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[54] **ELECTROLESS METAL DEPOSITION**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 523,902, Feb. 1, 1966, abandoned.

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[58] **Field of Search**..........117/47 R, 130, 130 E, 212; 106/1

[56] **References Cited**

UNITED STATES PATENTS

3,119,709	1/1964	Atkinson	106/1 X
3,257,215	6/1966	Schneble et al.	106/1
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[57] **ABSTRACT**

An improved method for enhancing the ductility of electroless metal deposits is provided in which an electroless metal bath contains an extraneous ion which has a preferential capacity for being coulombically adsorbed at the outer layer of an electric double layer present on an interface in contact with such bath on which said metal is electrolessly depositing, such ion being present in an amount sufficient to reduce the inclusion of hydrogen in the electrolessly deposited metal.

9 Claims, No Drawings

ELECTROLESS METAL DEPOSITION

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. application Ser. No. 523,902, filed Feb. 1, 1966, and now abandoned.

Generally stated, the subject matter of the present invention relates to a process for enhancing the ductility of electroless metal deposits. More particularly, the invention relates to a process for enhancing the ductility of electroless metal deposits which comprises employing a plating bath containing an extraneous ion which has a preferential capacity for being coulombically adsorbed at the outer layer of an electric double layer present on an interface in contact with such bath on which said metal is electrolessly depositing.

BACKGROUND OF THE INVENTION

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

Such solutions are particularly suitable for metallizing insulating substrata on surfaces which have been suitably treated to make them sensitive to the reception of electroless metal deposition. Such sensitization techniques include the well-known treatment with an acidic aqueous solution of stannous chloride ($SnCl_2$), followed by treatment with a dilute aqueous acidic solution of palladium chloride ($PdCl_2$). Alternatively, sensitization may be achieved by treating the insulating substrate 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 copending application Ser. No. 249,063, filed Jan. 2, 1963, and U.S. Pat. No. 3,146,125.

Most electroless metal solutions of the type described produce metal deposits which contain a substantial amount of hydrogen, for reasons which will be hereinafter clarified. Such deposits are brittle, break under vibration and bending, and otherwise exhibit poor ductility. For this reason, such solutions are not generally satisfactory for use where rugged, tenacious electroless metal deposits capable of withstanding rough mechanical handling and bending forces are desired. More particularly, the inherent tendency for electroless metal solutions to produce brittle metal deposits has severely retarded the widespread use of such solutions, for example, in the manufacture of printed circuits and the metallization of plastics generally.

The present invention has for an object the production of electroless metal having a reduced hydrogen content.

Another object is the production of ductile electroless metal deposits which are capable of withstanding bending forces.

A further object of the present invention is the provision of novel and improved processes for providing insulating substrates including plastics with adherent, ductile electroless metal deposits.

Still another object is the provision of novel and improved processes for the production of reliable, accurate and mechanically rugged printed circuits.

Other objects of the invention will in part be obvious from the following description and will in part be made clear hereinafter.

THE INVENTION

To achieve the foregoing objects, and in accordance with its purpose, as embodied and broadly described, the present invention provides an improved process for electrolessly depositing metal in which the ductility of the electroless metal deposits is enhanced. The process comprises maintaining in the electroless metal deposition solution an extraneous ion which is electrostatically adsorbed at the outer layer of the electric double layer present at the surface on which deposition is occurring. The effect of outer layer adsorption of the extraneous ion is to reduce or minimize inner layer adsorption at the deposition surface of hydrogen ions, thereby reducing the opportunity for hydrogen to be included in the electroless deposit.

By extraneous ion is meant an ion which does not interfere with and is not required for the main electroless deposition reaction to occur.

The invention will be particularly described with reference to electroless copper deposition, which is a preferred embodiment.

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., derived from a water-soluble copper salt, a reducing agent for cupric ions, a complexing agent for cupric ions, and a pH regulator.

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

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

Preferred reducing agents for cupric ion for use 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 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 release hydrogen when oxidized.

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 is the sulfuric acid.

In 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 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 in-

gredients and conditions of operation. Other factors which effect 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.

Electroless copper solutions having the basic constituents described produce copper deposits which contain a substantial amount of included hydrogen. Such deposits are brittle, break under vibration and bending, and otherwise exhibit poor ductility. Such deposits also exhibit a dull surface, of poor color, which may best be described as "smutty."

The electroless copper of this invention, as distinguished from that of the prior art, has a greatly reduced hydrogen content, is bright, and possesses enhanced ductility, as compared to the electroless copper of the prior art.

The precise mechanism by which electroless metal, e.g., copper, deposition occurs is complex and difficult of precise definition. Without wishing to be limited thereto, the ensuing theory affords a rational explanation for this phenomenon.

In electroless copper deposition from a solution containing a solvent, a source of cupric ions, a reducing agent for cupric ions, a complexing agent for cupric ions, and a pH regulator, the reducing agent is oxidized at deposition surface areas to release electrons to such areas. Cupric ions in contact with such areas pick up the free electrons and are reduced to copper atoms, which deposit on the adjacent surface areas and aggregate to form a copper metal deposit.

The potential at which the process takes place is a compromise, or mixed potential, between the two potentials which characterize the oxidization of the reducing agent and the reduction of the cupric ions.

To illustrate the mechanism, in one embodiment of a particularly useable electroless copper deposition solution, the reducing agent is formaldehyde, and the source of the cupric ions is a copper salt, such as cupric sulfate. Using the mixed potential theory heretofore described, the formaldehyde is oxidized to hydrogen and formate ions at the surface at which deposition is occurring, and an electron is given up to the surface for each molecule of formaldehyde oxidized. The released electron is in turn taken up by cupric ions at or in contact with the surface, to cause local deposition of copper.

The surface on which electroless metal deposition occurs may be considered a charged interface having the structure of an electric double layer. For a description of the electric double layer structure of such a charged interface, see: *Proc. Roy. Soc.* Series A, 1963, pp. 55–79; and Bockris, *Modern Aspects of Electrochemistry*, No. 1, 1954, pp. 103–173, which are herein incorporated by reference as part of the instant specification.

According to the present invention, the outer layer of the charged interface or surface at which deposition occurs, has electrostatically or coulombically adsorbed thereon extraneous ions which screen the surface at least in part from inner layer adsorption of hydrogen released by the reducing agent. To accomplish this result, there are maintained in the electroless copper solution, particularly one having a high plating potential, extraneous ions which are capable of being electrostatically or coulombically adsorbed at the outer layer of the deposition surface. The adsorbed, extraneous ions must be potentially dependent, i.e., they must have the capacity to be adsorbed at the potential of operation of the bath. They must also have the capacity to be preferentially adsorbed, compared to the ions normally present and required for successful operation of the bath. The potential of operation of the bath, the mixed potential, is between the potential which characterizes the reduction of the cupric ions on the absence of the reducing agent and the potential which characterizes the oxidation of the reducing agent in the absence of the cupric ions. The former is between −0.2 and −0.5 and the latter between −0.9 and −1.3 volts versus the saturated calomel electrode depending on temperature and composition of the bath. Thus, the adsorbed species must have the property to be adsorbed at the potentials between −0.2 and −1.3 volts versus the saturated calomel electrode.

The extraneous ions suitable for use must also, as stated previously, have the capacity of being electrostatically adsorbed at the outer layer of the electric double layer present at the surface on which deposition is occurring. The outer layer of the electric double layer may be considered as being separated from the charged interface by a distance of about 1 to 2 molecular diameters, or about 3 angstroms. The capacity of the extraneous ions suitable for use herein to be electrostatically adsorbed at the outer layer of the surface on which deposition is occurring distinguishes such ions from those which may be specifically adsorbed, i.e., chemisorbed, at the inner layer of the electric double layer.

The adsorbed extraneous ions of this invention screen the deposition surface from hydrogen ions which are released at the surface by the main deposition reaction. Accordingly, the greater the number of extraneous ions electrostatically adsorbed at the outer layer, the less the tendency for hydrogen adsorption. A decrease in the number of hydrogen ions adsorbed in the inner layer leads directly to a decrease in hydrogen inclusion in the electroless metal and a consequent increase in the ductility of the deposited metal.

Extraneous ions having a preferential capacity for the electrostatic or coulombic adsorption at the outer layer of the deposition interface and therefore suitable for use herein are ions which contain phosphorus and are derived, for example, from inorganic phosphorus containing salts, acids, and bases; including the phosphates, pyrophosphates, metaphosphates and polyphosphates. The phosphate, tetrapyrophosphate and hexametaphosphate salts of alkali and alkaline earth metals, and ammonia are preferred for use. Preferred for use are sodium, potassium and ammonium phosphates and polyphosphates.

The foregoing compounds are merely typical of those which are capable of providing phosphorus containing ions which are suitable for use herein.

The electrostatically absorbable ions described herein should be maintained in the electroless metal solutions averaging between about 0.02 and 0.1 mole per liter of solution, preferably between about 0.03 and 0.08 mole per liter.

It should be emphasized however that the amount of electrostatically absorbable ions will vary with the nature and activity of the ion used, and with makeup of the solution and the conditions, e.g., the temperature, concentration and pH, under which it is used. The upper limit of such ions is an amount which will prevent deposition of electroless metal under conditions of use. The lower limit is the least amount of ion which will be effective in manifesting the results described herein, again under the particular conditions of use.

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

Electroless metal salt	0.002 to 1.0 mole
Reducing agent	0.03 to 4 moles
Electroless metal complexing agent	0.7 to 40 times the moles of metal salt
Extraneous ion	0.02 to 0.1 mole
pH adjuster	sufficient to give desired pH
Water	sufficient to make 1 liter.

Embodiments of a high plating potential electroless copper solution comprise:

Copper salt	0.002 to 1 mole
Reducing agent	0.03 to 4 moles
Cupric ion complexing agent	0.7 to 40 times the moles of copper
Extraneous ion	0.02 to 0.1 mole
pH adjuster	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 moles
Alkali metal hydroxide, preferably sodium hydroxide, to give	pH of 10–14
Reducing agent, preferably formaldehyde	0.03 to 1.3 moles
Extraneous ion	0.03 to 0.08 mole
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 formulas 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 extraneous ions, and to adjust them to their optimum value as the bath is used.

Here it should be noted that the use of the electrostatically absorbable ions described are present in easily detectable amounts, thereby facilitating control of the operation.

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.

Particularly, results are achieved when the extraneous ions of this invention are added to or maintained in solutions which contain small effective amounts, e.g., between 5 micrograms and 500 milligrams per liter, of water soluble cyanide compounds. Typical of such cyanide compounds may be mentioned alkali cyanides, such as sodium and potassium cyanide, nitriles, such as chloroacetonitrile, alpha-hydroxy nitriles, e.g., glyconitrile and lactonitrile, and dinitriles, e.g., succinonitrile, iminodiactonitrile, and 3,3′ iminodipropionitrile.

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

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

TABLE I

Temperature (° C.)	pH	Na_3PO_4 (gm./l.)	$H_5P_3O_{10}$ (gm./l.)	Sodium tetraphyrophosphate (gm./l.)	Sodium hexametaphosphate (gm./l.)	Thickness of deposit (inch)	Ductility (bends)
60 (Control)	11.9					0.0004	1½
60	11.9	5				0.0002	4½
60	11.9	10				0.0001	3½
60	11.9	20				0.0001	2½
60	11.9	4				0.0007	3
60	11.9	5				0.0005	5½
60	11.9	6				0.0005	2½
60	11.9	0.5				0.0012	0
60	11.9	2				0.0009	0
80	11.9	5				0.0003	8
70	11.9	5				0.0003	5½
60	11.9		15			0.0006	½
60	11.9		30			0.0002	2½
60	11.9			30		0.0005	½
60	11.9			100		0.0002	5
60	11.9				20	0.0009	1
60	11.9			60		0.0007	1½
75	11.9	5				0.0003	5½
75	12.1	5				0.0005	3½
75	12.1	2				0.0006	2½
60	12.0	5				0.0003	6

NOTE.—All solutions contain copper sulfate, 15 gm./l.; tetrasodium salt of ethylenediaminetetraacetic acid, 40 gm./l.; formaldehyde, 6 ml./l.

In table I, the solutions contained about 1 ml./l. of an organic phosphate ester as a surfactant.

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

As shown in table I, the presence of phosphorus enhances the ductility of the copper deposits to a truly remarkable degree.

Use of the phosphorus compounds described also improved stability of the electroless copper solution to a marked degree.

In using the 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 brought out hereinabove.

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 metal baths and permitted to remain in the bath until a metal deposit of the desired thickness has built up.

As has been brought out heretofore, the solutions described herein are advantageous for use in production of printed circuits. For example, portions of the surface of an insulating substrate in the form of a desired circuit pattern may be sensitized for the reception of electroless metal. Following sensitization, the substrate 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 substrate. 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 substrate 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.

To enhance the stability of the electroless metal solutions described herein, divalent sulfur compounds, as well as sulfites, may be maintained therein during operation.

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 isothiazoles, 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-benzisothiazine, benzothiazine, and the like; thioamino acids, such as methinonine, cysteine, cystine, 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.

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

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.

Solutions containing small effective amounts of sulfur component are especially useful in the preparation of printed circuits. In the absence of sulfur, there is a tendency with electroless solutions of the type described for nonsensitized areas of the insulating substrates, following prolonged immersion in the solution, to become sensitized and to receive scattered spot deposits of metal. As will be readily appreciated, deposition of electroless metal in areas of the substratum where metal is not desired would raise havoc with control techniques in the preparation of printed circuits.

Additionally, when autocatalytic metal baths are used commercially, deposition of extraneous metal occurs on insulating walls of containers housing the electroless metal solution.

When sulfur is present, the tendency for such scattered spot deposits of metal to form is substantially reduced if not completely eliminated.

The extraneous ions described herein are especially suitable for use in electroless copper solutions which are to be run substantially free of ferric and ferrous ions.

According to copending application Ser. No. 523,863, of Frederick W. Schneble, Jr., John F. McCormack and Rudolph J. Zeblisky, filed Feb. 1, 1966, the reduction or substantial elimination from electroless metal deposition solutions of ions which have an oxidation potential greater than the oxidation potential of the ion of the metal sought to be electrolessly deposited also alleviates the problem of spontaneous decomposition ordinarily associated with such solutions. More specifically, the copending application suggests maintaining the concentration of such ions below about 25 parts per million.

The expression "oxidation potential" used herein should be understood as having the definition set forth in Latimer, *Oxidation Potentials*, 2nd ed., Prentice Hall, 1952.

In electroless copper solutions designed to be run for long periods of time, ions of iron, i.e., ferrous and ferric ions, are particularly troublesome in this respect, and the concentration should be maintained below about 25 parts per million.

The extraneous ions, e.g., phosphates, of this invention do not react with ferric and ferrous ions and therefore do not interfere with removal of ferrous and ferric ions from electroless copper solutions. Rather, with the extraneous ions of this invention, the electroless copper solutions may be continuously or periodically treated to remove the deleterious ions described immediately above, as by raising the pH of the solution to precipitate iron as the hydroxide.

It has also been discovered that the addition of complex cyanometallic compounds such as ferricyanides or ferrocyanides to electroless copper solutions of the type described herein results in an increase in the rate of deposition. Accordingly, the present invention contemplates the addition to or maintenance in the electroless metal solutions described of small effective amounts of water soluble ferrocyanide or ferricyanide salts, e.g., water soluble alkali metal, alkaline earth metal, and ammonium salts of hexacyanoferrate (II) and hexacyanoferrate (III). In general, the amount of such salts will range from about 1 to about 320 parts per million, calculated as iron (Fe).

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 is:

1. In a method for electrolessly depositing copper which comprises contacting a surface which is sensitive to the reception of electroless copper, with an electroless copper deposition solution containing an ion of copper, a complexing agent for said ion, a reducing agent for said ion, and a pH regulator; the improvement which comprises maintaining in the solution an inorganic extraneous ion which has a preferential capacity for being coulombically adsorbed at the outer layer of an electric double layer present at the electroless metal deposition surface, in an amount sufficient to reduce the inclusion of hydrogen in the electrolessly deposited metal and less than 0.08 mole per liter, said inorganic extraneous ion being derived from a compound which is a member selected from the group consisting of orthophosphoric acid, pyrophosphoric acid, metaphosphoric acid and polyphosphoric acid.

2. The method of claim **1**, wherein said extraneous ion not electrostatically adsorbed at the outer layer is chemisorbed at the inner layer of the electric double layer.

3. The method of claim **1**, wherein the extraneous ion is a phosphorus containing ion.

4. The method of claim **1**, wherein the electroless metal deposition solution comprises as a stabilizing agent a member selected from the group consisting of divalent sulfur compounds and sulfites.

5. The method of claim **1**, wherein the electroless metal deposition solution comprises as an agent for increasing the rate of deposition of the electroless metal a member selected from the group consisting of hexacyanoferrate (II) and hexacyanoferrate (III).

6. The method of claim **5**, wherein the electroless metal deposition solution comprises as a stabilizing agent a member selected from the group consisting of divalent sulfur compounds and sulfites.

7. The method of claim **1**, wherein the surface contacted with the electroless metal deposition solution is selectively sensitized in designated areas, thereby forming a printed circuit.

8. The method of claim **1**, wherein the electroless metal deposition solution comprises less than 25 parts per million of an ion having an oxidation potential greater than the oxidation potential of the particular ion being electrolessly deposited.

9. The method of claim **1**, wherein the extraneous ion is present in an amount of from about 0.02 to 0.08 mole per liter.

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