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(54) **Electroless copper plating solution**

(57) Provided is an electroless copper plating solution that forms a highly adhesive conductive film regardless of the degree of roughness of the resin surface and also has a fast deposition rate. The electroless copper plating solution of the present invention is characterized

in that it contains guanosine. The electroless copper plating solution of the present invention preferably also contains copper ion, reducing agent, copper ion complexing agent, and pH adjuster.

EP 2 826 886 A1

Description

Field of the Invention

5 **[0001]** The present invention relates to an electroless copper plating solution that forms a plating film having excellent adhesiveness with the article being plated. More specifically, it relates to an electroless copper plating solution that makes it possible to form a plating film having high adhesiveness even with an article being plated that has a low-roughness surface.

10 Background of the Invention

[0002] Electroless copper plating is used in a wide range of technical fields, such as plating on a functional insulating resin during build up and wiring formation in the manufacture of high-density printed circuit boards, plating inside the through holes for electrical connection between the layers of printed circuit boards, and the like. When electroless plating is performed on a resin, high adhesiveness is generally achieved by chemically roughening the resin surface and utilizing the so-called anchor (anchor) effect to improve the adhesiveness between the resin substrate and the conductive film.

[0003] Progress has been made in recent years in increasing signal speed and raising the frequency in association with improved IC chip performance in high-performance semiconductor packages, and formation of wiring having a smooth surface and finer wiring constituting the package substrate are being demanded. In addition, the high-performance resin materials being used recently as the resin substrate have high chemical resistance and mechanical properties, making it difficult to roughen the resin surface. Since it is difficult to actualize an anchor effect when forming a conductive film on these low-roughness surfaces, it was extremely difficult to form a conductive film having high adhesiveness with such resin surfaces. An electroless copper plating solution that makes it possible to form a film having high adhesiveness regardless of the roughness of the resin surface is therefore desired.

25 **[0004]** The plating solution is adjusted to the alkaline range (near pH 11-12) to maintain the reducing performance of the formaldehyde in electroless copper plating using formaldehyde as a reducing agent. A complexing agent must be added to prevent the copper ion from precipitating as copper hydroxide in alkaline copper plating solution. EDTA (ethylenediaminetetraacetic acid) is often used as a complexing agent for electroless copper plating solution. However, EDTA interferes with the neutralization and precipitation of heavy metals and poses a significant problem in waste water treatment. Electroless copper plating solution having equivalent performance without using EDTA is therefore desired. Tartrates are known as compounds having the ability to form complexes with metals. Nonetheless, the plating deposition speed is known to drop when tartrates are used as complexing agents for electroless copper plating solution. Therefore, electroless copper plating solution having a high plating deposition rate even while using tartrates is desired.

30 **[0005]** In JP Kokai 2010-106337, improvement of the adhesiveness of the resin substrate and plating film is intended by adding a specific compound in a conditioner to be used as a step prior to electroless copper plating. In JP Kokai 6-93457, an electroless copper plating solution containing copper ion, complexing agent, pH adjuster, reducing agent, and mercaptosuccinic acid is disclosed.

Summary of the Invention

40 **[0006]** Therefore, the first purpose of the present invention is to provide an electroless copper plating solution that presents high adhesiveness regardless of the roughness (degree of roughness of the surface) of the surface of the resin substrate and is capable of forming a plating film having a good appearance. The second purpose of the present invention is to provide an electroless copper plating solution having a high plating rate even without using EDTA which poses a problem in waste water treatment.

45 **[0007]** As a result of in-depth studies, the present inventors discovered that a plating solution that exhibits higher adhesiveness than past products and has a high plating rate even when using tartaric acid or a salt thereof as a complexing agent is obtained by adding guanosine to an electroless copper plating solution and thereby perfects the present invention.

[0008] Specifically, the present invention relates to an electroless copper plating solution containing guanosine.

50 **[0009]** Furthermore, the present invention relates to a method for forming a copper film on the surface of an article being plated using the above electroless plating solution.

Detailed Description of the Invention

55 **[0010]** In this specification, the terms "plating solution" and "plating bath" are used interchangeably. °C means degree Celsius; g/L means grams per liter; mg/L means milligrams per liter; μm means micrometer; kN/m means kilonewtons per meter; A/dm² and ASD mean amperes per square decimeter.

[0011] The electroless copper plating solution of the present invention is characterized in that it contains guanosine.

[0012] Guanosine is added to the electroless copper plating solution of the present invention to improve the adhesiveness between the resin substrate and the plating film and to raise the plating deposition rate. As will be shown below, adding guanosine to an electroless copper plating solution improves the adhesiveness of the plating film to resin substrates having various surface roughnesses. In addition, electroless copper plating solution with guanosine added obtains a satisfactory deposition rate even when tartaric acid or a salt thereof is used as a complexing agent without affecting the plating deposition rate.

[0013] The concentration of guanosine in the electroless copper plating solution is preferably 5.0 mg/L or higher, more preferably 5.0 mg/L to 30.0 mg/L, even more preferably 10.0 mg/L to 25.0 mg/L relative to the electroless copper plating solution as a whole. The electroless copper plating solution of the present invention may contain copper ion, reducing agent, copper ion complexing agent, and pH adjuster in addition to guanosine.

[0014] The copper ion is obtained by adding a copper compound that forms copper ion in the plating solution to the plating solution. Examples of the copper compound include salts of copper and an inorganic acid or organic acid, oxides, halides of copper, and the like. Specific examples include copper sulfate, copper chloride, copper acetate, copper nitrate, copper fluoroborate, copper methanesulfonate, copper phenylsulfonate, copper p-toluenesulfonate, copper hydroxide, copper oxide, and the like. Copper sulfate and copper chloride are especially preferred among them. These copper compounds can be used individually or in combinations of two or more types.

[0015] The content of copper ion in the plating solution is preferably 2.0 g/L or higher, more preferably 2.4 g/L or higher. At the same time, the content of copper ion is preferably 4.0 g/L or lower, more preferably 3.6 g/L or lower.

[0016] Furthermore, the electroless copper plating solution of the present invention may contain other metal ions as long as they do not harm the stability of the plating solution or the performance of the plating film obtained. For example, causing nickel to be contained is known to alleviate the stress of the film obtained by electroless copper plating. The addition of a trace of nickel to assist in the deposition of copper is also known in electroless copper plating solution using hypophosphorous acid as a reducing agent. Thus, nickel and other such metal ions other than copper can be contained in the electroless copper plating solution of the present invention. Examples of other metal ions include nickel, cobalt, tin, iron, and the like.

[0017] The reducing agent is a compound that itself is oxidized and decomposed in the plating bath and releases electrons. The metal ions in the plating solution receive these electrons and are reduced and deposit. Formalin having weak reducing power but a rapid oxidation rate is preferred as the reducing agent. Nonetheless, other compounds include hypophosphorous acid, glyoxylic acid, and the like. The concentration of reducing agent in the electroless copper plating solution is preferably 2.5 g/L or higher, more preferably 4.0 g/L or higher, relative to the electroless copper plating solution as a whole. At the same time, the concentration of reducing agent is preferably 7.5 g/L or lower, more preferably 5.5 g/L or lower.

[0018] A copper ion complexing agent is added to prevent the production of hydroxides of copper in the electroless copper plating solution which is alkaline. Examples of complexing agents include EDTA, tartaric acid, ethylenediamine-N,N,N',N'-tetra-2-propanol, malic acid, succinic acid, glycine, acetic acid, salts of these, and the like. It is preferable to use tartaric acid or a salt thereof in the present invention. The tartaric acid or salt thereof should form tartrate ion in the plating solution. Examples of salts of tartaric acid include a sodium salt, potassium salt, salts containing both of these, and the like. The concentration of copper ion complexing agent in the electroless copper plating solution is preferably 20.0 g/L or higher, more preferably 24.0 g/L or higher, relative to the electroless copper plating solution as a whole. At the same time, the concentration of copper ion complexing agent is preferably 50.0 g/L or lower, more preferably 36.0 g/L or lower.

[0019] A pH adjuster is added to keep the pH of the copper plating solution alkaline. Examples of pH adjusters include sodium hydroxide, potassium hydroxide, tetramethyl ammonium hydroxide, triethanolamine, monoethanolamine, and the like. However, sodium hydroxide or potassium hydroxide is preferred in the present invention.

[0020] The content of pH adjuster in the electroless copper plating solution is preferably 5.0 g/L or higher, more preferably 8.0 g/L or higher, relative to the electroless copper plating solution as a whole. At the same time, the concentration of pH adjuster is preferably 15.0 g/L or lower, more preferably 12.0 g/L or lower. Furthermore, the content of pH adjuster is the value measured by neutralization titration of the plating solution using a pH meter.

[0021] The electroless copper plating solution of the present invention can contain other additives in addition to the above compounds.

[0022] Examples of other additives include stabilizers to act on the monovalent copper produced in the plating solution and suppress the disproportionation reaction; compounds to improve the throwing power of the plating on the catalyst nuclei and stabilize the bath; agents to improve the film properties; agents to accelerate the plating deposition rate, and the like. Concrete examples include sulfur-containing compounds, for example, mercaptosuccinic acid, dithiodisuccinic acid, mercaptopyridine, mercaptobenzothiazole, thiourea, and the like; heterocyclic compounds, for example, pyridine, purine, quinoline, indole, indazole, imidazole, pyrazine, bipyridine, derivatives of these, and the like; alcohols, for example, alkyl alcohols, allyl alcohols, aryl alcohols, or cyclic phenols, and the like; hydroxy-substituted aromatic compounds, for example, methyl-3,4,5-trihydroxybenzoate, 2,5-dihydroxy-1,4-benzoquinone, 2,6-dihydroxynaphthalene,

and the like; carboxylic acids, for example, citric acid, tartaric acid, succinic acid, malic acid, malonic acid, lactic acid, acetic acid, salts of these, and the like; amines; amino acids; silicon compounds, for example, silane, siloxane, from low to intermediate molecule weight polysiloxane, and the like; polyalkylene glycols, cellulose compounds, alkyl phenyl ethoxylate, polyalkylene glycols, and the like.

[0023] The content of these additives in the electroless plating solution varies depending on the type, function, and the like of the additive. When 2,2'-bipyridine is used as an additive, it is preferably 3 mg/L or higher, more preferably 5 mg/L or higher, relative to the electroless copper plating solution as a whole. At the same time, it is preferably 30 mg/L or lower, more preferably 15 mg/L or lower. When mercaptosuccinic acid is used as an additive, it is preferably 1 mg/L or higher, more preferably 4 mg/L or higher, relative to the electroless copper plating solution as a whole. At the same time, it is preferably 20 mg/L or lower, more preferably 12 mg/L or lower.

[0024] Commonly known methods can be used when performing plating using the electroless copper plating solution of the present invention. Specifically, through holes are formed by drill, punch, or the like as needed in the article being plated, the surface of the article being plated is cleaned as needed, and roughening, neutralization, and catalyst-application steps are carried out, followed by formation of a copper film using the electroless copper plating solution of the present invention.

[0025] The electroless copper plating solution of the present invention can form a highly adhesive plating film on an article being plated (resin substrate) having a smooth surface with a surface roughness (Ra) of 30-500 nm, especially 90-300 nm. Examples of the resin substrate that is the article being plated include epoxy resin, polyimide resin, phenol resin, cyanate resin, ABS, bismaleimide-triamine resin, polyimide, mixtures of these, mixture of these resins and glass, and the like. The electroless copper plating solution of the present invention is especially useful in terms of its ability to form a highly adhesive conductive film even on epoxy resin, cyanate resin, and other such high-performance resin materials.

[0026] The temperature at which electroless copper plating is performed is preferably 20-40°C, more preferably 25-35°C, and the plating time is preferably 10-60 minutes, more preferably 15-30 minutes.

[0027] The electroless copper plating solution of the present invention can be used for a wide range of purposes to form a copper film by using electroless plating. However, it can be used in particular in through hole plating of a printed circuit board, electroless copper plating in a semi-additive process, and the like.

Examples

[0028] The present invention is explained below based on working examples. However, these examples do not limit the scope of the present invention.

Working Examples 1-3 and Comparative Examples 1-6

[0029] A test bath was produced by adding the compounds listed in Table 1 to the following base bath. The following various resin substrates were plated using the above test baths, and the test pieces obtained were evaluated. The results are shown in Table 2.

Base bath 1

[0030]

Cupric chloride dihydrate	5.4 g/L (2 g/L as copper)
Rochelle salt (potassium sodium tartrate)	30 g/L
Sodium hydroxide	10 g/L
Formaldehyde (23% aqueous solution)	20 mg/L (5.0 g/L as formaldehyde)

Working Example 4

[0031] The same procedure as in Working Example 1 was carried out except that the following plating bath was used, and the test piece obtained was evaluated. The results are shown in Table 2.

Plating bath

[0032]

EP 2 826 886 A1

Cupric chloride dihydrate	8.1 g/L (3 g/L as copper)
Guanosine	5 mg/L
Rochelle salt	20 g/L
Sodium hydroxide	10 g/L
Formaldehyde (23% aqueous solution)	20 mL/L (5.0 g/L as formaldehyde)

Table 1

[0033]

Table 1. Amounts of each compound added (unit: mg/L)

	Working Example				Comparative Example					
	1	2	3	4	1	2	3	4	5	6
Guanosine	10	20	30	5	--	--	--	--	--	--
Guanine	--	--	--	--	--	10	--	--	--	--
Uric acid	--	--	--	--	--	--	20	--	--	--
Caffeine	--	--	--	--	--	--	--	10	--	--
N,N'-bis(hydroxymethyl)urea	--	--	--	--	--	--	--	--	10	--
Adenine	--	--	--	--	--	--	--	--	--	20

Table 2

[0034]

Table 2. Evaluation results

Evaluation		Working Example					Comparative Example				
		1	2	3	4	1	2	3	4	5	6
Peel strength (kN/m)	Substrate 1	0.662	0.720	0.688	0.666	0.551	0.709	0.660	0.602	0.591	*
	Substrate 2	0.407	0.524	0.504	0.470	0.369	0.520	0.496	0.366	0.389	*
	Substrate 3	0.386	0.405	0.419	0.285	0.267	0.302	0.267	0.302	0.280	*
Film thickness (μm)	--	0.52	0.59	0.47	0.64	0.57	0.71	0.56	0.54	0.51	*
Appearance	--	Fairly dark	Fairly dark	Fairly dark	Fairly dark	Light	Dark	Dark	Light	Light	-- --
Overall evaluation	--	A	A	A	A	C	B	B	C	C	D
*: Plating did not deposit.											

Overall evaluation

[0035]

Table 3

Overall evaluation	Peel strength	Color of appearance
A	High	Fairly dark ^{Note 1)}
B	High	Dark
C	Low	Light ^{Note 2)}
D	Could not be measured	Chemical precipitation of copper powder
Note 1) Fairly dark shows a good appearance. Note 2) Means equivalent lightness to the unadded bath		

Resin substrate

[0036]

Substrate 1: Epoxy resin, surface roughness (Ra) 220-260 nm

Substrate 2: Epoxy resin, surface roughness (Ra) 90-160 nm

Substrate 3: Mixed resin of epoxy and cyanate, surface roughness (Ra) 250-300 nm

[0037] Resin for measurement of film thickness and checking appearance: Resin surface of MCL-E-67 (epoxy resin laminated on both sides by copper foil) manufactured by Hitachi Chemical Co., Ltd. exposed by detaching the copper foil from both sides by etching

Plating treatment

[0038] Each of the resin substrates shown in Table 1 was subjected to desmear treatment (swelling by Circuposit MLB Conditioner 211, resin etching by Circuposit MLB Promoter 213, neutralization of permanganic acid by Circuposit MLB 7832; all chemicals manufactured by Rohm and Hass Electronic Materials Co., Ltd.), and the surface roughness of the substrate was measured after drying. Conditioning (Circuposit Conditioner Neutralizer 3320, manufactured by Rohm and Hass Electronic Materials Co., Ltd.), soft etching using sulfuric acid, acid washing, catalyst pretreatment (Cataprep 404 Pre-dip, manufactured by Rohm and Hass Electronic Materials Co., Ltd.), catalyst application (Cataposit 44 Catalyst, manufactured by Rohm and Hass Electronic Materials Co., Ltd.), and catalyst activity [sic; activation] (Accelerator 19E, manufactured by Rohm and Hass Electronic Materials Co., Ltd.) were performed thereafter. Electroless plating was then carried out for 20 minutes at 30°C using the electroless plating solutions shown in Table 2. After drying, the thickness of the electroless copper plating film was measured, the appearance was checked visually, and the deposited shapes were checked by SEM. Firing, acid washing, copper electroplating (sulfuric acid copper plating, Copper Gleam ST901, manufactured by Rohm and Hass Electronic Materials Co., Ltd., 23°C, 90 minutes, 1.5 ASD), antioxidant treatment, and firing (180°C, 60 minutes) were performed thereafter. The peel strength was then measured.

Evaluation methods

1. Peel strength

[0039] The adhesive strength of the base resin and plating film was used to evaluate the adhesiveness. Specifically, each resin substrate was subjected to sulfuric acid copper plating in accordance with the process described above. After firing, the copper plating film obtained was cut to a width of 1 cm using a cutter, and the load when peeled at an angle of 90° and a pull rate of 50 mm/min in accordance with the printed circuit board test method JIS C5012 was measured using an Instron 5564 tester. Testing was repeated twice, and the average value is shown in Table 2.

2. Film thickness

[0040] Each resin substrate was subjected to electroless copper plating in accordance with the process described above, and the plating thickness was measured using an x-ray fluorescence film thickness meter SFT 9450.

3. Appearance

[0041] Each resin substrate was subjected to electroless copper plating in accordance with the process described above, and the film on the test piece obtained was examined visually.

[0042] As is evident from the above working and comparative examples, electroless plating solution with guanosine added exhibits good adhesive strength on various resin substrates and do not have any significant effect on the plating deposition rate or appearance. In contrast, when other compounds were added, the adhesive strength was low or the appearance of the plating film obtained was poor.

Claims

1. An electroless copper plating solution containing guanosine.
2. An electroless copper plating solution according to Claim 1 also containing copper ion, reducing agent, copper ion complexing agent, and pH adjuster.
3. An electroless copper plating solution according to Claim 1 wherein the content of guanosine is 5-30 mg/L relative to the plating solution.
4. An electroless copper plating solution according to Claim 2 containing tartaric acid or a salt thereof as a complexing agent.
5. A method for forming a copper film on the surface of an article being plated using an electroless copper plating solution of any of Claims 1-4.



EUROPEAN SEARCH REPORT

Application Number
EP 14 17 7591

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EPO FORM 1503 03.82 (PO4C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 3 793 038 A (MAGUIRE E) 19 February 1974 (1974-02-19) * column 4, line 29 * * column 6, lines 35-48 * * column 6, lines 56-65; examples 1-3 * * column 10, lines 5-10; tables II, V * * the whole document *	1-5	INV. C23C18/38
A,D	JP 2010 106337 A (ROHM & HAAS ELECT MATERIALS) 13 May 2010 (2010-05-13) * the whole document *	1-5	
A,D	JP H06 93457 A (HITACHI CHEMICAL CO LTD) 5 April 1994 (1994-04-05) * the whole document *	1-5	
			TECHNICAL FIELDS SEARCHED (IPC)
			C23C C25D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 27 November 2014	Examiner Suárez Ramón, C
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ON EUROPEAN PATENT APPLICATION NO.**

EP 14 17 7591

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27-11-2014

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3793038 A	19-02-1974	NONE	
JP 2010106337 A	13-05-2010	CN 101935828 A	05-01-2011
		EP 2275589 A1	19-01-2011
		JP 2010106337 A	13-05-2010
		KR 20100048929 A	11-05-2010
		TW 201026891 A	16-07-2010
		US 2010120962 A1	13-05-2010
JP H0693457 A	05-04-1994	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2010106337 A [0005]
- JP 6093457 A [0005]