solution includes a water soluble cyanide compound in an amount of 0.00002 to 0.06 moles per liter.

9. The process of claim **7**, wherein the said metal value is present in an amount of between about 0.1 and 3,000 microgram atoms per liter, said amount being insufficient to prevent autocatalytic deposition of copper from the solution at the conditions of use, but sufficient to enhance the stability of the solution at said conditions.

10. A process for electrolessly plating copper which comprises contacting a surface catalytic to the reception of electroless copper with an alkaline solution consisting essentially of:

water;

a water soluble copper salt, in an amount of 0.002 to 0.60 moles per liter;

a complexing agent for copper ion which is selected from the group consisting of tartrates, salicylates, ethyleneaminoacetic acids, triethanolamine, ammonium hydroxide, Rochelle salts, nitrilotriacetic acid, gluconic acid and glucono-Δ-lactone, in an amount of 0.7 to 2.5 times the moles of copper;

formaldehyde; and a compound soluble in the solution and providing a small effective amount of at least about 0.1 microgram atoms per liter of a metal value selected from the group consisting of molybdenum, niobium, tungsten, rhenium, rare earths of the actinide series, rare earths of the lanthanide series, and mixtures of the foregoing.

11. A solution for the electroless plating of copper which consists essentially of:

water;

a water soluble copper salt, from 0.002 to 0.60 moles per liter;

a complexing agent for copper ion, which is selected from the group consisting of tartrates, salicylates, ehtyleneaminoacetic acids, triethanolamine, ammonium hydroxide, Rochelle salts, nitrilotriacetic acid, gluconic acid and glucono-Δ-lactone, from 0.7 to 2.5 times the moles of the copper salt;

an alkali metal hydroxide, enough to give a pH of from 10.0 to 14.0;

formaldehyde, from 0.03 to 1.3 moles per liter; and a compound soluble in the solution and providing a small effective amount of at least about 0.1 microgram atoms per liter of a stabilizing metal value selected from the group consisting of molybdenum, niobium, tungsten, rhenium, rare earths of the actinide series, rare earths of the lanthanide series, and mixtures of the foregoing.

12. A solution for the electroless plating of copper which consists essentially of:

water;

a water soluble copper salt, from 0.002 to 0.2 moles per liter;

alkali metal hydroxide, enough to provide a pH of about 10 to 13;

a complexing agent for copper ion, which is selected from the group consisting of tartrates, salicylates, ethyleneaminoacetic acids, triethanolamine, ammonium hydroxide, Rochelle salts, nitrilotriacetic acid, gluconic acid and glucono-Δ-lactone, from 0.001 to 0.60 moles per liter;

formaldehyde, 0.06 to 0.50 moles per liter; and a compound soluble in the solution and providing a small effective amount of at least about 0.1 microgram atoms per liter of a stabilizing metal value selected from the group consisting of molybdenum, niobium, tungsten, rhenium, rare earths of the actinide series, rare earths of the lanthanide series, and mixtures of the foregoing.

13. The solution of claim **12** which includes an alkali metal cyanide in an amount of 0.00005 to 0.01 moles per liter.

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