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(71) Applicant: Kabushiki Kaisha Toshiba
72, Horikawa-cho Saiwai-ku
Kawasaki-shi Kanagawa-ken 210(JP)

(72) Inventor: Endo, Akira
c/o Kabushiki Kaisha Toshiba 72, Horikawa-cho
Saiwai-ku Kawasaki-shi Kanagawa-ken(JP)

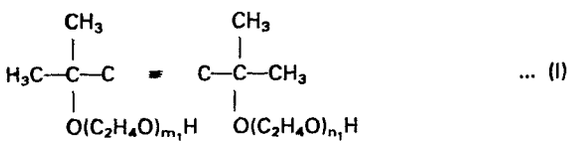
(72) Inventor: Takeda, Kazuhiro
c/o Kabushiki Kaisha Toshiba 72, Horikawa-cho
Saiwai-ku Kawasaki-shi Kanagawa-ken(JP)

(74) Representative: Lehn, Werner, Dipl.-Ing. et al,
Hoffmann, Eitle & Partner Patentanwälte Arabellastrasse
4 (Sternhaus)
D-8000 München 81(DE)

(54) Chemical copper plating solution.

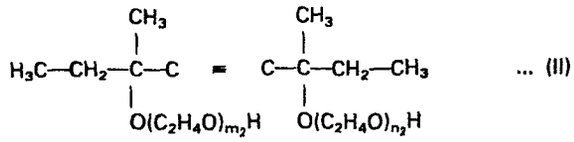
(57) There is disclosed a chemical copper plating solution containing a copper salt, a complexing agent, a reducing agent and a pH adjustor which further comprises at least one of the following Groups (A) and (B);

Group (A);
at least one non-ionic surface active agent selected from the group consisting of a non-ionic surface active agent having the formula:



... (I)

(wherein m_1 and n_1 each represent an integer of 1 or more) and a non-ionic surface active agent having formula:



... (II)

(wherein m_2 and n_2 each represent an integer of 1 or more), and at least one compound selected from the group consisting of 1,10-phenanthroline, a 1,10-phenanthroline derivative, 2,2'-dipyridyl, 2,2'-biquinoline and a water-soluble cyan compound;

Group (B);
an organic sulfur compound and an ethyleneamine compound.

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Chemical copper plating solution

BACKGROUND OF THE INVENTION

This invention relates to a chemical copper plating solution. More particularly, it is concerned with a chemical copper plating solution having a novel composition which makes it possible to deposit copper at a high speed and is stable over a prolonged period of application and can form a plated film having favourable mechanical properties.

A chemical copper plating solution may usually contain as essential components a water-soluble copper salt such as copper sulfate, cupric chloride, etc.; a complexing agent such as ethylenediaminetetraacetic acid (EDTA), N,N,N',N'-tetrakis-(2-hydroxypropyl)ethylenediamine, Rochelle salt, etc.; a reducing agent such as formaldehyde, dimethylaminoborane, sodium borohydride, etc.; a pH adjustor such as sodium hydroxide, potassium hydroxide, etc.; and, where necessary, a surface active agent such as a polyethylene oxide, a polyether, a polyester, etc.

However, a chemical copper plating solution having the composition of such components generally tends to lack stability and readily undergo self-decomposition; moreover, a plated film or deposited film made from said

chemical plating solution is brittle and insufficient in mechanical strength, particularly bending strength for practical utility.

In order to improve such defects, there has been proposed a chemical copper plating solution wherein there were further added a variety of additives, e.g., a dipyridyl, a phenanthroline, a water-soluble cyan compound, an inorganic or organic sulfur compound or a polymeric substance, in addition to prior plating components, i.e., a copper salt, a complexing salt, a reducing agent and a pH adjustor (see Japanese Patent Publications Nos. 1084/1965 and 11521/1968 and Japanese Provisional Patent Publication No. 68033/1977.).

However, even when the above-mentioned components would be added, stability of a plating solution and mechanical properties of a plated film have not yet been improved satisfactorily and, further, there have been inevitably presented problems of a slower deposit rate in plating and a reduced productivity owing to such components supplemented.

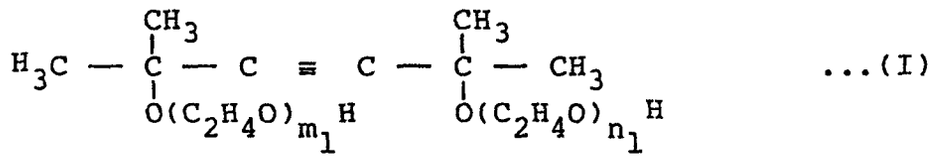
SUMMARY OF THE INVENTION

The primary object of this invention is to provide a chemical copper plating solution having a novel composition which can dissolve the aforesaid problems, show a good stability, without reducing high speed deposit in plating, and provide good mechanical properties, especially a favourable spreadability of the resultant plated film.

The chemical copper plating solution of this invention is a chemical copper plating solution containing a copper salt, a complexing agent, a reducing agent and a pH

adjustor, which further comprises at least one of the under-mentioned Groups (A) and (B):

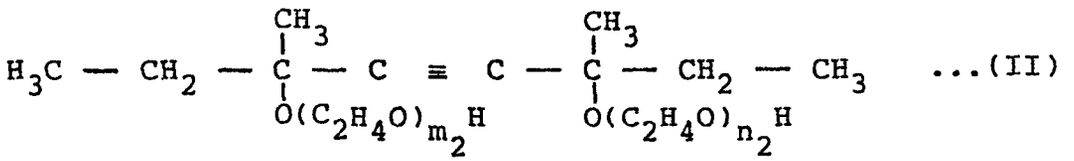
(A) at least one nonionic surface active agent selected from the group consisting of a non-ionic surface active agent having the formula (I):



...(I)

(wherein m_1 and n_1 each represent an integer of 1 or more); and

a nonionic surface active agent having the formula (II):



...(II)

(wherein m_2 and n_2 each represent an integer of 1 or more);

and at least one selected from the group consisting of 1,10-phenanthroline, a 1,10-phenanthroline derivative, 2,2'-dipyridyl, 2,2'-biquinoline and a water-soluble cyan compound,

(B) an organic sulfur compound and an ethyleneamine compound.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The chemical copper plating solution according to this invention is composed of, in addition to the four components of a copper salt, a complexing agnet, a

reducing agent and a pH adjustor, at least one selected from the group consisting of, as Group (A), a nonionic surface active agent mentioned below and at least one selected from the group consisting of 1,10-phenanthroline, a 1,10-phenanthroline derivative, 2,2'-dipyridyl, 2,2'-biquinoline and a water-soluble cyan compound; and as Group (B), an organic sulfur compound and an ethyleneamine compound.

Of these components, a copper salt may supply a copper ion, while a reducing agent may reduce said copper ion to a metallic state. A complexing agent may form a stable complex with copper ions to prevent, in a plating bath (alkaline), a formation of cupric hydroxide, while a pH adjustor may adjust the optimum plating deposit potential in a plating bath. These components may be of any of those usually employed for the preparation of a prior chemical copper plating solution.

Of the Group (A), the nonionic surface active agent may contribute to mechanical properties and deposit rate of a plating solution and is represented by the formula (I) or (II).

In the formulae (I) and (II), each of m_1, m_2, n_1 and n_2 is an integer of 1 or more. If any of them is 0 (zero), a nonionic surface active agent shows a low solubility so that a sufficient amount thereof to contribute to improvement in stability or mechanical properties of a plating solution could not be dissolved in a plating solution. On the other hand, as $m_1 + n_1$ or $m_2 + n_2$ is increased, stability and mechanical properties of a plating solution may be correspondingly improved. In any case, its effect may approximately reach the upper limit at the neighborhood of 20 to a saturated state. Thus, there is particularly no upper limit with regard to m_1 +

n_1 or $m_2 + n_2$, but not more than 500 is preferred in view of workability.

A concentration of the compound (I) or (II) in a plating solution is preferably in the range of 10 mg/l to 30 g/l. In particular, where each of $m_1 + n_1$ and $m_2 + n_2$ is less than 20, a range of 30 mg/l to 20 g/l is preferred. Where each of $m_1 + n_1$ and $m_2 + n_2$ is not less than 20, a range of 10 mg/l to 5 g/l is preferred.

In this invention, there is further added at least one of 1,10-phenanthroline, a 1,10-phenanthroline derivative, 2,2'-dipyridyl, 2,2'-biquinoline or a water-soluble cyan compound, in order that the aforesaid effects by nonionic surface active ageant, especially stability of a plating solution or mechanical properties of a plated film may be far more enhanced.

The 1,10-phenanthroline derivative may preferably have a substituent such as a lower alkyl group, e.g., a methyl group, an ethyl group, etc. or a phenyl group and there may illustratively be mentioned 2,9-dimethyl-1,10-phenanthroline, 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline and so on.

As the water-soluble cyan compound, there may be mentioned, for instance, potassium cyanide, sodium cyanide, sodium nitroprusside, potassium ferrocyanide, potassium ferricyanide, potassium tetracyanoniccolate and so on.

A total amount of 1,10-phenanthroline, a 1,10-phenanthroline derivative, 2,2'-dipyridyl and 2,2'-biquinoline to be added is preferably 1 - 200 mg/l, a range of 2 - 50 mg/l being particularly preferred. If the added amount is less than 1 mg/l, one could not obtain effects at all;

if said amount is more than 200 mg/l, there would undesirably produce a reduced stability of a plating solution or a reduced mechanical property of a plated film.

An amount of the water-soluble cyan compound to be added is preferably 1 mg/l to 3 g/l, a range of 5 mg/l to 1 g/l being particularly preferred. If the added amount is less than 1 mg/l, it does not at all contribute to improvement in stability and mechanical properties, while, if more than 3 g/l, there would undesirably produce a lowered deposit rate or a reduced mechanical property of a plated film.

Also, the organic sulfur compound added as the Group (B) may contribute to improved stability of a plating solution, while the ethyleneamine compound may contribute to speed-up of a deposit rate.

As the organic sulfur compound which may be employed as the Group (B), there may be mentioned, for instance, 2-mercaptobenzothiazole, thiourea, ethylene thiourea, 1-phenyl-2-thiourea, 1-allyl-2-thiourea, thiodiglycol, thiomalic acid, thiodiethanol, 2-mercaptobenzimidazole, dodecylmercaptan, thioglycolic acid, thiodiglycolic acid, etc. An amount of the organic sulfur compound to be added is preferably 0.01 mg/l to 10 mg/l, a range of 0.1 mg/l to 5 mg/l being particularly preferred. If the added amount is less than 0.01 mg/l, stability of a plating solution is not so much improved; if more than 10 mg/l, a deposit rate is extremely lowered, which leads to a reduced working efficiency.

As the ethyleneamine compound, there may be mentioned, for instance, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine,

pentaethylenehexamine and so on. An amount of the compound to be added is preferably 1 mg/l to 500 mg/l, a range of 5 mg/l to 100 mg/l being particularly preferred. If the added amount is less than 1 mg/l, a deposit rate of the plating solution or mechanical properties of the plated film is not so much improved; if more than 500 mg/l, a plating solution becomes unstable.

The present invention has the characteristics that at least one of the above Groups (A) and (B) is further incorporated, in addition to the four components of a copper salt, a complexing agent, a reducing agent and a pH adjustor; but, if the present plating solution contains only the above Group (A), stability and deposit rate of a plating solution and mechanical properties of a plated film may be far more improved by the addition of at least one of the organic sulfur compounds and ethyleneamine compounds.

Also, where the present plating solution contains only the above Group (B), at least one of a 2,2'-dipyridyl and a water-soluble cyan compound may be further added at a concentration in the plating solution of 1 - 100 mg/l, preferably 5 - 50 mg/l, in order to improve spreadability of a plated film and stability of plating solution. If the added amount is less than 1 mg/l, improvement in spreadability of a plated film or stability of a plating solution could not be expectable. If more than 100 mg/l, there will be produced a lowered deposit rate of a plating solution or a saturated effect for improved spreadability, which leads to useless increase in the added amount.

Therefore, the chemical copper plating solution of the present invention can become a chemical copper plating solution having respective merits of the compounds, that

is to say, the plating solution having an excellent stability and producing a highly spreadable plated film with a high speed deposit, when the above compounds having the above-mentioned functions are used in combination therewith at the predetermined proportion.

Preferable plating conditions, under which the present chemical copper plating solution may be applied, are the range of a temperature of 40 - 80 °C, more preferably 50 - 70 °C and a pH value of 10.8 - 13.0, more preferably 12.0 - 13.0. According to such plating condition, characteristic of the present plating solution can be fully put to use and there can be formed a plated film which can be deposited at a high speed and has a high spreadability.

This invention will be more fully illustrated by way of the following examples.

Examples 1 - 12

A stainless steel plate with a thickness of 0.3 mm was polished with a cleanser, dipped in a 10 % sodium hydroxide solution at 80 °C for one minute, taken out and washed with water. Then, it was dipped in a 10 % sulfuric acid at ordinary temperature for 30 seconds and washed with water to clean the surface thereof. The resultant stainless steel plate was then dipped in a solution having the composition of;

Stannic chloride	50 g/l
Hydrochloric acid	10 ml/l
Water	remainder

for 2 minutes and washed in a running water for one minute. Thereafter, the plate was dipped in a solution

having the composition of;

Palladium chloride	0.25 g/l
Hydrochloric acid	10 ml/l
Water	remainder

for one minutes and washed in a running water for one minute.

On the other hand, there were prepared various chemical copper plating solutions having the following compositions;

Copper sulfate (penta hydrates)	0.03 mole
Tetrasodium ethylenediamine-tetraacetate	0.06 mole
Paraformaldehyde	0.1 mole
Sodium hydroxide	amount required to bring a pH value to 12.5
Ingredient of the Group (A) indicated below	proper quantity
Ingredient of the Group (B) indicated below	proper quantity
Water	remainder

The chemical copper plating solutions thus prepared were measured for deposit rate of copper. Such a measurement was accomplished by dipping a copper foil with a thickness of 10 μm, the surface of which was previously cleaned, in the plating solution under conditions of a plating temperature of 60 ^{o}C and a pH value of the plating solution of 12.5 for one hour and calculating a deposit rate from the difference in weight before and after plating.

Then, the catalyzed stainless steel plate with a thickness of 0.3 mm as described above was treated with the chemical copper plating solution to deposit plated

films with a thickness of 30 - 35 μm over both sides thereof, respectively, using plating conditions of a plating temperature of 60 °C and a pH value of the plating solution of 12.5.

The copper plated film thus deposited was peeled off from the stainless steel plate and applied to a spreadability test. Spreadability was measured according to the following folding test at 180 °C; a plated film was first folded to one direction at 180 ° to make a fold and then restored to an original position and pressed to flat the fold. Such a procedure was counted as one folding and repeated until the plated film was broken at the folding portion. According to this test, spreadability of the plated film is represented in terms of the numbers of foldings which the plated film could resist.

Also, stability of the plating solution was evaluated by repeating dipping of the material to be plated, while properly supplementing a plating bath with components of respective plating compositions, counting as one cycle the point when all copper ions originally involved were deposited and measuring how many cycles the plating solution would be not usable by self-decomposition.

The results are summarized in Table 1, with regard to corresponding copper plating solutions, wherein deposit rate (μm/hr) of each copper plated film is also shown. The numbers of 1 - 12 in Table 1 indicate the Examples of the present invention.

And nonionic surface active agents of the formulae (I) and (II) are represented with A-x and B-x, respectively, said "x"s in A-x and B-x indicating $m_1 + n_1$ and $m_2 + n_2$, respectively.

Comparative Examples 1 - 2

In Comparative Example 1, a plating solution was prepared in the same manner as in the above Examples except for using a compound other than the present invention in place of the component other than the nonionic surface active agents in the Group(A).

While a plating solution for Comparative Example 2 was prepared in the same manner as in the above Examples except for using a compound other than the present invention in place of the nonionic surface active agent in the Group (A).

Then, similar tests as in the above Examples were carried out to those and the results are also shown in Table 1.

Table 1

	Sample No.	Group (A) Nonionic surface active agent	Added amount (mg/l)	Other component than nonionic surface active agent	Added amount (mg/l)	Group (B) Type	Added amount (mg/l)	Stability of plating solution (cycles)	Folding strength (numbers of times)	Deposit rate (μm/hr)
Example	1	A-10	100	2,9-Dimethyl-1,10-phenanthroline	10	2-Mercaptobenzothiazole	0.5	not less than 10	2.0	5.5
	2	"	"	2,2'-Dipyridyl	"	Ethylene thiourea	"	"	1.5	5.0
	3	"	"	2,2'-Biquinoline	"	Tetraethylene Pentamine	10	6.5	1.0	9.5
	4	"	"	2,2'-Dipyridyl	"	2-Mercaptobenzothiazole Tetraethylene pentamine	0.5 10	not less than 10	2.5	8.0
	5	"	"	Potassium cyanide	5	2-Mercaptobenzothiazole	0.5	"	3.0	3.5
	6	A-30	"	2,2'-Dipyridyl	10	Ethylene thiourea	"	"	2.0	"

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Table 1 (Contd.)

Example	7	B-10	100	2,2'-Dipyridyl	10	Ethylene thiourea	0.5	not less than 10	1.5	4.5
	8	"	"	"	"	2-Mercaptobenzo-thiazole Tetraethylene pentamine	0.5 10	"	1.0	9.0
	9	"	"	2,9-Dimethyl-1,10-phenanthroline	"	Thiomalic acid Pentaethylene hexamine	0.5 10	"	"	8.5
	10	"	"	Potassium cyanide	5	Thiodiglycolic acid	0.5	"	2.5	3.0
	11	"	"	2,2'-Dipyridyl	10	Triethylene tetramine	10	5.5	2.0	5.0
	12	B-30	"	"	"	Thiodiglycolic acid	0.5	not less than 10	"	4.0
Comparative Example	1	A-10	"	Magnesium sulfate	2000	2-Mercaptobenzo-thiazole	"	5.0	1.0	2.5
	2	Polyethy-leneglycol (MW 400)	"	2,2'-Dipyridyl	10	"	"	3.5	1.5	6.5

Examples 13 - 24

A stainless steel plate with a thickness of 0.3 mm was polished with a cleanser, dipped in a 10 % sodium hydroxide solution at 80 °C for 5 minutes, taken out and washed with water. Then, it was dipped in a 10 % hydrochloric acid at ordinary temperature for 5 minutes and washed with water to clean the surface thereof. The resultant stainless steel plate was dipped in a solution having the composition of;

Stannic chloride	50 g/l
Hydrochloric acid	10 ml/l
Water	remainder

for 2 minutes and washed in a running water for 1 minute. Then, it was dipped in a solution having the composition of;

Palladium chloride	0.25 g/l
Hydrochloric acid	10 ml/l
Water	remainder

for 1 minute and washed in a running water. Thereafter, a solution having the following composition was prepared;

Copper sulfate (penta hydrates)	0.03 mole
Ethylenediaminetetraacetic acid	0.06 mole
Paraformaldehyde	0.1 mole
GAFAC RE-610 (nonionic anionic surface active agent manufactured by Toho Kagaku Kogyo K.K.)	100 mg/l
Sodium hydroxide	amount required to bring a pH value to 12.3

Water	remainder

To 1 ℓ of the resultant solution was added an indicated amount of each additive as shown in Table 2 to form a chemical copper plating solution.

The chemical copper plating solution thus prepared was measured for deposit rate of copper. Such a measurement was accomplished by dipping a copper foil with a thickness of 10 μm, the surface of which was previously cleaned, in the plating solution for one hour under conditions of a plating temperature of 60 °C and a pH value of the plating solution of 12.3 and calculating a deposit rate from the difference in the weight before and after plating.

Then, by using such chemical copper plating solutions, a plated film with a thickness of 30 - 35 μm was deposited over both sides of a catalyzed stainless steel with a thickness of 0.3 mm. Spreadability of the plated film was tested in the same manner as in above Examples 1 - 12.

Then, stability of the copper plating solution was tested. That is to say, to 100 ml of the plating solution prepared at a plating temperature of 60 °C and a pH value of the plating solution of 12.3 were added two droplets of a solution having the composition of;

Palladium chloride	5 g/l
Hydrochloric acid	40 ml/l
Water	remainder

The time until the resultant plating solution was decomposed under the above-mentioned conditions was measured.

The results are summarized in Table 2, with regard to corresponding copper plating solutions of various compositions.

Comparative Examples 3 - 7

Plating solutions were prepared in the same manner as in the above Examples 13 - 24 except that either of an organic sulfur compound and an ethyleneamine compound was incorporated or none of both was added. Similar tests as in the above Examples 13 - 24 were carried out to those and the results are also shown in Table 2.

Table 2

Sample No.	Composition of chemicl copper plating solution						Deposit rate (μm/hr)	Folding strength (numbers of times)	Stability of plating solution (hr)
	Organic sulfur compound		Ethylene amine compound		2,2'-Dipyridyl	Potassium cyanide			
	Type	Added amount (mg/l)	Type	Added amount (mg/l)	Added amount (mg/l)	Added amount (mg/l)			
Example 13	2-Mercapto-benzothiazole	0.5	Tetraethylene pentamine	10	-	-	8.5	1.5	>5
14	Ethylene thio-urea	"	"	"	-	-	8.0	1.5	>5
15	1-Allyl-2-thio-urea	"	"	"	-	-	7.5	2.5	>5
16	Thiomalic acid	"	"	"	-	-	6.1	2.0	>5
17	Thiourea	"	"	"	-	-	7.8	2.0	>5
18	"	"	Pentaethylene hexamine	"	-	-	6.3	2.5	>5

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Table 2 (Contd.)

Example	19	Thiourea	0.5	Triethylene tetramine	10	-	-	6.0	2.5	>5
	20	2-Mercapto-benzothioazole	"	Tetraethylene pentamine	10	10	-	7.2	1.5	>5
	21	"	"	"	10	-	10	6.5	2.0	>5
	22	ethylene thio-urea	"	"	10	10	-	6.8	2.0	>5
	23	"	"	"	10	-	10	5.7	2.5	>5
	24	"	"	"	10	10	10	5.3	3.0	>5
Comparative Example	3	-	-	-	-	10	-	2.3	3.0	2>
	4	2-Mercapto-benzothiazole	0.5	-	-	-	-	4.5	1.0	>5
	5	"	"	-	-	10	-	2.8	1.5	>5
	6	-	-	Tetraethylene pentamine	10	-	-	9.5	1.0	1>
	7	- "	-	"	10	-	10	5.3	2.0	3>

As explained hereinabove, the chemical copper plating solution of the present invention can show an excellent stability usable over prolonged period, together with a high speed deposit, and produce a plated film having superior mechanical properties, inter alia, a good spreadability as illustrated with folding strength.

Accordingly, application of the chemical copper plating solution of the present invention can greatly improve working efficiency for plating and further enhance reliability in forming a plated film.

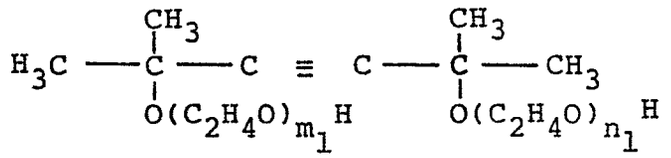
Therefore, the chemical copper plating solution of the present invention may be most suitable for production of, e.g., a continuity circuit in a print distributing plate and is highly valuable in an industrial field.

Claims:

1. A chemical copper plating solution containing a copper salt, a complexing agent, a reducing agent and a pH adjustor which further comprises at least one of the following Groups (A) and (B):

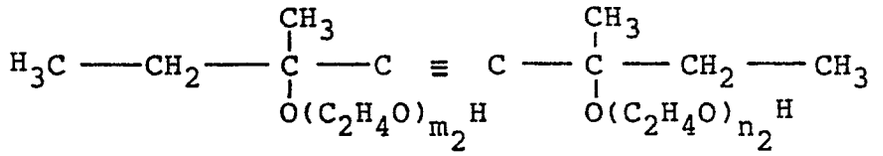
Group (A);

at least one nonionic surface active agent selected from the group consisting of a nonionic surface active agent having the formula:



...(I)

(wherein m_1 and n_1 each represent an integer of 1 or more) and a non-ionic surface active agent having the formula:



...(II)

(wherein m_2 and n_2 each represent an integer of 1 or more), and at least one compound selected from the group consisting of 1,10-phenanthroline, a 1,10-phenanthroline derivative, 2,2'-dipyridyl, 2,2'-biquinoline and a water-soluble cyan compound;

Group (B);

an organic sulfur compound and an ethyleneamine compound.

2. The chemical copper plating solution as claimed in

Claim 1, wherein the complexing agent is a cupric ion complexing agent.

3. The chemical copper plating solution as claimed in Claim 1, wherein the ethyleneamine compound is an ethylenepolyamine compound.

4. The chemical copper plating solution as claimed in Claim 1, wherein a concentration of the nonionic surface active agent of the formula (I) and (II) is 10 mg/l to 30 g/l.

5. The chemical copper plating solution as claimed in Claim 1, wherein the $m_1 + n_1$ and $m_2 + n_2$ are not more than 500.

6. The chemical copper plating solution as claimed in Claim 1, wherein a total concentration of 1,10-phenanthroline, a 1,10-phenanthroline derivative, 2,2'-dipyridyl and 2,2'-biquinoline is 1 - 200 mg/l.

7. The chemical copper plating solution as claimed in Claim 1, wherein a concentration of the water-soluble cyan compound is 1 mg/l to 3 g/l.

8. The chemical copper plating solution as claimed in Claim 1, wherein a concentration of the organic sulfur compound is 0.01 - 10 mg/l.

9. The chemical copper plating solution as claimed in Claim 1, wherein a concentration of the ethyleneamine compound is 1 - 500 mg/l.

10. A method for application of a chemical copper plating solution as claimed in Claim 1, wherein application condition is 40 - 80 ^{o}C and pH of 10.8 - 13.0.

11. The chemical copper plating solution as claimed in Claim 1, wherein there is contained a compound of the Group (A).

12. The chemical copper plating solution as claimed in Claim 11, wherein an organic sulfur compound or an ethyleneamine compound is further incorporated.

13. The chemical copper plating solution as claimed in Claim 1, wherein there is contained a compound of the Group (B).

14. The chemical copper plating solution as claimed in Claim 13, whrein at least one of a 2,2'-dipyridyl and a water-soluble cyan compound is further incorporated.

15. The chemical copper plating solution as claimed in Claim 14, wherein a concentration of the 2,2'-dipyridyl is 1 - 100 mg/l.

16. The chemical copper plating solution as claimed in Claim 14, wherein a concentration of the water-soluble cyan compound is 1 - 100 mg/l.