⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 164 580**
B1

⑫ EUROPEAN PATENT SPECIFICATION

㊺ Date of publication of patent specification: **20.09.89**

(51) Int. Cl.^{4}: **C 23 C 18/40**

㉑ Application number: **85105723.2**

㉒ Date of filing: **10.05.85**

---

(54) Electroless copper plating bath and plating method using such bath.

㉚ Priority: **17.05.84 US 611278**

㊸ Date of publication of application:
18.12.85 Bulletin 85/51

㊺ Publication of the grant of the patent:
20.09.89 Bulletin 89/38

(84) Designated Contracting States:
DE FR GB

(56) References cited:
FR-A-1 530 167
CHEMICAL ABSTRACTS, vol. 87, 1977, page 277, abstract no. 10159u, Columbus, Ohio, US; & JP-A-77 20 339 (HITACHI LTD.) 16-02-1977
METAL FINISHING ABSTRACTS, vol. 18, no. 1, 1976, page 18, right-hand column A, Electroless copper; & JP 50/26 730 (HITACHI K.K.) (11-07-1973)

(73) Proprietor: **International Business Machines Corporation**
Old Orchard Road
Armonk, N.Y. 10504 (US)

(72) Inventor: **Amelio, William Joseph**
161 Deyo Hill Road
Binghamton New York 13905 (US)
Inventor: **Bartolotta, Peter Gerard**
305 Adams Avenue
Endicott New York 13760 (US)
Inventor: **Markovich, Voya**
3611 Joel Drive
Endwell New York 13760 (US)
Inventor: **Parsons, Ralph Elliott**
18 Newberry Drive
Endicott New York 13760 (US)

(74) Representative: **Oechssler, Dietrich, Dr.rer.nat. Dipl.-Chem.**
Schönaicher Strasse 220
D-7030 Böblingen (DE)

EP 0 164 580 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

Description

The electroless plating of copper onto a substrate is well-known in the prior art. For instance, an electroless or autocatalytic copper plating bath usually contains a cupric ion source, a reducing agent for the cupric ion, a chelating or complexing agent, and a pH adjustor. In addition, if the surface being plated is not already catalytic for the deposition of the desired metal, a suitable catalyst is deposited on the surface prior to contact with the plating bath. Among the more widely employed procedures for catalyzing a substrate is the use of stannous chloride sensitizing solutuion and a palladium chloride activator to form a layer of metallic palladium particles.

Although the technology relative to electroless copper plating is continually being improved, there still remains room for additional improvement. Certain problems are especially pronounced when preparing articles of very high quality such as those to be employed in printed circuit applications (e.g., printed circuit boards which contain high-density circuitry and large numbers of holes such as through-holes and blind-holes).

A major reason for yield loss in electroless copper plating is the formation of what is known as extraneous copper or nodules. The formation of nodules in unwanted areas on a substrate can result in short-circuiting by forming contact between circuit lines on the substrate. In addition, such processes as providing protective coatings, providing solder, and pin insertion are adversely affected by the presence of nodules on the surface.

The problem of nodule formation can be avoided, however this has to be traded off by the judicious selection of the bath and the conditions of plating by providing a less-active bath.

It is the object of the invention to provide an electroless copper plating bath having improved stability and a method for electroless copper plating using this bath where in applying this method the formation of nodules is reduced if not entirely avoided and at the same time the rate of plating can be increased.

This object is achieved by a plating bath as disclosed in claim 1 and by a method as claimed in claim 10.

The plating bath of the present invention provides high-quality deposited copper of improved ductility. Moreover, the longevity of the baths of the present invention is relatively long (e.g., a bath can be used for about one week).

Advantageous embodiments of the inventive plating bath and the inventive method are disclosed in the subclaims.

The invention will become more apparent from the following detailed description.

According to the present invention, it has been found that electroless copper plating bath of improved stability and capable of providing of increased plating rates can be achieved by providing 1 part per 10^9 to 1,000 parts per 10^9 and preferably 1 part per 10^9 to about 500 parts per 10^9 of a cationic polymer from acrylamide and/or from methacrylamide.

It is believed that the cationic polymer, in the concentrations employed, helps in the oxidation of Cu^+, thereby preventing bulk precipitation of Cu_2O which, in turn, enhances the stability of the bath and helps in reducing nodule formation. Moreover, it is believed, in accordance with the present invention, that the cationic polymer acts as a complexing or chelating agent for the cupric ion. Moreover, it is believed that the presence of the cationic polymer in the plating bath acts as a bridging ligand between the metal ions and the surface to be coated, thereby enhancing the rate of the electrochemical reaction providing increased plating rate.

The preferred cationic polymers employed are available under the trade designation "Reten".

The polymer from acrylamide and/or methacrylamide is a multifunctional cationic material in that it must contain at least two active or available cationic moieties. The polymers are at least water-miscible and are preferably water-soluble or at least soluble in the water compositions employed in the present invention. The preferred cationic moieties are quaternary phosphonium and quaternary ammonium groups. Polymers containing at least two cationic moieties are commercially available and need not be described herein in any great detail. Examples of commercially available multifunctional cationic polymers are Reten 210, Reten 220, and Reten 300, marketed by Hercules, description of which can be found in "Water-Soluble Polymers", Bulletin VC-482A, Hercules Incorporated, Wilmington, Delaware 19899, disclosure of which is incorporated herein by reference.

Reten 210 is in powder form and is a copolymer of acrylamide and betamethacryloxyethyltrimethylammonium methyl sulfate having a Brookfield viscosity of a 1% solution of 600—1000 cps.

Reten 220 is in powder form and is a copolymer of acrylamide and betamethacryloxyethyltrimethylammonium methyl sulfate having a Brookfield viscosity of a 1% solution of 800—1200 cps.

Reten 300 is a liquid and is a homopolymer of betamethacryloxyethyltrimethylammonium methyl sulfate having a Brookfield viscosity of a 1% solution of 300-700 cps.

The molecular weight of the Reten polymers is usually relatively high and varies from about 50,000 to about 1,000,000 or more. These high molecular weight polymers are solid products and their main chemical backbone structure is polyacrylamide. The cationic Reten (positive charge) is obtained by attaching to the polyacrylamide various tetraalkyl ammonium compounds. These quaternary ammonium groups provide the number of positive charges of the polymer. The preferred copper electroless plating baths to which the cationic polymer from acrylamide and/or methacrylamide is added in accordance with the present invention and their methods of application are disclosed in U.S. Patents 3,844,799 and 4,152,467 disclosures of which are incorporated herein by reference.

Such copper electroless plating baths generally are aqueous compositions which include a source of cupric ion, a reducing agent, a complexing agent for the cupric ion, and a pH adjustor. The plating baths also preferably include a cyanide ion source and an anionic surface-active agent. The cupric ion source generally used is a cupric sulfate or a cupric salt of the complexing agent to be employed.

The cupric ion source is generally employed in amounts from about 3 to about 15 grams per liter and preferably about 8 to about 12 grams per liter calculated as cupric sulfate.

The most common reducing agent employed is formaldehyde which in the preferred aspects of the present invention are used in amounts from about 0.7 to about 7 grams per liter and most preferably from about 0.7 to about 2.2 grams per liter.

Examples of other reducing agents include formaldehyde derivatives or precursors such as paraformaldehyde, trioxane, dimethylhydantoin, and glyoxal; borohydrides such as alkali metal alkali borohydrides (sodium and potassium borohydride) and substituted borohydrides such as sodium trimethoxy borohydride; boranes such as amine borane (isoproply amine borane and morpholine borane).

Examples of some suitable complexing agents includes Rochelle Salts, ethylene diamine tetraacetic acid, the sodium (mono-, di-, tri-, and tetra-sodium) salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid and its alkali salts, gluconic acid, gluconates, triethanol amine, glucono(gamma)-lactone, modified ethylene diamine acetates such as N-hydroxy ethyl, ethylene diamine triacetate. In addition, a number of other suitable cupric complexing agents are suggested in U.S Patents 2,996,408; 3,075,856; 3,075,855; and 2,938,805 disclosures of which are incorporated herein by reference.

The amount of complexing agent is dependent upon the amount of cupric ions present in the solution as generally from about 20 to about 50 grams per liter or in a 3—4 fold molar excess.

The plating bath also preferably contains an anionic surface active agent which assists in wetting the surface to be coated. A satisfactory anionic surface active agent is, for instance, an organic phosphate ester available under the trade designation "Gafac RE-610". Generally, the anionic surface active agent is present in amounts from about 0.02 to about 0.3 grams per liter.

In addition, the pH of the bath is usually generally controlled, for instance, by the addition of a basic compound such as sodium hydroxide or potassium hydroxide in the necessary amount to achieve the desired pH. The preferred pH of the electroless plating bath employed in accordance with the present invention is between 11.8 and 12.5.

Also, preferably, the plating bath contains a cyanide ion and most preferably contains about 10 to about 25 milligrams per liter to provide a cyanide ion concentration in the bath within the range of 0.0002 to 0.0004 molar. Examples of some cyanides which can be employed according to the present invention are the alkali metal, alkaline earth metal, and ammonium cyanides. In addition, the plating bath can include other minor additives as known in the art.

The preferred plating baths employed have a specific gravity within the range of 1.060 to 1.080. Moreover, the temperature of the bath is preferably maintained between 70°C and 80°C and most preferably between 70°C and 75°C. For a discussion of the preferred plating temperature coupled with the preferred cyanide ion concentrations, see U.S. Patent 3,844,799.

In addtion, it is preferred to maintain the O_2 of the bath between 2 ppm and 4 ppm and preferably about 2.5 to about 3.5 ppm as discussed in U.S. Patent 4,152,467. The O_2 content can be controlled by injecting oxygen and an inert gas into the bath.

The overall flow rate of the gases into the bath is generally from about 28.32 to about 566.4 l per minute per 3785 l (about 1 to about 20 standard cubic feet per minute per thousand gallons) of bath and preferably from about 141.6 to about 283.2 l per minute per 3785 l (about 5 to about 10 standard cubic feet per minute per thousand gallons) of bath.

The preferred plating rates employed in accordance with the present invention are about 5.08 to about 7.62 μm (about 0.2 to about 0.3 mils) of plated copper thickness per hour.

The following non-limiting example is presented to illustrate the present invention.

Example 1

A plating bath containing about 9 grams per liter of cupric sulfate, about 2.0 grams per liter of formaldehyde, about 36 grams per liter of ethylene diamine tetraacetic acid, about 28 milligrams per liter of sodium cyanide, about 1.2 parts per 10^9 of Reten 210, and about 0.05 grams per liter of Gafac is preferred. The bath has a pH of about 12. The bath is fed through a plating tank at at temperature of about 73°C. The plating tank contains substrates having a thin layer of copper on the surface thereof. The oxygen content of the bath during plating is about 3 ppm. The rate of plating is about 5.08 μm per hour. The nodule rating of the substrate is 1 (nodule rating refers to nodules per 6.4516 cm^2 (1 square inch) with 1 being the best and 5 being the worst). Similar results are obtained with dielectric substrates catalyzed for plating copper electroless plating.

Claims

1. Electroless copper plating bath which comprises:

A. cupric ion source in an amount from about 3 to about 15 grams per liter calculated as cupric sulfate;

B. A reducing agent for the cupric ion source in an amount from about 0.7 to about 7 grams per liter calculated as formaldehyde;

C. a complexing agent for the cupric ion in an amount of about 20 to 50 grams per liter; and

D. 1 part per 10^9 to 1,000 parts per 10^9 of a cationic polymer from acrylamide or methacrylamide, or both.

2. Plating bath according to claim 1 which contains 1 part per 10^9 to about 500 parts per 10^9 of said cationic polymer.

3. Plating bath according to claim 1 or 2 which contains an anionic surface-active agent, preferably in an amount from about 0.02 to about 0.3 grams per liter.

4. Plating bath according to any one of claims 1 to 3 having a pH of about 11.8 to about 12.5.

5. Plating bath according to any one of claims 1 to 4 which also contains about 10 to about 25 milligrams per liter of a cyanide ion.

6. Plating bath according to any one of claims 1 to 5 wherein said cationic polymer is a multifunctional cationic polmer.

7. Plating bath according to any one of claims 1 to 6 wherein said cationic polymer is a copolymer of acrylamide and ammonium quaternary compound.

8. Plating bath according to any one of claims 1 to 7 which also contains between about 2 and about 4 ppm O_2.

9. Plating bath according to any one of claims 1 to 8, which contains the cupric ion source in an amount from about 8 to about 12 grams per liter calculated as cupric sulfate, the reducing agent in an amount from about 0.7 to about 2.2 grams per liter calculated as formaldehyde and as complexing agent ethylene diamine tetraacetic acid or salt thereof for the cupric ion in an amount of about 20 to 50 grams per liter.

10. Method for coating a substrate which comprises contacting the substrate with an electroless copper plating bath according to claim 1.

11. Method according to claim 10 wherein said electroless copper plating bath is maintained at a temperature of about 70°C to about 80°C.

Patentansprüche

1. Bad zum stromlosen Verkupfern, folgendes enthaltend:

A. eine Kupfer (II)-Ionenquelle in einer Menge von ca. 3 bis ca. 15 g/l kalkuliert als Kupfer (II)-sulfat;

B. ein Reduzierungsmittel für die Kupfer (II)-Ionenquelle in einer Menge von ca. 0,7 bis ca. 7 g/l kalkuliert als Formaldehyd;

C. einen Komplexbildner für das Kupfer(II)-Ion in einer Menge von ca. 20 bis 50 g/l; und

D. 1 Teil pro 10^9 bis 1,000 Teile pro 10^9 eines kationischen Polymers aus Akrylamid oder Methakrylamid, oder aus beiden.

2. Plattierungsbad nach Anspruch 1, welches 1 Teil pro 10^9 bis ca. 500 Teile pro 10^9 des kationischen Polymers enthält.

3. Plattierungsbad nach Anspruch 1 oder 2, welches ein anionisches oberflächenaktives Mittel enthält, bevorzugt in einer Menge von ca. 0,02 bis ca. 0,3 g/l.

4. Plattierungsbad nach einem der Ansprüche 1 bis 3, mit einem pH von ca. 11,8 bis ca. 12,5.

5. Plattierungsbad nach einem der Ansprüche 1 bis 4, welches außerdem ca. 10 bis ca. 25 mg eines Zyanidions/1 enthält.

6. Plattierungsbad nach einem der Ansprüche 1 bis 5, bei dem das kationische Polymer ein polyfunktionelles kationisches Polymer ist.

7. Plattierungsbad nach einem der Ansprüche 1 bis 6, bei dem das kationische Polymer ein Kopolymer aus Akrylamid und einer quaternären Ammoniumverbindung ist.

8. Plattierungsbad nach einem der Ansprüche 1 bis 7, das außerdem zwischen ca. 2 und ca. 4 ppm O_2 enthält.

9. Plattierungsbad nach einem der Ansprüche 1 bis 8, welches die Kupfer(II)-Ionenquelle in einer Menge von ca. 8 bis ca. 12 g/l kalkuliert als Kupfer(II)-Sulfat, das Reduzierungsmittel in einer Menge von ca. 0,7 und ca. 2,2 g/l kalkuliert als Formaldehyd, und als Komplexbildner Äthylendiamin-Tetraessigsäure oder ein Salz derselben für das Kupfer(II)-Ion in einer Menge von ca. 20 bis 50 g/l enthält.

10. Verfahren zum Plattieren eines Substrats, bei dem das Substrat mit einem Bad zum stromlosen Verkupfern nach Anspruch 1 kontaktiert wird.

11. Verfahren nach Anspruch 10, bei dem das Bad beim stromlosen Verkupfern auf einer Temperatur zwischen ca. 70°C und ca. 80°C gehalten wird.

Revendications

1. Bain de dépôt chimique de cuivre qui comprend:

A. une source d'ions cuivriques dans une proportion allant d'environ 3 à environ 15 grammes par litre, ceci étant calculé pour du sulfate cuivrique;

B. un agent réducteur de la source d'ions cuivriques dans une proportion allant d'environ 0,7 à environ 7 grammes par litre, ceci étant calulé pour le formaldéhyde;

C. un agent complexant de l'ion cuivrique dans une proportion d'environ 20 à environ 50 grammes par litre; et

D. une partie par 10^9 à 1000 parties par 109 d'un polymère cationique de l'acrylamide ou du méthacrylamide ou des deux.

2. Bain de dépôt selon la revendication 1, qui contient une partie par 10^9 à environ 500 parties par 10^9 du polymère cationique.

3. Bain de dépôt selon la revendication 1 ou 2, qui contient un agent surfactant anionique, de préférence dans une proportion d'environ 0,02 à environ 0,3 gramme par litre.

4. Bain de dépôt selon l'une quelconque des revendictions 1 à 3, ayant un pH d'environ 11,8 à environ 12,5.

5. Bain de dépôt selon l'une quelconque des revendications 1 à 4, qui contient aussi environ 10 à environ 25 milligrammes par litre d'ion cyanure.

6. Bain de dépôt selon l'une quelconque des revendications 1 à 5, dans lequel le polmère cationique est un polymère cationique polyfonctionnel.

7. Bain de dépôt selon l'une quelconque des revendications 1 à 6, dans lequel le polymère cationique est un copolymère de l'acrylamide et d'un composé d'ammonium quaternaire.

8. Bain de dépôt selon l'une quelconque des revendications 1 à 7 qui contient aussi entre environ 2 et environ 4 ppm O_2.

9. Bain de dépôt selon l'une quelconque des revendications 1 à 8, qui contient la source d'ions cuivrique dans une proportion d'environ 8 à environ 12 grammes par litre, ceci étant calculé pour du sulfate cuivrique, l'agent réducteur dans une proportion allant de 0,7 à environ 2,2 grammes par litre, ceci étant calulé pour le formaldéhyde et comme agent complexant de l'ion cuivrique de l'acide éthylène diamine tétraacétique ou un sel de celui-ci dans une proportion d'environ 20 à 50 grammes par litre.

10. Méthode de revêtement d'un substrat qui comprend la mise en contact du substrat avec un bain de placage chimique de cuivre selon la revendication 1.

11. Méthode selon la revendication 10 dans laquelle ledit bain de placage chimique de cuivre est maintenu à une température comprise entre 70°C. et 80°C. approximativement.