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AUTOCATALYTIC METAL PLATING SOLUTIONS

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ABSTRACT OF THE DISCLOSURE

The present invention relates to autocatalytic plating of metal, and more particularly, to improved autocatalytic metal plating solutions having an enhanced rate of deposition.

SUMMARY

Autocatalytic copper solutions which are capable of depositing copper continuously over long periods of time without the use of electricity, i.e., electrolessly, are now well known in the art. Such solutions ordinarily comprise a water soluble copper salt, a complexing agent for cupric ion, a reducing ion for cupric ion, and a pH adjustor. In the operation of such solutions, the rate of deposition and bath stability are important parameters from a commercial standpoint. Generally speaking, it can be said that slowing the rate of deposition will tend to increase the stability of the solution. Conversely, increasing the rate of deposition will tend to decrease stability.

An object of the present invention is to enhance the rate of deposition from autocatalytic copper solutions without adversely affecting stability.

According to this invention, it has been discovered that this and other objects may be achieved by adding to autocatalytic copper solutions small effective amounts of osmium.

DETAILED DESCRIPTION

According to the present invention it has been discovered that it is possible to enhance the rate of deposition from autocatalytic copper solutions without adversely affecting stability by adding to and/or maintaining in the solutions osmium. The osmium is preferably in the form of osmium containing compounds. Preferred are certain water soluble osmium compounds, such as osmium tetroxide and salts of osmic acid, such as alkali metal salts of osmic acid, e.g., potassium osmiate.

The osmium or osmium compound should be maintained in the solution in small amounts effective to control the plating rate. The amount of these materials will generally vary so as to maintain between about 0.001 milligram per liter and 10 milligrams per liter of osmium in the solution. It should be emphasized that the osmium content of the bath will vary with the nature and activity of the osmium compounds used, and with the particular results desired.

The selection of the water soluble copper salts for the electroless copper solutions of this invention 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 gluconoδ-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, 3,075,856, 3,075,855 and 2,938,805.

Preferred reducing agents for cupric ion which have been used in alkaline electroless metal baths include formaldehyde, and formaldehyde precursors or derivatives, such as paraformaldehyde, trioxane, 1-hydroxymethyl 5,5-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 trimethoxy borohydride. 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 reducing agents for cupric ion in acid electroless copper solutions are hypophosphites, such as sodium and potassium hypophosphite, and the like.

Reducing agents of the type described, when oxidized, release hydrogen.

The pH adjustor or regulator may consist of any acid or base. The pH adjustor on the alkaline side is preferably potassium or sodium hydroxide, with particularly good results being obtained by the use of potassium 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 normal operation of the bath, the copper salt serves as a source of cupric ions, and the reducing agent reduces the cupric ions to metallic form. When reducing agents of the type described above are oxidized to provide electrons for the reduction of the cupric ions, hydrogen is released at the site of deposition. The complexing agent serves to complex the cupric ion, and at the same time makes the cupric ion 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 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 continually being consumed, so that the bath is in a constant state of change. Replenishment of the bath ingredients is therefore necessary for continuous or long term operation.

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

Electroless metal salt—0.002 to 1.0 gram mole
Reducing agent—0.005 to 4 gram moles
Electroless metal complexing agent—0.7 to 40 times the gram moles of metal salt
Osmium compound (as osmium)—0.001 to 30 milligrams
pH adjustor—Sufficient to give desired pH
Water—Sufficient to make 1 liter

Preferred embodiments of highly active electroless copper solutions comprise:

A soluble cupric salt, preferably cupric sulfate—0.002 to 0.60 gram mole
Alkali metal hydroxide, preferably sodium or potassium hydroxide, to give—pH of 10–14

Reducing agent, preferably formaldehyde—0.03 to 1.3 gram moles
Osmium compound (as osmium)—0.1 to 2 milligrams
Cupric ion complexing agent—0.7 to 15 times the moles of copper
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 ingredients, 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, which may be obtained under the trade names Gafac RE 610 and Triton QS–15, respectively.

The potassium salts in general are preferred over the corresponding sodium salts in preparing the solutions of this invention.

The osmium compounds of this invention may be used alone, or in combination with other activation ions, such as phosphorus, sulfur, or cyanide ions, or ions containing phosphorus, sulfur or cyanide.

As the source of cyanide ions may be mentioned alkali cyanides, such as sodium and potassium cyanide, and nitriles, such as chloroacetonitrile and alpha hydroxynitriles, e.g., glyconitrile and lactonitrile, and dinitriles, e.g., succinonitrile, iminodiacetonitrile and 3,3′-iminodipropionitrile.

As the source of sulfur may be used any sulfur compound, preferably one containing divalent sulfur, capable of forming a stable but dissociable chelate with cuprous ion.

Among the organic sulfur compounds may be mentioned the following: 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 iso-thiazoles, e.g., 2-mercapto benzol thiazole and the like; dithiols, e.g., 1,2-ethanedithiol and the like; 6-membered heterocyclics containing S—N in the ring, such as thiazines, e.g., 1,2-benziso-thiazine, benzothiazine, and the like; thioamino acids, such as methionine, cystine, cysteine, and the like; thio derivatives of alkyl glycols, such as 2,2′-thiodiethanol, dithiodiglycol and thioglycollic acid; and the like. Among the inorganic sulfur compounds may be mentioned: alkali metal sulfides, e.g., sodium sulfide, potassium sulfide, sodium polysulfide, potassium polysulfide; alkali metal thiocyanates, such as sodium and potassium thiocyanates; and alkali metal dithionates, such as sodium and potassium dithionate.

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 thereof.

The foregoing sulfur compounds are merely typical of sulfur compounds which are capable of stabilizing autocatalytic copper baths as taught herein.

As the phosphorus ion source, which may be presented in small effective amounts between about 0.02 and 0.1 mole per liter may be mentioned the organic and inorganic phosphorus containing salts, acids and bases, such as the water soluble phosphate, tetrapyrophosphate and hexametaphosphate acids and salts, including alkali and alkaline earth metals.

The amount of sulfur compound required is a small effective amount and will vary, depending upon the particular compound used, from a trace to about 300 parts per million (p.p.m.) or more. For most sulfur compounds 1 p.p.m. will be the upper limit and about 0.001 p.p.m. the lower limit. A good working limit for most

sulfur compounds is between about 0.01 and 0.02 p.p.m.

The amount of the cyanide compound to be added to the bath is between about 0.00001 to 0.06 mole per liter, preferably between about 0.00005 to 0.01 mole per liter.

In Examples 1–2 below a bath formulation, designated A, was employed. It had the following composition:

Bath A

Copper sulfate ——g. mole/liter	0.06
Tetrasodium salt of ethylene-diaminetetraacetic acid (1.3 molar solution) ——g. mole/liter	0.09
Formaldehyde (37% solution) ——g. mole/liter	0.07
Sodium cyanide ——g. mole/liter	0.0005
Gafac RE 610 (20% solution) ——g./liter	1

KOH—enough to maintain desired pH.

In the examples, steel test strips (approximate area of 10 square centimeters) were immersed in the solution which was maintained at 60° C. for the time specified.

EXAMPLE 1

Various additions of osmium tetroxide were made to Bath A which was maintained at pH 12.3. The results obtained were as follows:

Concentration of osmium tetroxide	Copper deposited (g.)	Time, hrs.
None	0.0223	3
1.0 mg./l.	0.0423	3
0.5 mg./l.	0.0463	3

EXAMPLE 2

Various concentrations of osmium tetroxide were made to Bath A which was maintained at a pH of 11.9 with KOH. The results obtained were as follows:

Concentration of osmium tetroxide	Copper deposited (g.)	Time, hrs.
None	0.0379	5
.5 mg./l.	0.0691	5
0.2 mg./l.	0.057	5

The results shown in the examples demonstrate that the presence of small amounts of osmium in the solution produces an appreciable increase in the rate of copper deposition.

The electroless copper solutions described herein 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 ($PdCl_2$). Alternatively, sensitization may be achieved by treating the insulating 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 sensitization of insulating substrata to the reception of electroless copper are disclosed in co-pending application Ser. No. 249,063, filed Jan. 2, 1963 and U.S. Pat. No. 3,146,125.

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 plated is immersed in autocatalytic metal baths, and permitted to remain in the bath until a metal deposit of the desired thickness has 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 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 substratrum to the electroless metal solution. In this embodiment, electroless metal builds up on the circuit pattern, as well as on the walls surrounding the holes to form interconnections.

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 a bath for the electroless plating of copper which comprises a water soluble copper salt, a complexing agent for cupric ion, a pH adjustor and a reducing agent for cupric ion; the improvement which comprises in combination therewith a soluble osmium compound in an amount, calculated as osmium, sufficient to enhance the rate of deposition of electroless copper.

2. The bath of claim 1 wherein the osmium is present in the form of a water soluble osmium compound.

3. The bath of claim 1 wherein the osmium is present in the form of a compound selected from the group consisting of osmium tetroxide and potassium osmiate.

4. The bath of claim 2 wherein the osmium is present in the bath in an amount between about 0.001 and 30 milligrams per liter.

5. The bath of claim 1 wherein a cyanide compound is maintained in the bath.

6. The bath of claim 1 wherein a sulfur compound is maintained in the bath.

7. The bath of claim 5 wherein the cyanide compound is a member selected from the group consisting of inorganic cyanides and organic nitriles.

8. The bath of claim 6 wherein the sulfur compound is a member selected from the group consisting of thio derivative of alkyl glycols; a aliphatic S—N compounds; 5-members heterocyclics containing S—N in the 5-membered ring; dithiols; 6-membered heterocyclics containing S—N in the ring; thioamino acids; alkali metal sulfides; alkali metal polysulfide; alkali metal thiocyanate; alkali metal dithionates; and mixtures of the foregoing.

9. The bath of claim 1 wherein the water soluble copper salt is present in an amount from about 0.002 to 1.0 mole per liter; the complexing agent for cupric ion is present in an amount between 0.7 to 40 times the moles of copper salt; the pH adjustor is an alkali metal hydroxide which is present in an amount sufficient to maintain a pH of from about 10.0 to 14.0; and the reducing agent is formaldehyde and is present in an amount between 0.005 to 4.0 moles per liter.

10. A process of electroless copper plating which comprises immersing a receptive surface to be plated in the electroless copper solution of claim 1.

11. Electroless copper produced from the bath of claim 1.

References Cited

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CERTIFICATE OF CORRECTION

Patent No. 3,515,563 Dated June 2, 1970

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, lines 6 and 7, "derivative of alkyl glycols; a aliphatic S-N compounds; 5-members heterocyclics containing S-N in the 5-", should read

-- derivatives of alkyl glycols; aliphatic S-N compounds; 5-membered heterocyclics containing S-N in the 5- --.

SIGNED AND
SEALED
OCT 20 1970

(SEAL)
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