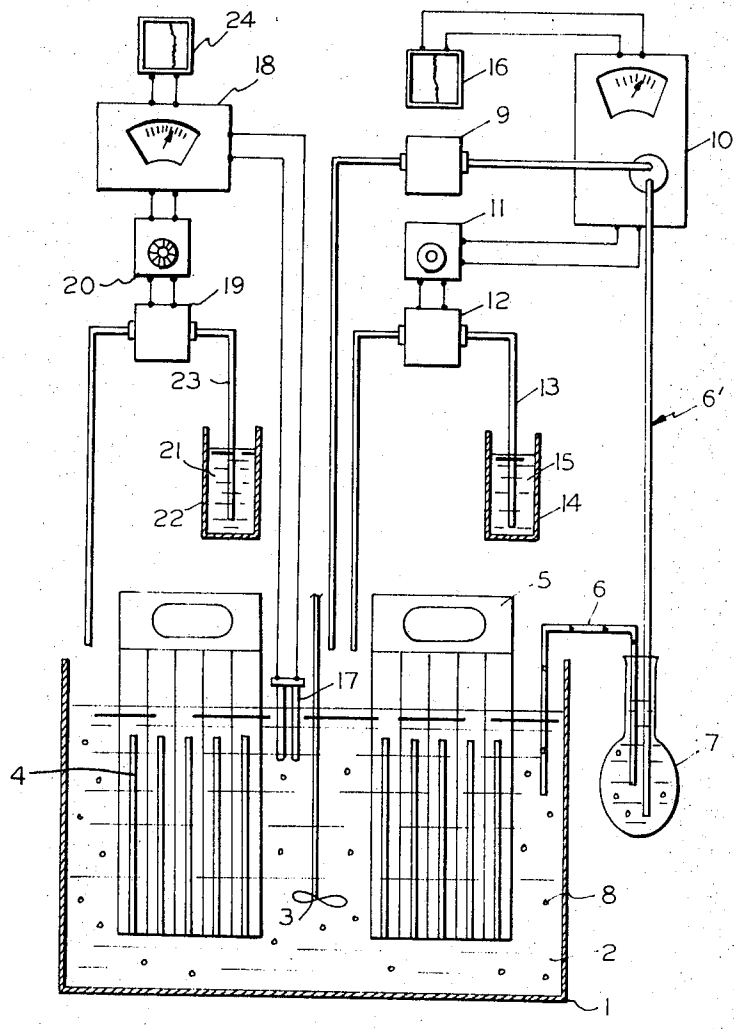
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ELECTROLESS COPPER PLATING PROCESS

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Hyogo Hirohata,
Masahiro Oita and
Katsuhiko Honjo
INVENTORS

BY Wenderoth, Lind & Ponack
ATTORNEYS

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ELECTROLESS COPPER PLATING PROCESS

Hyogo Hirohata, Neyagawa-shi, Masahiro Oita, Kashiwara-shi, and Katsuhiko Honjo, Kadoma-shi, Japan, assignors to Matsushita Electric Industrial Co. Ltd., Osaka, Japan

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ABSTRACT OF THE DISCLOSURE

In an electroless copper plating process, the improvement which comprises measuring the pH of a bath consisting of an aqueous solution of formaldehyde, a copper salt, a complexing agent and an alkali hydroxide; removing the hydrogen gas included in said aqueous solution; measuring the copper ion concentration in said bath; holding the pH at a predetermined value by feeding into the bath a concentrated aqueous solution of an alkali hydroxide; and supplying a mixture of formaldehyde and copper salt in a predetermined mole ratio to said aqueous solution so as to hold the concentrations of formaldehyde and copper salt at predetermined values.

FIELD OF THE INVENTION

This invention relates to an electroless copper plating process utilizing a bath consisting of an aqueous solution of formaldehyde, a copper salt, a complexing agent and an alkali hydroxide, and more particularly relates to a method for automatically holding the concentration of copper ions and formaldehyde in said bath at a predetermined value for a long plating time.

DESCRIPTION OF PRIOR ART

An electroless copper plating process has been widely used for plating a metal film onto non-conductive plastics and for making printed circuit boards. The process usually utilizes a bath consisting of a strongly basic aqueous solution of a copper salt, a complexing agent and a reducing agent such as formaldehyde or its derivative. Conventionally, the copper salt is copper sulfate, copper nitrate or copper chloride and the complexing agent is ethylenediaminetetraacetic acid, its alkali salt, tartaric acid or its alkali salt.

In the bath an activated substrate is coated with a copper film deposited by an autocatalytic reaction expressed by a chemical Equation 1:

$$Cu^{+2}+2HCHO+4OH^- \rightarrow Cu^\circ+H_2+2H_2O+2HCO_2^- \quad (1)$$

The deposited copper promotes catalytically the reaction of Equation 1 and increases the thickness of plated film. The above autocatalytic reaction is accompanied by undesirable reactions such as a Cannizzaro reaction (2), cuprous oxide formation reaction (3) and disproportionation reaction (4).

$$2HCHO+OH^- \rightarrow CH_3OH+HCO_2^- \quad (2)$$

$$2Cu^{+2}+HCHO+5OH^- \rightarrow Cu_2O+HC_2^-+3H_2O \quad (3)$$

$$Cu_2O+H_2O \rightarrow Cu^\circ+Cu^{+2}+2OH^- \quad (4)$$

A highly concentrated bath increases the deposition rate of the copper, but at the same time promotes decomposition of the bath composition due to the reactions (3) and (4). The cuprous oxide formed according to the reaction (3) is converted into metallic copper by the reaction (4). The metallic copper so produced promotes the autocatalytic reaction (1) and consequently causes a copper deposition over all the surface of substrate including the portion which it is not desired to plate. Another great disadvantage of conventional electroless copper plating is a decrease in the concentration of the bath during the course of plating, which decrease is not observed in a copper electroplating process in which anodic copper is provided for continuously supplying copper ions to the bath. In addition to the decrease in the copper ions in the electroless copper plating bath, the concentrations of formaldehyde and alkali hydroxide also decrease during the copper deposition according to the reaction (1). The decrease can be prevented to some extent by employing a large bath and a concentration of bath as high as possible, but not so high as to cause the decomposition of the bath. These methods, however, cannot effectively prevent the decrease of, and finally result in an extremely small rate of copper deposition. Therefore, the bath is required to be renewed frequently even though it still has a remainder of active materials. Therefore, by electroless copper plating according to prior art methods, it is difficult to produce a thick plated film, and accordingly it is used as a pretreatment which enables one to make non-coductive materials electrically conductive for a subsequent copper electroplating.

BRIEF SUMMARY OF THE INVENTION

An object of this invention is to provide an electroless copper plating process in which a bath composition is kept at a given value for a long period of plating time.

Another object of this invention is to provide an electroless copper plating process which produces a thick plated film, the thickness being approximately in proportion to the plating time.

A further object of this invention is to provide an electroless copper plating process in which a bath is stable without chemical decomposition during plating and which results in low waste.

The electroless copper plating process according to the invention comprises utilizing a bath consisting of an aqueous solution of formaldehyde, a copper salt, a complexing agent and an alkali hydroxide such as sodium hydroxide or potassium hydroxide, and according to the invention the pH and copper ion concentration in said bath are simultaneously measured; the pH is held at a predetermined value by feeding into the bath a concentrated aqueous solution of alkali hydroxide; and a combination of formaldehyde and a copper salt in a predetermined mole ratio is fed to said bath so as to hold the concentrations of formaldehyde and copper ions at a predetermined value. The apparatus for carrying out the method includes means for feeding automatically both the necessary alkali hydroxide and the combination of formaldehyde and copper salt, in response to variations in the pH and copper ion concentration of the bath with the plating time.

It is possible to use any soluble copper salt such as copper nitrate, copper sulfate or copper chloride.

An operable complexing agent is ethylenediaminetetraacetic acid, or its alkali derivative, which prevents the bath from decomposing even at a high pH value, and also protects the plated film from surface oxidation due to a low pH of the bath.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be set forth in detail in the following description taken together with the accompanying drawing showing diagrammatically an electroless copper plating apparatus according to the invention.

DETAILED DESCRIPTION

The preferred bath is an aqueous solution having the following composition

TABLE 1

	Mole/l.
Cupric sulfate	0.001–0.09
Ethylenediaminetetraacetic acid	0.001–0.20
Formaldehyde	0.01–1.5
Sodium hydroxide	0.01–1.0

It has heretofore been difficult to measure and control continuously the concentration of formaldehyde in the bath during plating. No prior art disclosure concerning an electroless copper plating process has been found in which the concentration of formaldehyde is automatically controlled during plating.

It has been discovered according to the present invention that formaldehyde is consumed during electroless copper plating by a mole ratio of more than 2:1 and less than 3:1 with respect to consumed copper ions. Therefore, the concentration of formaldehyde in the bath can be determined by the determining of the concentration of copper ions, which can be measured by a colorimetric analysis. The copper ions in the bath form complexed copper ions with the complexing agent dissolved in the bath and have the absorbence characteristic of the complexed copper ions. For example, the copper ions combined with ethylenediaminetetraacetic acid show maximum absorbence at a wave length of 760 mμ when the pH is 11 to 13.

The intensity of absorbence is not affected by the presence of such as SO_4^{-2}, NO_3^-, Cl^- and $HCOO^-$ and other compounds such as methanol, formaldehyde and excess ethylenediaminetetraacetic acid which may be included in the bath, but decreases with an increase in the pH. At a constant pH value in the bath, the concentration of copper ions can be measured exactly by colorimetric analysis. The pH value of the bath can be kept constant by continuously measuring the pH and automatically feeding a concentrated alkali hydroxide solution to the bath in response to the variation in the pH in a manner set forth hereinafter.

The continuous colorimetric analysis indicates what amounts of copper ions and formaldehyde are present at any time, and the analysis apparatus is electrically coupled with the means for feeding copper salt and formaldehyde into the bath so as to keep the bath at the predetermined concentration of copper ions and formaldehyde. There can be employed any feeding method in which the amount of copper salt fed into the bath is in a mole ratio of from 1:2 to 1:3 with respect to the formaldehye fed into the bath. A preferable feeding method is one in which a mixture of copper salt and formaldehyde in the above mole ratio is supplied to the bath. The mixture can be a powder on a solution.

The operable mole ratio depends upon the plating conditions such as temperature, the volume of the bath, the concentration of the bath and the size of the object to be plated, and ranges from 1:2 to 1:3. The exact mole ratio must be predetermined by a test run for the process without feeding into the bath the mixture of copper salt and formaldehyde. A mole ratio higher than 1:2 results in an extremely small rate of copper deposition and a mole ratio lower than 1:3 causes decomposition of the bath.

Referring to FIG. 1, a bath container **1** made of any material inert to the bath contains a solution **2** for plating and a stirrer **3** is provided for circulating the bath to keep the composition uniform throughout. Samples **4** activated by a conventional method are imersed in the bath while being supported by any suitable holder means **5**. The bath solution **2** is supplied through a glass tube **6** to a bubble eliminator **7** by a siphon. It is necessary for accurate colorimetric analysis to eliminate bubbles of hydrogen gas included in the bath solution. Hydrogen gas **8** contained in the bath solution evaporates from the bubble eliminator **7**. The degassed solution is drawn by a pump means **9**, through a glass tube **6'** to a spectrocolorimeter **10** for measuring the concentration of cupric ions by colorimetric analysis. The solution is then fed back to the bath by the pump means **9** after colorimetric analysis. The spectrocolorimeter **10** generates an electric signal, the strength of the signal depending upon the difference between the measured concentration of copper ions and a predetermined value of concentration. The generated electric signal is amplified by an amplifier **11** and supplied to a feeding pump **12** so as to control the feed of an aqueous solution of formaldehyde and copper salt in the aforesaid mole ratio to the bath through a pipe **13** from a container **14** containing said aqueous solution **15**. Alternatively the amplifier can be an on-off type amplifier which is actuated to drive the pump when the signal falls below a predetermined value. The spectrocolorimeter **10** is electrically connected to a recorder **16** for recording the concentration of copper ions.

In association with the control of concentrations of formaldehyde and copper ions in the bath, the pH of the bath **2** is continuously measured by a glass electrode **17** connected electrically to a pH meter **18**. The pH meter **18** generates an electric signal, the strength of the signal depnding upon the difference between the measured pH and a predetermined pH value. The generated electric signal drives a feeding pump **19** after it is amplified by an amplifier **20**. A concentrated alkali hydroxide solution **21** in an alkali hydroxide container **22** is fed through a glass tube **23** to the bath by said feeding pump so as to hold the pH of the bath at a predetermined value. Alternatively the amplifier can be an on-off type amplifier which is actuated to drive the pump when the signal falls below a predetermined value. The pH meter **18** is electrically connected to a recorder **24** for convenience in recording the pH value of the bath.

In such a way the bath can be controlled both with respect to the pH and the concentration of formaldehyde and copper ions so as to facilitate electroless plating at a predetermined rate for a long period of time. In the bath according to the invention, there is no decrease in the pH or the concentrations of formaldehyde and copper ions which lowers the plating rate, and there is no need to employ an initially high concentration of the bath which is apt to result in the decomposition of the bath.

When the mixture of formaldehyde and copper salt is in a finely divided powder form, one form of feeding means can be a container having at the bottom a small hole which can be closed and opened by a stopper means. The electrical signal supplied from the spectrocolorimeter **10** actuates a switch to move the stopper means to open said hole so as to feed the mixture into the bath in powder form. The powder form of the mixture has the advantage that the volume of the bath is not remarkably increased by the addition thereof, whereas a solution of the mixture has the advantage that the bath composition can easily be made uniform.

The electroless copper plating process according to the invention can be made fully automatic by using a belt conveyor which moves through the bath at a given rate, because the bath is controlled so as to have a composition which results in a constant plating rate over a long period of plating time. The activated objects to be plated can be placed on the belt conveyor and immersed in the bath for a given period and then withdrawn automatically from the bath by the moving belt conveyor after being plated on the surface to a given thickness which depends upon the plating conditions and immersion time.

The following example is a specific embodiment of the invention and should not be construed as limitative.

EXAMPLE

The bath composition used is an aqueous solution of 0.02 mole/l. of cupric sulfate, 0.03 mole/l. of ethylenediaminetetraacetic acid, 0.20 mole/l. of sodium hydroxide,

and 0.15 mole/l. of formaldehyde. A plastic container having a 100 liter capacity is filled with 60 l. of the said aqueous solution. A phenolic resin board is given a conventional activation treatment by employing a $SnCl_2$ and a $PdCl_2$ solution respectively, and is then immersed in the bath. The aqueous solution is kept at 30° C. and is stirred by a plastic three blade stirrer which is rotated at 750 r.p.m. during the plating operation.

The aqueous solution is supplied through a glass tube having a 5 mm. diameter to a bubble eliminator at a flow rate of 20 ml./min. by siphon as shown in FIG. 1. The bubble eliminator is a round bottom glass flask having a 300 ml. volume. Hydrogen gas contained in the aqueous solution evaporates off at the bubble eliminator. The refined aqueous solution is fed, by a quantitative suction pump, CV–I type of Tokyo Instrument Co., to a spectrocolorimeter, Sp–20 type of Shimazdu Corporation, for measuring continuously the concentration of cupric ions in the aqueous solution. After measurements of the concentration, the aqueous solution is fed back to the bath at a rate of 20 ml./min. The measured concentration of cupric ions is converted into an electric signal by a conventional method. The thus produced electric signal is supplied to an on-off amplifier which operates when the signal indicates a concentration of less than 0.02 mole/l. of cupric ions, and which activates a quantitative suction pump when the measured concentration of cupric ions is lower than 0.02 mole/l. The activated suction pump supplies an aqueous solution of 0.5 mole/l. of cupric sulfate and 1.2 mole/l. of formaldehyde to the bath at a rate of 30 ml./min. from a storage bottle until the measured concentration of cupric ions reaches 0.02 mole/l. The pH of the bath is continuously measured by a pH meter which is coupled with an on-off amplifier which operates when the pH value falls below 12.0. The on-off amplifier activates a quantitative suction pump when the measured pH value is lower than 12.0. The suction pump supplies an aqueous solution of 6 N sodium hydroxide to the bath at a rate of 30 ml./min. until the measured pH becomes 12.0. According to the method it is possible to keep the composition of bath constant, within a tolerance of ±10%, for 10 days, with 5 hours' operation per day, and to produce a constant deposition rate of copper ranging from 2.0 to 2.5 micron/hour thickness.

What we claim is:

1. In an electroless copper plating process wherein an article is plated with copper by immersing said article in an aqueous solution of formaldehyde, copper ions, a complexing agent, and an alkali metal hydroxide for establishing a pH ranging from 11 to 13, the improvement comprising measuring the pH of said solution during said process; feeding into said solution an alkali metal hydroxide in response to said pH measurement to maintain the pH of said solution at said pH ranging from 11 to 13; measuring the copper ion concentration in said solution during said process by means of a spectrocolorimeter which generates a corresponding electric signal; and feeding into said solution in response to said corresponding electric signal a combination of formaldehyde and said copper ions in a mole ratio from 1:2 to 1:3 to maintain the initial concentration of copper ions and formaldehyde in said solution constant during said plating process.

2. The improvement as claimed in claim 1, wherein said complexing agent is ethylenediaminetetraacetic acid.

3. The improvement as claimed in claim 1, wherein said complexing agent is an alkali metal salt of ethylenediaminetetraacetic acid.

4. The improvement as claimed in claim 1, wherein said combination of formaldehyde and copper salt is in powder form.

5. The improvement as claimed in claim 1, wherein said combination of formaldehyde and copper salt is in aqueous solution.

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JULIUS FROME, Primary Examiner

L. B. HAYES, Assistant Examiner

U.S. Cl. X.R.

117—47, 130, 160

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,532,519 Dated October 6, 1970

Inventor(s) Hyogo Hirohata, Masahiro Oita, Katsuhiko Honjo

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

In the Specification

Column 3, line 59, change "1:2 to 1:3" to -- 2:1 to 3:1 --;

line 62, change "1:2" to -- 2:1 --;

line 64, change "1:3" to -- 3:1 --.

In the Claims

Claim 1, line 16, change "1:2 to 1:3" to -- 2:1 to 3:1 of formaldehyde with respect to copper --.

Signed and sealed this 25th day of December 1973.

(SEAL)
Attest:

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