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⑤④ Method of formulating and operating an electroless plating bath solution for forming copper deposits which are essentially free of fissures.

⑤⑦ Electroless metal plating solutions are formulated and controlled to provide high quality metal deposits by establishing the intrinsic cathodic reaction rate of the solution less than 110% of the intrinsic anodic reaction rate. Electroless copper plating solutions contaning plating rate accelerators containing delocalized pi bonds and having the concentration of the reducing agent no greater than 1,2 times the concentration of the cooper ion can deposit copper on printed wiring boards of quality sufficient to pass a thermal stress of 10 seconds contact with molten solder at 288 °C without cracking the copper deposits on the surface of the printed wiring boards or in the holes. As the plating solution ages by buildup of plating reaction by-products or by-products and contamination, the quality of the copper deposited can be maintained by increasing the copper ion concentration and pH of the solution, while reducing or maintaining substantially constant the concentration of the reducing agent.

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Method of Formulating and Operating an Electroless Plating Bath Solution for Forming Copper Deposits which are Essentially free of Fissures

Copper deposits on substrates produced by electroless deposition or electroless deposition reinforced by electroplating are an important part of many processes for the manufacture of printed circuit boards. Fully additive printed circuit boards are made with the total copper deposit formed by electroless deposition.

5 In order to provide reliable printed circuit boards for use in military and, increasingly, commercial applications the citeria for such boards are based on the ability to meet the requirements of MIL Spec. P-55110-D stress test specification.

Frequently, electrolessly formed copper deposits have been found not to pass this thermal stress test: the plated-through hole wall plating would fracture during a 10 seconds exposure to molten solder, the 10 fracture usually occurring at the intersection of the hole wall with the surface, the corners of the holes.

It was found that the buildup of by-products and of trace contaminations in electroless copper deposition solutions has major detrimental effects on the quality of copper deposits. Contaminants can enter the plating solution through trace contaminants in chemical addition solutions, water supplies, air or from the work placed in the electroless copper bath solution. Many of the inorganic contaminants, such as cuprous 15 ions, iron, silver, gold, antimony, arsenic and other metals and their compounds, as well as many organic species, can cause deleterious results for both bath operation and quality of copper deposits, even when only present in parts per million concentrations.

The following definitions are used herein:

By the term:

20 "anodic reaction rate" is meant the rate of oxidation of the reducing agent on a metal surface in an electroless metal deposition solution;

"cathodic reation rate" is meant the rate of reduction of metallic ions to metal on a metallic surface in an electroless deposition solution;

"intrinsic anodic reaction rate", r_a' is meant the anodic reaction rate as measured on a metallic surface in 25 an electroless plating solution by imposing a potential slightly more positive than the mixed potential on the metallic surface;

"intrinsic cathodic reaction rate", r_c', is meant the cathodic reaction rate as measured on a metallic surface in an electroless plating solution by imposing a potential slightly more negative than the mixed potential on the metallic surface;

30 "electroless plating reaction under cathodic control" is meant that the cathodic reation controls the overall plating rate, i.e., the plating rate depends on the concentration of the cathodic reactants, the concentration of the metal ions, or the concentration of depolarizers for the half reaction involving the metal ions;

"electroless plating reaction under anodic control" is meant that the anodic reaction controls the overall plating rate, i.e., the plating rate depends on the concentration of the anodic reactants, the concentration of 35 the reducing agents, or depolarizers for the half reaction involving the reducing agent;

"thermal stress test" is meant a test of printed circuit specimens containing plated through holes wherein the specimens are conditioned at 120°C to 150°C for a minimum period of 2 hours to remove moisture; after conditioning, the specimens are placed in a desiccator on a ceramic plate to cool; the specimens are then fluxed (type RMA of MIL Spec. F-14256) and floated in a solder bath (Sn 63 +/- 5%), and maintained 40 at 288°C +/- 5°C for a period of 19 seconds: subsequently, the specimens are placed on a plate to cool; then they are microsectioned in a vertical plane at the center of the hole and examined for cracks at 50 to 100 magnifications. A minimum of one microsection containing at least three holes is made for each sample tested. Any cracks forming in the copper deposit on the specimens will indicate thermal stress failure;

"high quality copper" is meant copper that has small crystals with a grain size less than 10 micrometer and 45 low frequency of crystal dislocations, defects and twinning. High quality copper on printed circuit boards will pass the thermal stress test. When referring to electrolessly deposited copper, by the term "satisfactory copper quality" is meant also high quality copper.

"fissure free copper deposits" are meant electroless copper deposits free of internal cracks or fissures or internal defects capable of causing cracks or fissures when the copper is thermally stressed. "Fissure 50 resistant copper" means copper deposits that will not form fissures or cracks when exposed to thermal stress, thermal cycling or in use.

It is an object of the invention to provide a method of operating and maintaining an electroless copper plating solution which ensures the deposition of copper having good physical properties and being free of fissures.

it is a further object to provide a method for formulating electroless copper plating solutions that are capable of depositing copper free of fissures and resistant to cracking under thermal stress, and more specifically under thermal stress testing at 288° C.

The foregoing objects are achieved by the method of the invention of formulating and operating an electroless plating bath solution for forming copper deposits being substantially free of fissures, said solution comprising copper ions, a complexing ligand for copper ions, a pH adjustor, a reducing agent, a stabilizer and/or ductility promoter; and having a desired initial ratio of the intrinsic anodic to the intrinsic cathodic reaction rates, being characterized in that, as the solution ages in use by the buildup of by-products of the electroless plating reactions, or said by-products and contaminants, the copper ion concentration and the pH are increased to maintain copper deposits substantially free of fissures.

In one aspect of the invention, the copper ion concentration and pH are sufficiently increased and the redu cing agent concentration is sufficiently decreased for substantially maintaining the original plating rate.

In another aspect, copper ion concentration and pH are sufficiently increased and the reducing agent concentration decreased for maintaining the ratio of intrinsic anodic to intrinsic cathodic reaction rates at or below the ratio originally selected for the plating bath solution.

Further embodiments described hereinafter include methods of maintaining constant plating rates and methods for increasing plating rates.

The plating bath solution of the present invention is characterized in that the mole concentration of the reducing agent is no greater than 1,2 times the mole concentration of the copper ion and preferably equal to the latter.

Fig. 1 is a schematic diagram of apparatus suitable for carrying out electrochemical measurements referred to in this invention.

Fig. 2 is the plot of the potential applied in making the measurements vs. time as described in Example 1.

Fig. 3 is the plot of the current produced vs. the potential applied as described in Example 1.

While the invention will be described in the context of alkaline electroless plating bath solutions, its scope is not limited to such solutions.

There are many electroless copper plating bath solution formulations which will initially deposit high quality copper. However, experience has shown that, as the plating baths age, the quality of the deposit deteriorates, and the bath must be replaced in whole or in part. The age of an electroless plating solution is determined by buildup of plating reaction by-products and contaminants. The buildup of by-products can be measured by the change in solution density or specific gravity. Only under fixed operating conditions, the contaminants also will build up in proportion to the change in solution density. The teaching of this invention allows the extension of the useful life of such solutions by controlling the mole ratio of the reducing agent to copper, and increasing the copper concentra tions and the pH of such solutions to obtain adequate plating rates at the desired mole ratio.

Among copper compounds that are suitable as sources of copper ions are copper sulfates, copper nitrates, copper halides, copper acetates, copper phosphates, copper oxides, copper hydroxides, basic copper sulfates, halides and carbonates and soluble copper complexes. Copper(II) sulfate and copper(II) chloride are commonly used. Another source of copper ions is metallic copper which may be electrochemically dissolved into the electroless plating solution, or electrochemically dissolved into an electrolyte and diffused through a membrane into the electroless plating solution.

The lower limit for the concentration of the copper compound in the electroless plating solution should be high enough to maintain the intrinsic cathodic reaction rate grater than 90% of the intrinsic anodic reaction rate. The upper limit is the concentration where copper metal precipitates homogeneously throughout the solution instead of only forming copper deposits on preselected catalytic surfaces. The upper limit also depends on the stabilizer additive used to control homogeneous precipitation. For most electroless copper plating bath formulations, the concentration will be above 0,01 molar and below 0,2 molar.

In one embodiment of the invention, the copper concentration and the pH of the electroless plating solution are increased as the by-products and contaminants build up in the solution. In this embodiment, in order to obtain fissure free copper deposits when contaminants and/or by-products build up in the solution the copper concentration is increased 20 to 200%, preferably 40 to 100%, while the pH is also increased.

Among the reducing agents that are suitable for the reduction of copper ions are formaldehyde reducing agents including compounds such as formaldehyde, formaldehyde bisulfite, paraformaldehyde, dimethylhydantoin, and trioxane. Other suitable reducing agents are boron hyrides such as boranes and borohydrides such as alkali metal borohydrides.

The upper limit for the reducing agent in the electroless plating solution is the concentration at which the intrinsic anodic reation rate is 100% the intrinsic cathodic reaction rate. The lower limit is the concentration at wich copper plating on a clean copper surface does not occur, i.e., the plating solution is passive. Preferably, the lower limit is the concentration at which the intrinsic anodic reactions rate is 75% to 85% of the intrinsic cathodic reaction rate. For formaldehyde reducing agents, the limits depend on additives, pH and very strongly on the temperature. In solutions where the intrinsic anodic and cathodic reaction rates have not been determined, the concentration of formaldehyde will preferably be set above 0,01 molar and below 1, 2 times the molar concentration of copper ions, and more preferably maintained at or below the molar concentration of the copper ions.

Suitable pH adjusting compounds include the alkali metal hydroxides and copper oxide. In the operation of an alkaline, electroless copper plating solution, the pH usually drops during plating, and hydroxides are added to raise or maintain pH. If the pH need to be lowered, an acidic compound would be used as a pH adjusting ion. When a formaldehyde reducing agent is used, the activity of the reducing agent depends on the pH as well as the concentration of the reducing agent. Therefore, to increase the activity of the reducing agent and thus increase the intrinsic anodic reaction rate as described hereinbelow, either the concentration of the formaldehyde reducing agent or the concentration of the hydroxide compound (i.e., pH) may be increased. In operating an electroless copper solution when the intrinsic anodic reaction is to be increased, preferably pH is increased and formaldehyde concentration is held substantially constant or even decreased.

In one embodiment of the invention, as the solution ages, the intrinsic cathodic reation rate is increased by raising the copper concentration by 40 to 100% and the anodic reaction rate is increased less than the cathodic raction rate by raising the pH 0,1 to 1 pH unit, more preferably by 0,2 to 0,6 pH unit.

For formulations with formaldehyde type reducing agents, the pH (measured at room temperature) is usually set between 9,5 and 14. When the ratio of the mole concentration of the reducing agent to the mole concentration of the metal ion is less than about 1,2, the pH is preferably greater than 11,9, more preferably greater than 12,2.

Suitable complexing agents for electroless copper plating solutions are well known to those skilled in the art. Among the complexing agents useful for eletroless copper plating solutions are ethylenedinitrilotetraacetic acid (EDTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetrinitrilopentaacetic acid (DTPA), nitrilotriacetic acid (NTA), triethanolamine, tetrakis (2-hydroxypropyl)ethylenediamine (THPED), pentahydroxypropyldiethylenetriamine, and tartaric acid and its salts (Rochelle salts).

Many additives have been proposed for use in electroless copper plating solutions. These additives may be classified by function into different groups. Most additives have more than a single effect on the electroless copper plating solutions, so classification of additives into groups may be somewhat arbitrary. Almost all the additives affect the rate of the oxiation of the reducing agent (the anodic reaction) or the reduction of the copper ion to metal (the cathodic reaction).

One group of additives are anionic, nonionic, amphoteric or cationic surfactants. The choice of sufactants may vary depending on the operating temperature and the ionic strength of the electroless plating solution employed. Preferably, the surfactant is used at solution temperatures and ionic strengths below its cloud point. Surfactants containing polyethoxy groups or fluorinated surfactants are preferred. Among the preferrd surfactants are alkylphenoxypolyethoxy phosphates, polyethoxy polypropoxy block copolymers, anionic perfluoroalkyl sulfonates and carboxylates, nonionic fluorinated alkyl alkoxylates and cationic fluorinated quaternary ammonium compounds.

A second group of additives are stabilizers which prevent the spontaneous decomposition of the plating solution and/or the indiscriminate formation of copper deposits outside of, or extraneous to, the desired deposit, so called "extraneous copper". Among the additives that have found use a stabilizers and to inibit extraneous copper are oxygen (e.g., oxygen added to the plating solution by stirring or air agitation of the solution), divalent sulfur compounds (e.g., thiols, mercaptans, and thioethers), selenium compounds (e.g., selenocyanates). covalent mercury compounds (e.g., mercuric chloride and phenylmercury), and copper(I) complexing agents (e.g., cyanides, 2,2′-dipyridyl and 1, 10-phenanthrolines).

A third group of additives may be classified as ductility promoters and/or additives to retard hydrogen inclusion in the deposit. This group would include polyalkylene ethers, cyanides, nitriles, compounds of vanadium, arsenic, antimony and bismuth, nickel salts, 2,2′-dipyridyl, 1,10-phenanthrolines and some organic silicones.

The ductility promoters also act as stabilizers and are used alone or in combination with other stabilizers. The amount of stabilizer and/or ductility promotor in the electroless copper plating solution depends on the stabilizers or ductility promotors selected and on the concentration of copper ions, reducing

agent and pH. In general, they should be present in an amount sufficient to prevent extraneous plating, i.e., plating on masks or resists, and substantially less than the amount that would cause passivation of metal surfaces being plated or that would stop the plating reaction.

A fourth class of additives is the group of plating rate accelerators (also known as depolarizers) as disclosed in US-A 4,301,196. These are compounds containing delocalized pi bonds such as heterocyclic aromatic nitrogen and sulfur compounds, aromatic amines and non-aromatic nitrogen compounds having at least one delocalized pi bond. Among such compounds are purines, pyrimidines, pyridines, thiazines, triazines, and thiol derivatives.

Preferably, the depolarizing or accelerating agent will be present in a small effective amount, i.e., generally at least 0,0001 to 2, 5 grams per liter, more specifically 0,0005 to 1, 5 grams per liter, and preferably from 0,001 to 0,5 grams per liter. In general, the amount of depolarizing or accelerating agent used will vary depending upon the particular agent employed and the formulation of the solution.

Although electrolessly deposited copper has been known for many years to be inferior to electrolytically deposited copper in resistance to thermal stress, ductility and other physical properties, surprisingly it has been found that if electroless copper deposition solutions are formulated and controlled to have an intrinsic anodic reaction rate less than 110% of the intrinsic cathodic reaction rate, copper deposits with superior physical properties, including resistance to thermal stress, may be obtained.

The intrinsic rate ratio can be determined by measuring the reaction rates for the two half reactions in the neighborhood of the mixed potential, i.e., at +10 mV for the one and at -10 mV for the other half reaction; or by sweeping the potential on the one and the other side of the mixed potential and measuring the current.

In one method, the intrinsic anodic reaction rate at the mixed potential is estimated from the current required to vary the potential on a working electrode which is electrolessly depositing copper. The potential between the working electrode and a reference electrode is varied in a potential ramp between the mixed potential ($_{mp}$) and +/-30 mV from $_{Emp}$ by passing current between the working electrode and a counter electrode and simultaneously measuring the potential and the anodic current as the potential changes. Alternatively, if the counter electrode is at E_{mp} and very much larger than the working electrode, it can also serve as a reference electrode since the current passed between it and the working electrode would be too small to shift the counter electrode potential. The intrinsic anodic reaction rate at E_{mp} may be determined from the slope of a current vs. voltage plot as it approaches E_{mp}.

Similarly, the intrinsic cathodic reaction rate may be determined from the slope of the current vs. voltage plot between -30 mV from E_{mp} and E_{mp}.

When the intrinsic cathodic deposition rate is maintained greater than the intrinsic anodic deposition rate, or when the ratio of the intrinsic anodic deposition rate to the intrinsic cathodic deposition rate, r_a'/r_c', is less than 1,1 and preferably less than 1,05 and more preferably less than 1,0 it had been found that copper with superior physical properties is deposited. In order to maintain the desired ratio, it may be desirable to increase the rate of the intrinsic cathodic reaction, or increase the intrinsic cathodic rate more than an increase in the rate of the intrinsic anodic reaction.

Among the methods for increasing the rate of the intrinsic cathodic reaction are (1) raising the concentration of the cathodic constituent, i.e., the metal ion concentration; (2) addition of a catalyst or depolarizer to accelerate the cathodic reaction; and (3) increasing the surface area available for the cathodic reaction (e.g., by reducing the contaminants or the stabilizer concentration and the surface area blocked by contaminants or stabilizer; this may be accomplished by diluting the solution with fresh solution or by carbon treatment of the solution to remove contaminants blocking the surface area available for the cathodic reaction). When the metal ion concentration becomes too high, extraneous metal deposition in the bulk of the solution or outside the desired metal pattern may be observed. For many electroless copper plating solutions, this occurs at copper ion concentrations above the range of 0.08 to 0.12 moles per liter.

As electroless plating solutions build up by-products and contamination, the ratio usually will increase. The ratio, r_a/r_c, may be maintained less than 1 while increasing both the anodic and cathodic reaction rates, by increasing the rate of the intrinsic anodic reaction less than an increase in the rate of the cathodic reaction. The rate of the intrinsic anodic reaction may be increased by (1) decreasing the concentration of the reducing agent (i.e., lower formaldehyde) while increasing the pH; or (2) increasing the concentration of anodic depolarizers such as heterocyclic aromatic nitrogen or sulfur compounds. If the concentration of the formaldehyde is lowered too much, the E_{mc} of the solution may rise by 50-200 mV and the solution becomes passive, i.e., there is no electroless deposition. Frequently, the solution will become active again at a higher temperature. It has been found that to increase the concentration of the anodic reactants, the product of the formaldehyde concentration and the square root of the hydroxide ion concentration, $(CH_2O)(OH^-)^{0.5}$, must be increased. Although the formaldehyde concentration may be decreased, held constant,

or even increased, the product, $(CH_2O)(OH^-)^{0.5}$, is increased to maintain the intrinsic anodic reaction rate less than the cathodic rate as the cathodic rate is increased.

For plating solutions operating above room temperature, the square root of the hydroxide ion concentration $(OH^-)^{0.5}$ may be conveniently estimated using the room temperature (25 °C) pH of the solutions.

In the event, that bath contaminants cause reduction of deposition rate and inadequate copper quality because of temporary, localized passivation of the plating surface, the condition must be compensated for by increasing the plating current produced by the anodic half-reaction, i.e., by increasing pH. Since this will increase intrinsic anodic reaction rate, the copper concentration must be increased to bring the ratio of r_a/r_c to the original value before the solution became contaminated, or a value below 1,1 and adequate for the resulting plating rate.

Measurement of the intrinsic rate of the partial reactions

We have determined the ratio of the intrinsic rate of the partial anodic and cathodic reactions from measurements of current-potential relationships in a narrow potential range (e.g., from -30 to +30 mV from the mixed potential, E_{mp}). This relationship is used in two ways. Both methods give similar conclusions regarding conditions for producing copper of preferred qualities.

In one embodiment, the cathodic current, i_c, at the potential which is 10 mV negative with respect to the E_{mp} (i.e., the overpotential, Eta = -10 mV vs. E_{mp}) is taken as the rate of the cathodic partial reaction, $(r_c)_{-10mv}$, or simplified r_c; the anodic current i_a at the potential which is 10 mV positive with respect to the mixed potential, E_{mp}, (i.e., the overpotential, Eta = +10 mV vs. E_{mp}) is taken as the rate of the anodic partial reaction, $(r_a)_{+10\,mV}$, or simplified r_a.

Alternatively, in a computerized method, the intrinsic rates of the partial reactions are determined using the rate expression.

$$r' = \sum_{j=1}^{n} (i_j E_j) / \sum_{j=1}^{n} ((E_j)^2)$$

where r' is the partial rate, i_j is the current density at an overpotential, η_j (Eta), referenced to the mixed potential, E_{mp}, and E_j is calculated from the overpotential vs. E_{mp}, η_j (Eta), according to the equation

$E_j = 10^{\eta_j/b_a} - 10^{(\eta_j/b_c)}$

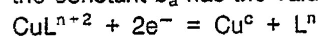
where b_a and b_c are the Tafel slopes. For an electrochemical reaction, a plot of the overpotential, n, from the thermodynamic equilibrium potential vs. logarithm of the current, log i, was found by Tafel to be of the form

$\eta = a - b (\log i)$.

For many electroless solutions, the anodic reaction,

$CH_2O + 2OH^- = HCOO^- + H_2O + 1/2H_2 + e^-$

the constant b_a has the value 940 mV/decade, and for the cathodic reaction



$CuL^{n+2} + 2e^- = Cu^c + L^n$

b_c has the value 310 mV/decade.

The rate of the cathodic partial reaction, r_c', is obtained, in this invention, by applying the above equation to a set of pairs of experimental values (i_j, E_j) from the cathodic potential range which is, e.g., from -30 mV vs. E_{mp} to E_{mp}. The rate of the partial anodic reaction, r_a, is obtained by applying the above equation to a set of pairs of experimental values obtained from the anodic potential range which is, e.g., from E_{mp} to E = +30 mV vs. E_{mp}.

The currents used to calculate intrinsic raction rates are measured at potentials near Emp, e.g., 10-50 mV from Emp, which may introduce some errors in the determination of the intrinsic reaction rates. The equations strictly apply only close to the mixed potential. If one examines both positive and negative overpotentials and currents for a particular solution, one will find near the mixed potential, the overpotential departs from the Tafel (semilogarithmic) relationship. The current measurements for determination of the intrinsic anodic and cathodic reaction rates must be in the range where the semilogarithmic relationship is non-linear. This range is often within +/-40 mV of the Emp, but can be larger or smaller depending on the electroless plating solution formulation. The admissible error depends on the set point of the ratio of the intrinsic anodic and cathodic reaction rates and thus on the formulation of the electroless plating solution.

An experimental setup for carrying out electrochemical measurements of r_a, r_a', r_c and r_c', according to this invention, is shown in Fig. 1. The setup is composed of an electrochemical cell (100), a potentiostat with function generator (120) and a recorder (130).

In a typical test, an all-glass, single compartment cell with three electrodes was used. The test electrode was a platinum wire, 3,8 mm^2 in area (length 2 mm, diameter 0,6 mm), and the auxiliary electrode a platinum cylinder (about 10 mm^2 in area), both electroplated with copper. Plating was done in an acid copper solution $CuSO_4.5H_2O$ - 188 g/l, H_2SO_4 - 74 g/l) at 10 mA/cm^2 for 1 to 5 minutes. A saturated calomel electrode (SCE) was used as a reference electrode.

The current potential curves where obtained with an IBM Instruments Inc. EC/225 Voltammetric Analyzer^{TRADEMARK} (120 in Fig. 1) and recorded on an IBM Instruments Inc. 7424 X-Y-T Recorder^{TRADEMARK} - (130).

The test electrode (111), an auxiliary electrode (112), and a reference electrode (113) are connected to the potentiostat (120). The potentiostat with function generator was used in a DC operating mode, for linear sweep voltammetry (LSV). The sweep waveform as shown in Fig. 2 is a linear ramp; the current is continuously sampled; when the potential reached a final value it is left at this value for a short period of time and then reset to the initial value, or an automatic can reversal to the initial value can be used.

EXAMPLE 1

An electroless copper plating solution was prepared with a high copper concentration and a correspondingly high specific gravity. The ration of the mole concentration of the formaldehyde reducing agent to the mole concentration of the copper was 0,67. The formulation was as follows:

Copper sulfate	0,12 moles/l
Ethylenedinitrilotetraacetatic acid	0,20 moles/l
Formaldehyde	0,08 moles/l
pH (25 °C)	11,9
$(CH_2O)(OH^-)^{0,5}$	0,007 $(m/l)^{1,5}$
Cyanide (Orion electrode)	110 mV vs. SCE
Vanadium pentoxide	5 mg/l
Specific gravity	1,124
Operating temperature	75 °C
r_a	0,14 mA/cm^2
r_c	0,16 mA/cm^2
Ratio (r_a/r_c)	0,88
r_a'	1,13 mA/cm^2
r_c'	1,96 mA/cm^2
Ratio' (r_a'/r_c')	0,58

Additive printed circuit boards were plated in this solution and after plating, tested by the thermal stress test at 288 °C for 10 seconds. There were no cracks formed in the copper by the thermal stress test which confirmed the results from the ratio of the intrinsic anodic and cathodic reaction rates.

EXAMPLE 2

A solution from a working, production, electroless copper plating bath was operated to the formulation below as far as its formulated bath constituents are concerned. The formulation was known to be able to produce high quality copper. However, the ratio of formaldehyde to copper was greater than 1,2 so the solution would not consistently deposit high quality copper as the by-products and contaminants built up and the ratio changed. Electrochemical analysis of the solution gave a ratio of 1,1 and a ratio' of 1,05, indicating borderline performance. The deviation of the electrochemical ratio results from the good ratio results indicates the presence of an unknown contaminant. Fully additive printed wiring boards were prepared on adhesive coated, epoxy glass laminates in this electroless copper plating bath. Thermal stress

testing showed cracks in 20% of the copper hole walls.

The solution had the following formulation:

Copper sulfate	0,028 moles/l
EDTA	0,076 moles/l
Formaldehyde	0,049 moles/l
pH (25° C)	11,6
$(HCHO)(OH^-)^{0,5}$	0,0031 $(moles/l)^{1,5}$
Sodium cyanide (Orion Electrode)	-110 mV vs. SCE
Vanadium pentoxide	0,0012 g/l
Specific gravity (at 25° C)	1,094 g/l
Temperature	75° C
r_a	0,33 mA/cm^2
r_c	0,30 mA/cm^2
Ratio	1,10
r_a'	2,87 mA/cm^2
r_c'	2,74 mA/cm^2
Ratio'	1,05
Thermal stress	20% cracks

In order to deposit copper that would pass the thermal stress test, a similar solution was prepared with a pH of 11,9 and a ratio of formaldehyde to copper of 0,84. The solution had the following formulation:

Copper sulfate	0,056 moles/l
EDTA	0,110 moles/l
Formaldehyde	0,047 moles/l
pH (at 25° C)	11,9
$(CH_2O)(OH^-)^{0,5}$	0,0042 $(moles/l)^{1,5}$
Sodium cyanide (by Orion electrode)	-110 mV vs. SCE
Vanadium pentoxide	0,004 g/l
Specific gravity	1,066 (at 25° C)
Temperature	75° C
r_a	0,33 mA/cm^2
r_a	0,40 mA/cm^2
Ratio	0,83
r_a'	1,69 mA/cm^2
r_c'	1,98 mA/cm^2
Ratio'	0,85
Thermal stress	no cracks

Because the solution was under anodic control and the anodic rate was only slightly increased, the increase in the copper ion concentration to twice the concentration did not cause a corresponding increase in the plating rate. The copper metal was deposited at approximately the same rate, and it required 17 hours to deposit 35 micrometers thick.

In order to accelerate the plating rate, since the concentration of the cathodic reactant had already been doubled, the pH was increased to 12,2. The changes in the formulation are shown below:

pH (at 25 °C)	12,2
$(CH_2O)(OH^-)^{0,5}$	0,006 $(moles/l)^{1,5}$
Sodium cyanide	-110 mV vs, SCE
Specific gravity	1,070 (at 25 °C)
r_a	0,47 mA/cm^2
r_c	0,49 mA/cm^2
Ratio	0,96
r_a'	5,02 mA/cm^2
r_c'	5,30 mA/cm^2
Ratio′	0,95
Thermal stress	no cracks

This solution deposited high quality copper 35 micrometers thick in less than 8 hours. This example illustrates how the principles of the invention may be used to obtain copper with superior physical properties at fast plating rates.

EXAMPLE 3

In this example, a test solution was deliberately contamined to show how the teaching of this invention may be used to adjust the formulation, or reset the control parameters, to obtain fissure free copper deposits from a solution in which contaminants have built up over a period of time as the solution is used.

An electroless copper plating test solution was prepared with a stabilizer system using both vanadium and cyanide additions agents. In the Table below, this solution is marked A. The electrochemical analysis of the solution gave a ratio of the intrinsic anodic reaction rate to the intrinsic cathodic reaction rate, Ratio′ = r_a'/r_c', of less than 1,1 indicating the solution would deposit fissure free copper.

As a deliberate contaminant, 2-mercaptobenzothiazole (2-MBT), 1 mg/1, was added to the test solution. The addition of the contaminant turned the solution passive, i.e., stopped the electroless plating reaction, and the mixed potential of the copper electrode in the test solution was shifted outside the electroless plating range.

The conventional practice in the prior art was to increase the formaldehyde and the pH in order to regain a mixed potential sufficient for electroless copper plating. Following this conventional procedure, formaldehyde was added to the solution to triple the concentration and enough sodium hydroxide was added to increase the pH by one pH unit. In addition, copper was added to increase the cathodic reaction rate. The modified formulation is listed in the Table as solution B. While these adjustments overcame the passivation and increased the rate of deposition, the ratio of formaldehyde to copper was 2,4, and thus greater than 1,2. As expected, the electrochemical analysis of the intrinsic anodic and cathodic reaction rates gave a ratio′ greater than 1,1 indicating the copper deposits would be subject to fissures.

To lower the intrinsic anodic reaction rate relative to the intrinsic cathodic reaction rate, the solution was reformulated with the original formaldehyde concentration and a formaldehyde to copper ratio of 0,7; this is solution C. The ratio′ was reduced to less than 1,1, so the solution would deposit copper resistant to fissures.

To achieve a preferred ratio′ of the intrinsic anodic reaction rate to the intrinsic cathodic reaction rate, the concentration of the anodic reactant, formaldehyde, was further reduced. The formulation is listed as soluton D. The ratio′ of the intrinsic anodic reaction rate to the intrinsic cathodic reaction rate for this solution is less than 1,0 and thus the solution can provide a high quality, fissure free copper deposit.

Solution	A	B	C	D
$CuSo_4$ (mol/l)	0,028	0,056	0,056	0,056
EDTA (mol/l)	0,101	0,101	0,157	0,157
CH_2O (mol/l)	0,04	0,133	0,04	0,02
pH (25 °C)	11,50	12,50	12,50	12,50
$(CH_2O)(OH^-)^{0,5}$ $(m/l)^{1,5}$	0,002	0,024	0,007	0,005
Gafac RE-610 (mg/l)	40	40	40	40
V_2O_5 (mg/l)	1	1	1	1
NaCN (mg/l)	20	20	20	20
2-MBT (mg/l)	0	1	1	1
Temperature (°C)	75	75	75	75
E_{mp} vs. SCE (mV)	-749	-820	-810	-786
r_a' (mA/cm2)	1,41	3,25	3,50	2,65
r_c' (mA/cm2)	1,49	2,90	3,32	2,79
Ratio′	0,9	1,12	1,05	0,95
Plating Rate (µm/hr)	1,70	3,60	4,00	3,30

This example shows that under the given conditions mercaptobenzothiazole acts as an accelerator or depolarizing agent, and with increased copper concentration and pH, with the same or decreased formaldehyde concentration, leads to faster plating rates and high quality copper deposits. The plating rate of solution A without the accelerator or depolarizing agent was 1,4 micrometers per hour. The plating rates of solutions C and D with the accelerator or depolarizing agent were 4,0 and 3,3 micrometers per hours, respectively.

EXAMPLE 4

The procedure of Example 3 was repeated using a plating tank equipped with an electroless copper plating bath controller which continuously measured the solution parameters such as the copper and formaldehyde concentrations, the pH, the cyanide ion activity and the temperature. The plating bath controller automatically compared the measured parameters to the set points and made additions to the solution to maintain the solution within the preset operating limits.

The plating solution was operated to deposit approximately 6 turnovers. (A turnover is replacing the copper salt content of the solution once). This raised the specific gravity of the solution due to the formation of by-product sodium sulfate and sodium formate. The intrinsic anodic and cathodic reaction rates were measured by electrochemical analysis, and the ratio′ of the intrinsic anodic reaction rate to the intrinsic cathodic reaction rate was found to be less than 1,1 which indicates that the copper deposit is resistant to fissures. The soluton was used to made additive printed circuits by the electroless deposition of copper to form surface conductors and plated through holes. The printed circuits were thermally stressed by contact with molten solder at 288 °C for 10 seconds. After thermal stress, the plates through holes were microsectioned and examined for cracks in the deposited copper. There was no evidence of cracks or fissures in the copper conductors or pated through holes. The formulation tested in shown in the table below.

The operating solution found to deposit fissure free copper was then treated with 0,5 mg of 2-mercaptobenzothiazole (2-MBT) as a deliberate contaminant to simulate the effect of contamination of the plating solution by organic compounds. Organic contamination is a frequent problem in electroless copper plating, especially in solutions operated for five or more turnovers. Sources of contamination include leaching from plastic substrates being electrolessly plated, from the plating resist, or from fortuitous contamination.

After the addition of the contaminant, the plating solution became substantially passive. The plating rate was about 0,03 micrometers of copper per hour and the solution would no longer deposit copper on the hole walls of the insulating base material. The ratio′ of the intrinsic anodic and cathodic reaction rates was grater than 1,1, so even if copper would have deposited on the hole walls, the formed deposit, and thus the plated through holes, would fail the thermal stress test. This solution is more fully described below.

Following the procedures of Example 3 in a sample of the solution, the pH was raised to provide a more active plating solution, and the copper concentration was increased to adjust the ratio′ of the intrinsic anodic

and cathodic reaction rates to less than 1,1. The increase in the copper concentration reduced the ratio of formaldehyde to copper from 1,7 to 0,85. When the ratio′ of less than 1,1 was achieved with the sample solution, the set points on the electroless plating bath controller for copper concentration and pH were reset. Additive printed circuit boards were plated in the contaminated electroless plating solution using the new set points. The copper deposited on these printed circuit boards was tested by thermal stress with molten solder at 288° C for 10 seonds and was found free of cracks of fissures. The formulation, set points and test data for this solution are also given below.

		Original good Solution	Solution with Reset Controls
$CuSO_4$	mol/l	0,028	0,040
EDTA	mol/l	0,087	0,100
CH_2O	mol/l	0,047	0,047
pH	25° C	11,75	12,40
$(CH_2O)(OH^-)^{0,5}$	$(m/l)^{1,5}$	0,0035	0,007
Gafac RE-610	mg/l	40	40
NaCN (Orion electrode vs.SCE)	mV	-130	-130
V_2O_5	mg/l	1	1
Specific gravity	g/cm^3	1,066	1,066
Temperature	°C	75	75
Emp vs. SCE	mV	-764	-687
Plating rate	um/hr	1,7	2,9
r_a'	mA/cm^2	1,44	2,57
r_c'	mA/cm^2	1,39	2,40
Ratio′		1,04	0,93
Thermal stress		pass	pass

In this example, a passive, contaminated solution was restored to active plating, and then by adjustment of the formulation, according to the teachings of this invention, the intrinsic anodic and intrinsic cathodic reaction rates of the contaminated solution were adjusted to deposit high quality copper. The addition of 2-mercaptobenzothiazole, a heterocyclic nitrogen and sulfur compound, and increasing the copper concentration and pH resulted in a 70% increase in the plating rate.

EXAMPLE 3

In this example, fissure resistant copper was deposited from an electroless copper deposition solution operating at low temperature. A first electroless copper plating solution was formulated to operate at 30° C. The formaldehyde concentration was higher than similar solutions at 75° C as is the common practice in electroless copper solutions operating near room temperature. The ratio of the formaldehyde concentration to copper concentration was 2,4. The solution plated slowly, depositing 25 micrometers of copper in three days. This first solution composition is given in the table below. As reported in the table, the ratio of the intrinsic anodic reaction rate to the intrinsic cathodic reaction rate is grater than 1,1 and the additive printed circuit boards prepared in the soluton failed the thermal stress test.

Following the teachings of this invention, the concentration of the formaldehyde reducing agent was reduced to lower the anodic reaction rate relative to the cathodic reaction rate. The ratio of the formaldehyde concentration to the copper concentration was reduced to 0,5. The resulting solution is the second soluton in the table below.

		Solution	
		1st	2nd
$CuSO_4$	mol/l	0,028	0,028
EDTA	mol/l	0,087	0,087
Formaldehyde	mol/l	0,067	0,013
pH	25 °C	12,5	12,5
$(CH_2O)(OH^-)^{0,5}$	$(m/l)^{1,5}$	0,012	0,002
NaCN	mg/l	20	20
V_2O_5	mg/L	3	3
Temperature	°C	30	30
Emp vs. SCE	mV	-783	-750
r_a'	mA/cm^2	0,341	0,323
r_c'	mA/cm^2	0,280	0,304
Ratio'		1,22	1,06

The second solution is used to plate additive printed circuit boards with copper 25 micrometers thick. It is difficult to initiate electroless plating on catalytic adhesive and catalytic base materials at low temperatures and low formaldehyde concentration. Therefore, before plating the additive circuit boards, the conductive pattern including the plated through holes is covered with a thin layer of copper about 0,2 micrometer thick in an electroless strike solution which has a formaldehyde concentration of 0,13 moles/liter.

These additive printed circuit boards from the second solution pass the thermal stress test, demonstrating that maintaining a formaldehyde to copper ratio in an electroless plating solution less than 1,2 can provide fissure free copper deposits.

Claims

1. A method of formulating and operating an electroless plating bath solution for forming copper deposits being substantially free of fissures, said solution comprising copper ions, a complexing ligand for copper ions, a pH adjustor, a reducing agent, a stabilizer and/or ductiliy promoter; and having a desired initial ratio of the intrinsic anodic to the intrinsic cathodic reaction rates, characterized in that as the solution ages in use by the buildup of by-products of the electroless plating reactions or said by-products and contaminants, the copper ion concentration and the pH are increased to maintain copper deposits substantially free of fissures.

2. The method of claim 1, characterized in that the copper ion concentration and the pH are sufficiently increased and the reducing agent concentration is sufficiently decreased for substantially maintaining the original plating rate.

3. The method of claim 1, characterized in that the copper ion concentration and/or the pH are sufficiently increased and/or the reducing agent concentration is sufficiently decreased for maintaining the ratio of the intrinsic anodic to the intrinsic cathodic reaction rates at or below the ratio originally selected.

4. The method of one or more of claims 1 to 3, characterized in that the mole concentration of the reducing agent is not greater than 1,2 times the mole concentration of the copper ions.

5. The method of claim 4, characterized in that the mole concentration of the reducing agent is not greater that the mole concentration of the copper ions.

6. The method of one or more of claims 1 to 5, characterized in that the reducing agent is formaldehyde.

7. The method of claims 1 to 6, characterized in that the bath solution further comprises an accelerator selected from (i) heterocyclic aromatic nitrogen and sulfur compounds; (ii) non-aromatic nitrogen compounds having at least one delocalized pi bond; and (iii) aromatic amines and mixtures of the foregoing; and that the pH is adjusted to at least 11,9 as measured at 25 °C.

8. The method of claim 7, characterized in that the pH is adjusted and maintained to at least 12,2 and preferably to 12,5.

9. The method of claims 1 to 8, characterized in that the copper ion concentration and the pH are increased sufficiently to maintain the ratio of the intrinsic reaction rates at or below the initially selected value; and that the reducing agent concentration is sufficiently decreased to maintain the initially selected and established plating rate.

10. An electroless copper plating solution comprising copper ions, a complexing ligand for copper, a pH adjustor, and a stabilizer or ductility promoter, characterized in that the mole concentration of the reducing agent is no greater than 1,2 times the mole concentration of the copper ion.

11. The plating bath solution of claim 10, characterized in that the mole concentration of the reducing agent is no greater than the mole concentration of the copper ion.

12. The plating bath solution of claims 10 or 11, characterized in that it further comprises an accelerator containing a delocalized pi bond, selected from (i) heterocylic aromatic nitrogen and sulfur compounds, (ii) non-aromatic nitrogen compounds having at least one delocalized pi bond, and (iii) aromatic amines, and mixtures of the foregoing.

13. The plating bath solution of claims 10 to 12, characterized in that the reducing agent is a formaldehyde compound.

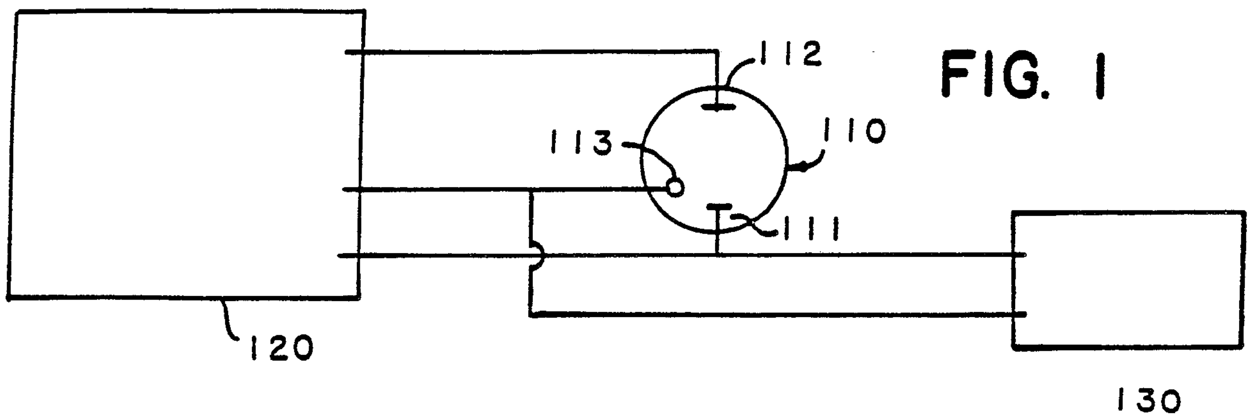


FIG. 1
112
113
110
111
120
130

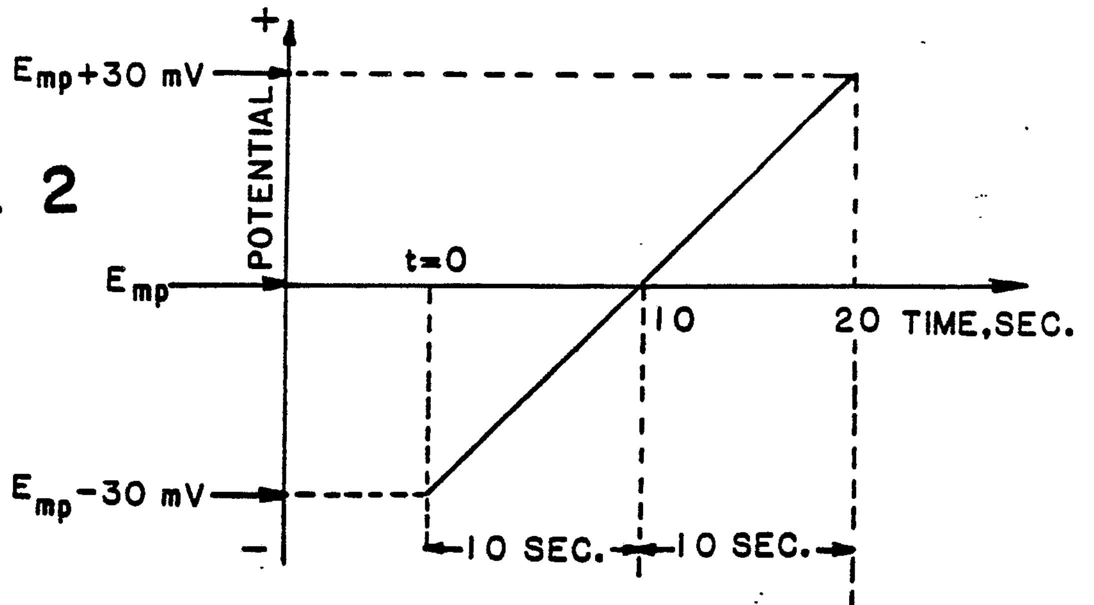


FIG. 2
+
-
POTENTIAL
Emp+30 mV
Emp
Emp-30 mV
t=0
10
20 TIME,SEC.
10 SEC.
10 SEC.

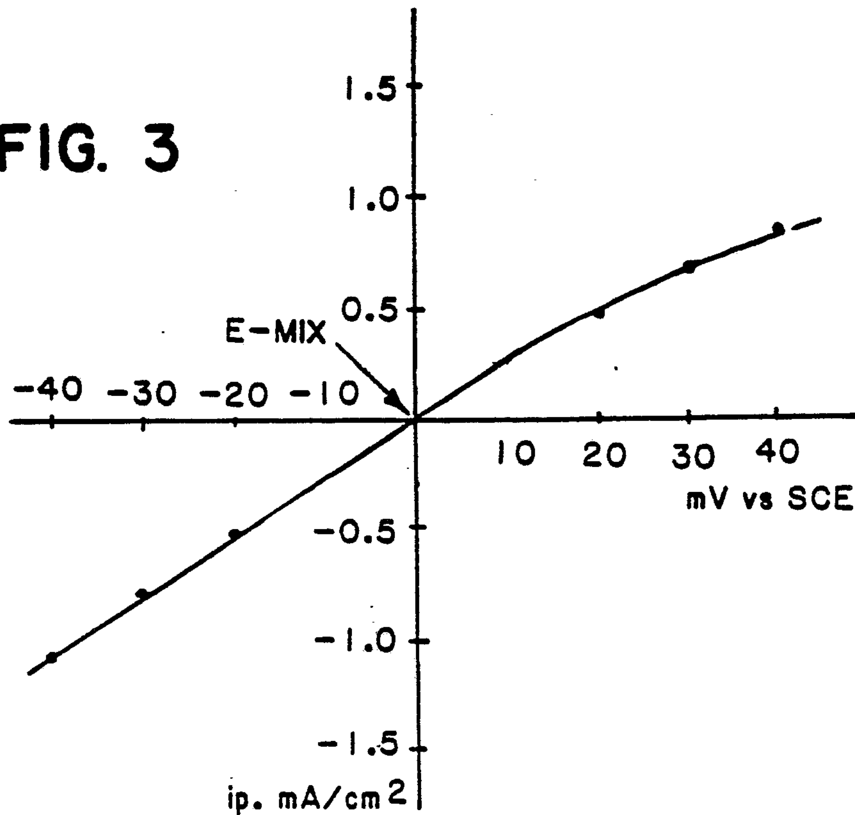


FIG. 3
1.5
1.0
0.5
E-MIX
-40 -30 -20 -10
10 20 30 40
mV vs SCE
-0.5
-1.0
-1.5
ip. mA/cm2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 10 7716

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP-A-0 242 745 (IBM) * Claim 10; page 4, lines 6-29; page 5, lines 4-13 *	1-3,6-9	C 23 C 18/16 C 23 C 18/40
D,Y	FR-A-2 436 192 (KOLLMORGEN TECHNOLOGIES CORP.) * Claims 1-20; page 12, line 1 - page 13, line 20 *	1-3,6-9	
P,X	EP-A-0 265 901 (KOLLMORGEN CORP.) * Claims 1-20 *	1-3,6-9	
P,X	WO-A-8 803 181 (KOLLMORGEN TECHNOLOGIES CORP.) * Claims 1-25; examples *	1-13	
X	FR-A-1 522 048 (PHOTOCIRCUITS CORP.) * Claims 1,2; page 7, table *	10,12, 13	
X	US-A-4 632 852 (H. AKAHOSHI et al.) * Table 5; examples 11-15,18-19 *	10,12, 13	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)**
A	JOURNAL OF ELECTROCHEMICAL STY, vol. 127, no. 2, February 1980, pages 365-369, Princeton, US; M. PAUNOVIC: "An electrochemical control system for electroless copper bath"	1	C 23 C G 01 N

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-08-1989	DE ANNA P.L.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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