



US 20070284258A1

(19) **United States**

(12) **Patent Application Publication**
Yoshimoto et al.

(10) **Pub. No.: US 2007/0284258 A1**

(43) **Pub. Date: Dec. 13, 2007**

(54) **METHOD FOR SILVER PLATING**

(30) **Foreign Application Priority Data**

(76) Inventors: **Masakazu Yoshimoto**, Kyogo-Ken
(JP); **Shingo Kitamura**,
Hyogo-Ken (JP); **Seiji Omori**,
Hyogo-Ken (JP); **Toshifumi**
Kadokawa, Hyogo-Ken (JP)

Jun. 9, 2006 (JP) 2006-161049

Publication Classification

(51) **Int. Cl.**
C25D 3/46 (2006.01)

(52) **U.S. Cl.** **205/263**

(57) **ABSTRACT**

Correspondence Address:

MARSHALL, GERSTEIN & BORUN LLP
233 S. WACKER DRIVE, SUITE 6300, SEARS
TOWER
CHICAGO, IL 60606

The invention provides a method for silver plating using a non-cyanide acid silver plating bath to form a silver plating film exhibiting good adhesiveness while suppressing dissolution of resist in pattern plating. The method includes conducting strike plating using a non-cyanide acid strike plating bath prior to the silver plating.

(21) Appl. No.: **11/759,417**

(22) Filed: **Jun. 7, 2007**

METHOD FOR SILVER PLATING

FIELD OF THE INVENTION

[0001] The present invention relates to a method for silver electroplating with a non-cyanide bath, and in particular to a method for forming a silver plating film using an acid plating bath, exhibiting good adhesiveness while suppressing dissolution of resist in pattern plating.

BACKGROUND OF THE INVENTION

[0002] Silver is widely used not only for functional plating as it is excellent in properties such as electric conductivity and solderability, but also for decorative plating as it is also excellent in aesthetic appearance. In the current industrial practices, almost all the silver plating processes are operated with a cyanide bath.

[0003] Much research has been reported on a non-cyanide bath for silver plating. Some of the reports include the development of an acid silver-plating bath. It has been known since a long time ago that silver plating may be also conducted from an acid bath. For example, "Electroplating Baths for Silver A Review of Cyanide-Free Formulations: S. R. Natarajan & R. Krishnan, Metal Finishing, February 1971, P51", which was published about 30 years ago, discloses acid silver-plating baths. However, the baths disclosed in the literature were not suitable for industrial applications in terms of adhesiveness and film properties, etc.

[0004] Studies have been continued over the years for the improvement of the acid silver-plating baths. Examples of silver-plating baths that can be reportedly used under acid condition include those described in the following literatures.

[0005] JP H02-290993A discloses a bath using potassium iodide as a complexing agent and teaches that the pH is in the range of 1 to 11, preferably 3 to 6. JP H07-166391A discloses a silver-plating solution using succinimide as a complexing agent at a pH of 4 to 10.

[0006] Plating solutions using hydantoin as a complexing agent are also disclosed. Though hydantoin is generally used in alkaline baths at a pH of 7 or more as disclosed in JP H08-104993A, hydantoin-containing silver-plating solutions and strike plating solutions used at a pH of 3.0 to 10.0 are described in JP H07-180085A. JP2000-34593A discloses "a phosphine-containing aqueous solution for reduction-deposition of metal". In the Example, a silver electroplating solution at a pH of 0.98 is disclosed in the same. JP Patent No. 3365866 discloses a silver-plating solution containing at least one of alkane sulfonic acid ion and alkanol sulfonic acid ion, and a non-ionic surfactant. Though there is no description about pH, it is deemed to be a strong acid bath judging from the disclosed composition.

[0007] Acid baths are more suitable to partial plating and pattern plating than alkaline baths as the former are less likely to attack resist than the latter. In particular, among the acid baths, strong acid silver-plating baths made with simple salt at pH of less than 3 are advantageous as they can be stable without using a complexing agent and thereby can be formed and operated at lower cost.

[0008] Silver exhibits noble potential and thus has a problem of readily causing displacement deposition. Though some literature references have disclosed baths that can

reduce or prevent deposition by adding additives or using other methods, such baths cannot prevent it in an industrially applicable way.

SUMMARY OF THE INVENTION

[0009] Accordingly, it is an object of the present invention to provide a method for acid silver plating to form a dense silver plating film exhibiting good adhesiveness while suppressing dissolution of resist in pattern plating.

[0010] Accordingly, the subject matter of the present invention is a method for silver plating onto a substrate using a non-cyanide acid silver plating bath (A), comprising conducting strike plating onto the substrate using a non-cyanide acid strike plating bath (B) prior to the silver plating.

[0011] In one embodiment of the method according to the present invention, both the non-cyanide acid silver plating bath (A) and the non-cyanide acid strike plating bath (B) have a pH of less than 3.

[0012] In another embodiment of the method according to the present invention, the non-cyanide acid strike plating bath (B) is an acid silver strike plating bath (B1) or an acid copper strike plating bath (B2).

[0013] In a further embodiment of the method according to the present invention, either or both of the non-cyanide acid silver plating bath (A) and the non-cyanide acid strike plating bath (B) contain at least a sulfonate ion.

[0014] In a further embodiment of the method according to the present invention, either or both of the non-cyanide acid silver plating bath (A) and the non-cyanide acid strike plating bath (B) contain at least an aliphatic phosphine.

[0015] In a further embodiment of the method according to the present invention, the acid copper strike plating bath (B2) contains at least a sulfate ion.

[0016] In a further embodiment of the method according to the present invention, either or both of the non-cyanide acid silver plating bath (A) and the non-cyanide acid strike plating bath (B) further contain an azole compound and/or a thiophene compound.

[0017] In a further embodiment of the method according to the present invention, either or both of the non-cyanide acid silver plating bath (A) and the non-cyanide acid strike plating bath (B) further contain a surfactant and/or a surface-active polymer compound.

[0018] In a further embodiment of the method according to the present invention, the method further comprises the step of conducting displacement deposition prevention treatment to the substrate between the strike plating and the silver plating and wherein the strike plating is conducted using the acid copper strike plating bath (B2).

[0019] In a further embodiment of the method according to the present invention, the method further comprises the step of conducting pretreatment using an acid degreasing bath prior to the strike plating.

[0020] In a further embodiment of the method according to the present invention, either or both of the non-cyanide acid silver plating bath (A) and the non-cyanide acid strike plating bath (B) comprise an ion-exchange membrane therein to separate an anode and a cathode.

[0021] Since the method for non-cyanide silver plating according to the present invention uses an acid bath for both the strike plating step and the main silver plating step, it can solve the following two problems:

[0022] (1) decrease in adhesiveness of a plating film due to alkaline components remaining on the substrate (e.g. metal surface) to be plated in the main silver plating step, and

[0023] (2) dissolution of resist due to an alkaline strike plating bath.

[0024] Therefore, the present invention can provide a method for forming a silver plating film exhibiting good adhesiveness suitable for partial or pattern plating using resist.

[0025] In addition, since the method according to the present invention uses a strong acid silver-plating bath made with simple salt at a pH of less than 3, the present invention can provide a method that can be carried out at lower cost despite using a non-cyanide bath. The method can be applied not only to functional plating to form a plating film excellent in properties such as solderability but also to decorative plating.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0026] Since a stronger acid generally dissolves base metal more easily, strike plating is necessary prior to silver plating for good adhesiveness. However, unlike other metal plating processes, no study has been done for using an acid strike plating bath in case of a silver plating process using an acid plating bath because the acid strike plating bath is deemed to cause displacement deposition easily.

[0027] However, even when an acid silver plating bath is used to avoid dissolution of resist, dissolution of resist may occur if an alkaline strike plating bath is used in the previous step. In addition, if an alkaline strike plating bath is used before an acid silver plating bath, since alkaline components in the alkaline strike plating bath may remain on the metal surface to be plated after completion of the strike plating, good plating film may not be formed in the subsequent silver plating process. The present inventors have determined that one or more improvements can be made by strike plating using a strong acid bath prior to silver plating using a strong acid silver plating bath.

[0028] The present invention, in various embodiments, may have one or more advantages including, but not limited to, suppressing dissolution of resist in pattern plating, preventing alkaline components from remaining on the metal surface to be plated, and forming a dense plating film with good adhesiveness.

[0029] The silver plating method of this invention will be described in further detail below.

[0030] One embodiment of the invention provides a method for silver plating onto a substrate using a non-cyanide acid silver plating bath (A), comprising conducting strike plating onto the substrate using a non-cyanide acid strike plating bath (B) prior to the silver plating.

[0031] Both the silver plating bath (A) and the strike plating bath (B) are required to be acidic. Preferably, both baths have a pH of less than 3. As for the main silver plating bath (A), it goes without saying that the bath should be acidic for the purpose of preventing resist dissolution. The bath (A) having a pH of less than 3 eliminates the need for a complexing agent for stability, allowing the plating process to be operated at lower cost. Accordingly, in one type of embodiment of the invention, the silver plating bath is essentially free of or completely free of a complexing agent. Further, by adjusting the acidity of the both baths to the pH

of less than 3, adhesion of alkaline components onto the substrate possibly occurring in the previous strike plating step, which may affect the adhesiveness, can be avoided.

[0032] The pH is preferably less than 3 and more preferably less than 2.

[0033] Silver strike plating is preferably adopted as the strike plating step. Copper strike plating is also adopted as the strike plating bath. In such case, depending on the desired properties of the plating film, displacement prevention treatment or silver strike plating may be preferably conducted between the copper strike plating step and the silver plating step.

[0034] Any or all of the silver plating bath (A), the copper strike plating bath (B1) and the silver strike plating bath (B2) may contain any known acid alone or in combination as the acid component for keeping the bath acidic. Sulfonic acids are preferably used in terms of appearance of the plating film and electric properties such as surface resistivity of the plating film, etc. Among the sulfonic acids, aliphatic and aromatic sulfonic acids may be preferably used and aliphatic sulfonic acids may be more preferably used.

[0035] Preferable aliphatic sulfonic acids include alkane sulfonic acids and alkanol sulfonic acids. Examples of alkane sulfonic acids include methanesulfonic acid, ethanesulfonic acid, 1-propanesulfonic acid, 2-propanesulfonic acid, 1-butanesulfonic acid, 2-butanesulfonic acid and pentanesulfonic acid, etc. Examples of alkanol sulfonic acids include 2-hydroxyethane-1-sulfonic acid (isethionic acid), 2-hydroxypropane-1-sulfonic acid (2-propanolsulfonic acid), 2-hydroxybutane-1-sulfonic acid and 2-hydroxypentane-1-sulfonic acid, as well as 1-hydroxypropane-2-sulfonic acid, 3-hydroxypropane-1-sulfonic acid, 4-hydroxybutane-1-sulfonic acid and 2-hydroxyhexane-1-sulfonic acid, etc.

[0036] In a preferred embodiment of the invention, either or both of the silver plating bath (A) and the strike plating bath (B) may at least contain one or more aliphatic or aromatic phosphines represented by the Formula (1):



wherein X_1 , X_2 and X_3 , which may be the same or different, each represent a hydrogen atom, a substituted or unsubstituted C_1 to C_{10} alkyl group, or a substituted or unsubstituted benzene ring, one or more substituents for the substituted alkyl or the substituted benzene ring being selected from the group consisting of a hydroxyl group, a carboxyl group, a sulfonic group and an amino group, provided that all of X_1 , X_2 and X_3 are not hydrogen atoms at the same time.

[0037] Among the phosphines, lower alkyl phosphines represented by the Formula (2):



wherein Y_1 , Y_2 and Y_3 , which may be the same or different, each represent an unsubstituted C_1 to C_3 alkyl group or a C_1

to C₃ alkyl group substituted with one or more substituents selected from the group consisting of a hydroxyl group, a carboxyl group, a sulfonic group and an amino group,

[0038] may be more preferably used.

[0039] Preferable examples of the phosphines include unsubstituted alkyl phosphines in which each alkyl group is a methyl group, an ethyl group or a propyl group; and substituted alkyl phosphines in which each alkyl group is substituted by one or more substituents selected from the group consisting of a hydroxyl group, a carboxyl group, a sulfonic group and an amino group. The substituted alkyl phosphines include hydroxy lower alkyl phosphines having a hydroxymethyl group, a hydroxyethyl group or a hydroxypropyl group; carboxy lower alkyl phosphines having a carboxymethyl group, a carboxyethyl group or a carboxypropyl group; sulfo lower alkyl phosphines having a sulfo-methyl group, a sulfoethyl group or a sulfopropyl group; and amino lower alkyl phosphines having an aminomethyl group, an aminoethyl group or an aminopropyl group.

[0040] Tris(hydroxy lower alkyl)phosphines, in which one hydrogen atom on each lower alkyl group is substituted by a hydroxyl group to form each hydroxy lower alkyl selected from the group consisting of a hydroxymethyl group, a hydroxyethyl group and a hydroxypropyl group, may be more preferably used among these phosphines from the viewpoints of cost and stability. Tris(3-hydroxypropyl)phosphine may be most preferably used.

[0041] The copper strike plating bath (B1) of the present invention preferably contains at least a sulfate ion as one of the bath components.

[0042] Any or all of the silver plating bath (A), the copper strike plating bath (B1) and the silver strike plating bath (B2) of the present invention may further contain an azole and/or thiophene compound.

[0043] As the azole compounds, tetrazoles, imidazoles, benzimidazoles, pyrazoles, indazoles, thiazoles, benzothiazoles, oxazoles, benzoxazoles, triazoles and derivatives thereof may be preferably used.

[0044] Among these compounds, imidazoles, pyrazoles, indazoles and triazoles may be more preferably used, and triazoles may be most preferably used. Examples of these compounds are listed below.

[0045] Preferred imidazoles include imidazole, 1-methylimidazole, 1-phenylimidazole, 2-methylimidazole, 2-ethylimidazole, 2-propylimidazole, 2-butylimidazole, 2-phenylimidazole, 4-methylimidazole, 4-phenylimidazole, 2-aminoimidazole, 2-mercaptoimidazole, imidazole-4-carboxylic acid, benzimidazole, 1-methylbenzimidazole, 2-methylbenzimidazole, 2-ethylbenzimidazole, 2-butylbenzimidazole, 2-octylbenzimidazole, 2-phenylbenzimidazole, 2-trifluoromethylbenzimidazole, 4-methylbenzimidazole, 2-chlorobenzimidazole, 2-hydroxybenzimidazole, 2-aminobenzimidazole, 2-mercaptobenzimidazole, 2-methylthiobenzimidazole, 5-nitrobenzimidazole, benzimidazole-5-carboxylic acid, tris(2-benzimidazolylmethyl)amine and 2,2'-tetra (or octa) methylene-dibenzimidazole, etc. More preferred imidazoles include imidazole, benzimidazole, tris(2-benzimidazolylmethyl)amine and 2,2'-tetra (or octa) methylene-dibenzimidazole.

[0046] Preferred pyrazoles or indazoles include pyrazole, 3-methylpyrazole, 4-methylpyrazole, 3,5-dimethylpyrazole, 3-trifluoromethylpyrazole, 3-aminopyrazole, pyrazole-4-carboxylic acid, 4-bromopyrazole, 4-iodopyrazole, inda-

zole, 5-aminoindazole, 6-aminoindazole, 5-nitroindazole, 6-nitroindazole, etc. More preferred pyrazoles include pyrazole and 3-aminopyrazole.

[0047] Examples of compounds other than imidazoles, pyrazoles and indazoles include tetrazoles, thiazoles, benzothiazoles, oxazoles, benzoxazoles and triazoles. Preferred tetrazoles and derivatives thereof include tetrazole, 5-aminotetrazole, 5-mercapto-1-methyltetrazole and 5-mercapto-1-phenyltetrazole, etc. Preferred thiazoles or benzothiazoles and derivatives thereof include thiazole, 4-methylthiazole, 5-methylthiazole, 4,5-dimethylthiazole, 2,4,5-trimethylthiazole, 2-bromothiazole, 2-aminothiazole, benzothiazole, 2-methylbenzothiazole, 2,5-dimethylbenzothiazole, 2-phenylbenzothiazole, 2-chlorobenzothiazole, 2-hydroxybenzothiazole, 2-aminobenzothiazole, 2-mercaptobenzothiazole and 2-methylthiobenzothiazole, etc. Preferred oxazoles or benzoxazoles and derivatives thereof include isoxazole, anthranil, benzoxazole, 2-methylbenzoxazole, 2-phenylbenzoxazole, 2-chlorobenzoxazole, 2-benzooxazolinone and 2-mercaptobenzoxazole, etc. Preferred triazoles and derivatives thereof include 2H-1,2,3-triazole-2-ethanol, N-trimethylsilyl-1,2,4-triazole, 3-amino-5-methyl-1,2,4-triazole, 5,5'-diamino-3,3'-bis-1,2,4-triazole, 4H-1,2,4-triazole-4-propanol, 1,2-dihydroxy-5-(phenylmethyl)-3H-1,2,4-triazole-3-thione, 1,2,4-triazole-1-acetic acid, 1,2,3-triazole, 1,2,4-triazole, 1H-1,2,4-triazole-1-ethanol, 1,5-dimethyl-1H-1,2,3-triazole-4-carboxylic acids, 5-amino-1,2,4-triazole-3-carboxylic acids, 2H-1,2,3-triazole-2-acetic acid, 1,2,4-triazole-3-carboxylic acids, 1-methyl-1,2,4-triazole-3-carboxylate esters, 3-amino-1,2,4-triazole, 4-amino-1,2,4-triazole, 1H-1,2,3-triazole-1-ethanol, 1,2,4-triazole-3-ethylcarboxylates, 3-amino-5-mercapto-1,2,4-triazole, 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, 4-methyl-3-(methylthio)-5-phenyl-4H-1,2,4-triazole, 3-mercapto-1,2,4-triazole, 1,2-dihydroxy-5-(3-pyridinyl)-3H-1,2,4-triazole-3-thione, 1,2,4-triazole sodium salt, 1H-1,2,3-triazole-1-ethylacetate, 1H-1,2,3-triazole-1-acetic acid, 2H-1,2,3-triazole-1-ethylacetate, 2H-1,2,3-triazole-1-acetic acid, 1-(3-aminopropyl)-1H-1,2,3-triazole dihydrochloride, 3-amino-5-methylmercapto-1,2,4-triazole, 5-methylmercapto-1,2,3-triazole, ethyl-2-(1H-1,2,4-triazole-1-yl) acetic acid, 5-mercapto-1,2,3-triazole sodium salt, 4-(2-hydroxyethyl)-1,2,4-triazole, 5-methyl-1,2,4-triazole-3-thiol, 1-hydroxybenzotriazole, 5-methyl-1H-benzotriazole, benzotriazole sodium salt, benzotriazole-5-carboxylic acids, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 6H,12H-benzotriazolo [2,1-a]benzotriazole, 4-methylbenzotriazole, 2-(2'-hydroxy-5'-octylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-*t*-butylphenyl)benzotriazole, 2-(3',5'-di-*tert*-butyl-2'-hydroxyphenyl)chloro-2H-benzotriazole, tolyltriazole sodium salt, tolyltriazole potassium salt, 1,2,3-benzotriazole and 2-(2'-hydroxy-5'-methacryloxy ethylphenyl)-2H-benzotriazole, etc.

[0048] Preferred thiophenes and derivatives thereof include thiophene, 2-bromothiophene, 2-thiophenenitrile, 3-dodecylthiophene, 4-dibenzothiophene-4-boric acid, tetrahydrothiophene, benzothiophene-3-boric acid, tetrahydrothiophene-1,1-dioxide, 2-(acetylthio)thiophene, 2-benzoylthiophene, 3-thiopheneacetonitrile, 2-amino-5-methylthiophene-3-nitrile, 4-methyl-2-thiophenecarboxylic acids, 2-chloro-3-methylthiophene, 3-[(chloroacetyl)amino]-2-thiophenemethylcarboxylates, 3-acetylthiophene, 5-chlorothiophene-2-boric acid, 5-methylthiophene-2-boric acid, 2-thiophenesulfonylchloride, 4-bromo-2-thiophenecarboxy-

lic acids, 3-chloromethyl-2-methylbenzothiophene, 3-formylthiophene-2-boric acid, 3-formyl-2-thiopheneboric acid, 3-chloro-4-methylthiophenemethylcarboxylates, 3-methoxythiophene, 3-aminothiophene, 4-bromothiophene-2-carbaldehyde, 2-thiopheneacetic acid, 5-methyl-2-thiophenecarboxylic acids, 2-amino-3,5-dinitrothiophene, 5-acetyl-2-thiopheneboric acid, 2-thiopheneacetonitrile, 2-(acetylamino)-3-thiophenemethylcarboxylates, 2-thiophenecarboxylic acid hydrazides, 3-methyl-2-thiophenecarboxylic acids, 5-chlorothiophene-2-carboxylic acids, 2,5-dimethyl-3-formylthiophene, 4-bromo-3-methyl-2-thiophenecarbonylchloride, 5-chlorothiophene-2-sulfonylchloride, 2-thiophenemethylamine, thiophene-2-methylamine, 3-chloro-6-methoxybenzothiophenecarboxylic acids, 3-methylbenzothiophene-2-carboxylic acids, 2,4-dibromothiophene, 2,3,5-tribromothiophene, 2,5-dibromothiophene, 2,5-dichlorothiophene, 2-iodothiophene, 4-bromo-2-propionylthiophene, 4-bromo-2-propylthiophene, 3-bromo-5-methyl-2-thiophenecarbaldehyde, 2,5-dichloro-3-acetylthiophene, α -(phenylmethylene)-2-thiopheneacetonitrile, thiophene-2-acetylchloride, 3-bromo-2-chlorothiophene, 4-bromo-5-(1,1-dimethylethyl)-2-thiophenecarboxylic acid, 5-acetyl-2-thiophenecarboxylic acids, 2,5-carboxythiophene, 2,5-thiophenedicarboxylic acids, 2,5-bis(methoxycarbonyl)thiophene, 2-formylthiophene-3-boric acid, 3-formyl-4-thiopheneboric acid, 5-bromothiophene-2-carbaldehyde, 2,5-diacetylthiophene, thiophene-3-carbaldehyde, 3-hydroxy-3-thiophene methylcarboxylates, thiophene-2-carboxylic acids, 2-thiophenecarbonylchloride, 5-bromo-4-methyl-2-thiophenecarboxylic acids, 2,5-dichlorothiophene-3-sulfonylchloride, 2-thiopheneethylacetate, thiophene-2-carboxamide, 3-methyl-2-thiophenecarbaldehyde, 3-thiophene methyl acetate, 2-iodomethylthiophene, 4-chlorothiophene-2-carboxylic acid, 2-nitrothiophene, 3-methyl-2-thiophenecarbonylchloride, etc.

[0049] The above-stated compounds may be used preferably in the range of 0.01 to 50 g/L and more preferably in the range of 0.05 to 10 g/L.

[0050] Any or all of the silver plating bath (A) and the strike plating bath (B) may further contain a surfactant and/or surface-active polymer compound. The addition of the surfactant and/or surface-active polymer compound may improve one or more properties including throwing power, refinement and uniformity in grain size, and adhesiveness, etc.

[0051] Preferred surfactants include known cationic surfactants, anionic surfactants, nonionic surfactants and amphoteric surfactants, which may be used alone or in combination as necessary.

[0052] Preferred cationic surfactants include tetra(lower alkyl)ammonium halides, alkyl trimethylammonium halides, hydroxyethylalkylimidazolines, polyoxyethylene-alkylmethylammonium halides, alkylbenzalkonium halides, dialkyldimethylammonium halides, alkyl dimethyl benzilammonium halides, alkylamine hydrochlorides, alkylamine acetates, alkylamine oleates, alkylaminoethylglycines, alkylpyridinium halides, etc.

[0053] Preferred anionic surfactants include alkyl(or formalin condensate)- β -naphthalene sulfonic acid(or salt thereof), fatty acid soaps, alkylsulfonates, α -olefinsulfonates, alkyl benzene sulfonates, alkyl(or alkoxy)naphthalenesulfonates, alkyl diphenylether disulfonates, alkylether-

sulfonates, alkylsulfate salts, polyoxyethylenealkylethersulfate salts, polyoxyethylene alkylphenol ether sulfate salts, higher-alcohol monophosphate salts, polyoxyalkylene alkylether phosphates, polyoxyalkylenealkylphenylether phosphates, polyoxyalkylene phenylether phosphates, polyoxyethylene alkylether acetates, alkylol sarcosines, alkylol sarcosinates, alkylolmethyl alanine salts, N-acylsulfocarboxylates, alkyl sulfacetates, acyl methyl sodium taurate, alkyl fatty acid glycerine sulfates, hardened coconut oil fatty acid glyceryl sodium sulfates, alkyl sulfocarboxylates, alkyl sulfosuccinates, dialkyl sulfosuccinates, alkyl polyoxyethylene sulfosuccinic acids, monooleyamide sulfosuccinate (sodium salt, ammonium salt, and TEA salt), etc.

[0054] Preferred nonionic surfactants or surface-active polymer compounds include polyoxyalkylene alkyl ethers (or esters), polyoxyalkylene phenyl(or alkyl phenyl)ethers, polyoxyalkylene naphthyl(or alkyl naphthyl)ethers, polyoxyalkylene styrenated phenyl ethers(or derivatives thereof having a polyoxyalkylene chain added to the phenyl group), polyoxyalkylene bisphenol ethers, polyoxyethylene polyoxypropylene block polymers, polyoxyalkylene sorbitan fatty acid esters, polyoxyalkylene sorbitan fatty acid esters, polyethylene glycol fatty acid esters, polyoxyalkylene glycerine fatty acid esters, polyoxyalkylene alkyl amines, condensation adducts of ethylenediamine and polyoxyalkylene, polyoxyalkylene fatty acid amides, polyoxyalkylene castor (or and hardened castor) oils, polyoxyalkylene alkyl phenyl formalin condensates, glycerin (or polyglycerin) fatty acid esters, pentaerythritol fatty acid esters, sorbitan mono-(and sesqui- and tri-)fatty acid esters, higher fatty acid mono-(and di-)ethanol amides, alkyl alkylode amides, oxyethylene alkyl amines, polyalkylene glycols, polyalkylene diamine, polyvinyl pyrrolidone and polyethylene-imine, etc.

[0055] Preferred amphoteric surfactants include 2-alkyl-N-carboxymethyl (or ethyl)-N-hydroxyethyl(or methyl)imidazolium betaines, 2-alkyl-N-carboxymethyl(or ethyl)-N-carboxymethylpolyoxyethylimidazolium betaines, dimethyl alkyl betaines, N-alkyl- β -aminopropionic acids (or salts thereof), alkyl(poly)aminoethyl glycines, N-alkyl-N-methyl- β -alanines (or salts thereof), fatty acid amido propyldimethyl aminoacetic acid betaines, etc.

[0056] The content of these surfactants, which may be chosen as appropriate, is generally in the range of 0.001 g/L to 50 g/L and preferably in the range of 0.01 g/L to 50 g/L.

[0057] The acid strike plating bath and the silver plating bath used in the silver plating method of the invention may contain a grain refiner, a smoother and a brightener, etc., alone or in combination, in addition to the above-stated surfactants. The content thereof is generally in the range of 0.01 to 50 g/L and preferably in the range of 0.1 to 30 g/L.

[0058] Any or all of the silver plating bath (A) and the strike plating bath (B) used in the invention may further contain a displacement deposition prevention agent. Any known displacement deposition prevention agents may be used. Examples of the agent include heterocyclic thione compounds, amide or imide compounds, amino acids, open chain secondary amines having a sulfur atom and a double bond, cyclic thiol compounds having a sulfur atom with a double bond, amino or thiol compounds having a pyridine, pyrimidine, piperidine, piperazine or triazine skeleton, etc. Specific examples of the agent include 3-amino rhodanine, 3-thiourazole, 2-thiouramil, 4-thiouramil, 2,5-dioxo-4-thiohexahydropyrimidine, 4,6-dioxo-2-thiohexahydropyrimi-

dine, 2,6-dioxo-4-thio-hexahydropyrimidine, glutamic acid imide, succinimide, glutamic acid, arginine, valine, diethylthiourea, dimethylthiourea, thioacetamide, allylthiourea, thiosemicarbazide, dimercaptothiadiazole, thiosalicylic acid, benzoxazole, thiobenzamide, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, aminopyrimidine, N-aminopyrrolidine, N-aminomethylpyrrolidine, N-aminoethylpyrrolidine, N-aminopiperidine,

N-aminomethylpiperidine, N-aminoethylpiperidine, N-aminopiperazine, N-aminomethylpiperazine, N-aminoethylpiperazine, triazinethiol, etc. The agent may be added as appropriate in the range of 0.001 g/L to 50 g/L.

[0059] The invention may further comprise a displacement deposition prevention treatment step after the strike plating in case where the copper strike plating bath (B2) is used for the strike plating.

[0060] The displacement deposition prevention agents as mentioned above that may be contained in the silver plating bath (A) and/or the strike plating bath (B) may be contained in the solution used for this step.

[0061] According to the invention, an acid degreasing bath may be preferably used in the degreasing step, which is conducted prior to the silver or copper strike plating. In the degreasing step, though it is not limited to using the acid bath and an alkaline bath may be also used, it is recommendable to use the acid degreasing bath in the degreasing step if the resist or masking agent used for patterning has a weak resistance to alkali.

[0062] According to the invention, either or both of the silver plating bath (A) and the strike plating bath (B) include an ion-exchange membrane to conduct the silver plating and/or the silver strike plating with an anode being separated from a cathode. Though the ion-exchange membrane may be preferably applied to any of the silver plating bath (A) and the strike plating bath (B), it may be more preferably applied to the strike plating bath (B). Furthermore, it may be still more preferably applied to the strike plating bath that is stabilized by a complexing agent. It can bring a remarkable effect to the strike plating bath using a phosphine compound as the complexing agent. Though either of a cation-exchange membrane or an anion-exchange membrane may be used, the anion-exchange membrane may be preferably used. By separating the cathode and the anode with the ion-exchange membrane, the disintegration of the complexing agent, smoother, and brightener, etc., added in the plating bath or the strike plating bath may be prevented. The adverse effect on the plating film of compounds generated by consumption or disintegration of these additives may be also prevented. The ion-exchange membrane may also prevent an increase in silver concentration in the bath when a silver anode is used, facilitating the control of metal concentration in the bath.

[0063] By separating the cathode and the anode, accordingly the cathode chamber and the anode chamber (i.e. catholyte and anolyte), an insoluble anode may be used. As the insoluble anode, that made of any known materials such as a carbon anode, a platinum anode, a platinum-coated titanium anode, a ruthenium oxide-coated electrode and iridium oxide-coated electrode, etc. may be used. Accordingly, the silver anode and the insoluble anode as stated above may be used alone or in combination as the anode.

[0064] The method of silver plating using the acid bath according to the invention generally comprises the successive steps of, but not limited to, degreasing, acid activation, strike plating and silver plating. Water washing is usually conducted between each step.

[0065] The acid silver strike plating is generally conducted under the following conditions. The bath temperature is preferably 10 to 50 degrees C. and more preferably 20 to 35 degrees C. The electric current density is preferably 0.5 to 5 A/dm² and more preferably 2 to 3 A/dm². The plating time is preferably 10 to 300 seconds and more preferably 20 to 100 seconds.

[0066] The acid copper strike plating is generally conducted under the following conditions. The bath temperature is preferably 20 to 40 degrees C. and more preferably 25 to 35 degrees C. The electric current density is preferably 0.2 to 10 A/dm² and more preferably 1 to 5 A/dm². The plating time is preferably 10 to 300 seconds and more preferably 20 to 100 seconds.

[0067] The silver plating is generally conducted under the following conditions. The bath temperature is preferably 10 to 50 degrees C. and more preferably 15 to 40 degrees C. The electric current density is preferably 0.1 to 10 A/dm² and more preferably 0.5 to 5 A/dm². The plating time changes as appropriate in accordance with the desired thickness of plating film.

EXAMPLES

[0068] The invention will be explained in more detail based on the following Examples. However, it is to be understood that the invention is not intended to be limited to these examples. The invention may be variously modified within the scope of the technical idea of the present invention.

[0069] Each plating process was evaluated from the aspects of both adhesiveness of plating film and existence of dissolution of resist. Adhesiveness of plating film was evaluated by a bending test. In the bending test, each test piece was bent 90 degrees twice in accordance with JIS-H8504 standards before checking whether peeling of plating film occurred or not. The dissolution of resist was checked during or after conducting each plating process onto a test piece having a simulated pattern formed with a plating resist. As for the plating resist, developer and resist stripper, PHOTO FINER PER-2000 series (Taiyo Ink MFG, Co., Ltd) was applied for the formation of the simulated pattern under the standard conditions.

[0070] Since the dissolution of resist was observed when employing a commonly-used alkaline-type degreasing agent, acid CLEANER AC-100 (Daiwa Fine Chemical Co., Ltd.) for general purpose use was used instead as the degreasing agent so as to evaluate the process.

Comparative Example 1

[0071] Acid degreasing, silver cyanide strike plating, acid silver plating and drying were applied to a copper substrate in this order. Washing was conducted between each step. The composition of the treatment bath used in each step is as follows.

Silver cyanide strike plating	
silver cyanide(as silver)	3.6 g/L
potassium cyanide	80 g/L
temperature	25 degrees C.
electric current density	2 A/dm ²
plating time	60 sec

Silver plating bath	
silver methanesulfonate (as silver)	30 g/L
methanesulfonic acid	80 g/L
3-amino-1,2,4-triazole	5 g/L
1,2,4-triazole	3 g/L
2-mercaptobenzimidazole	0.1 g/L
temperature	25 degrees C.
electric current density	1 A/dm ²
plating time	5 min

[0072] In the test piece having a simulated pattern, resist dissolution was observed during the silver cyanide strike plating.

[0073] In case where washing was conducted extremely cautiously and carefully between the silver cyanide striking plating and the acid silver plating, neither cracking nor peeling of the plating film was observed in the bending test, showing a good flexibility and adhesiveness. However, in case where the washing was conducted in a common way with water, peeling of the plating film was observed.

Comparative Example 2

[0074] Acid degreasing, alkaline pyrophosphate copper strike plating, displacement prevention treatment, 5% methanesulfonic acid dipping, acid silver plating, and drying were applied to a 42 alloy substrate in this order. Washing was conducted between each step. The composition of the treatment bath used in each step is as follows.

Alkaline copper pyrophosphate strike plating bath	
copper pyrophosphate (as copper)	25 g/L
pyrophosphoric acid	200 g/L
ammonium nitrate	7 g/L
temperature	55 degrees C.
electric current density	4 A/dm ²
plating time	60 sec

Silver plating bath	
silver methanesulfonate (as silver)	30 g/L
methanesulfonic acid	80 g/L
3-amino-1,2,4-triazole	5 g/L
1,2,4-triazole	3 g/L
2-mercaptobenzimidazole	0.1 g/L
temperature	25 degrees C.
electric current density	1 A/dm ²
plating time	5 min

[0075] In the test piece having a simulated pattern, resist dissolution was observed during the alkaline copper strike plating. Exfoliation of the plating film was observed in the bending test.

Example 1

[0076] Acid degreasing, acid silver strike plating, acid silver plating and drying were applied to a copper substrate

in this order. Washing was conducted between each step. The composition of the treatment bath used in each step is as follows.

Silver strike plating bath	
silver methanesulfonate (as silver)	3 g/L
tris(3-hydroxypropyl)phosphine	15 g/L
methanesulfonic acid	40 g/L
temperature	25 degrees C.
electric current density	2.5 A/dm ²
plating time	60 sec

Silver plating bath	
silver methanesulfonate (as silver)	30 g/L
methanesulfonic acid	80 g/L
3-amino-1,2,4-triazole	5 g/L
1,2,4-triazole	3 g/L
2-mercaptobenzimidazole	0.1 g/L
temperature	25 degrees C.
electric current density	1 A/dm ²
plating time	5 min

[0077] Neither cracking nor peeling of the plating film was observed in the bending test, showing a good flexibility and adhesiveness. No sign of resist dissolution and peeling was observed in the test piece having a simulated pattern.

Example 2

[0078] Acid degreasing, acid activation, silver strike plating, silver plating and drying were applied to a copper substrate in this order. Washing was conducted between each step. The composition of the treatment bath used in each step is as follows. In Example 2, the anode and the cathode were separated by an anionic exchange membrane in the silver strike plating bath. Iridium oxide was used as the anode. 5% methanesulfonic acid solution was used as anolyte.

Silver strike plating bath	
silver methanesulfonate (as silver)	3 g/L
tris(3-hydroxypropyl)phosphine	15 g/L
methanesulfonic acid	40 g/L
temperature	25 degrees C.
electric current density	2.5 A/dm ²
plating time	60 sec

Silver plating bath	
silver methanesulfonate (as silver)	30 g/L
methanesulfonic acid	80 g/L
polyvinyl pyrrolidone	1 g/L
2-(2'-hydroxy-5'-methylphenyl)benzotriazole	0.1 g/L
2-aminothiazole	0.5 g/L
temperature	25 degrees C.
electric current density	1 A/dm ²
plating time	5 min

[0079] Neither cracking nor peeling of the plating film was observed in the bending test, showing a good flexibility and adhesiveness. No sign of resist dissolution and peeling was observed in the test piece having a simulated pattern. In case where the ionic exchange membrane was not used, 10% or more of the complexing agent for silver, tris(3-hydroxypropyl)phosphine, added to the silver strike plating bath was consumed by the electrolysis at 5 A/hr/L. On the other hand, in case where the ionic exchange membrane was used, only about 1% of the complexing agent was consumed.

Example 3

[0080] Acid degreasing, silver strike plating, silver plating and drying were applied to a 42 alloy substrate in this order. Washing was conducted between each step. The composition of the treatment bath used in each step is as follows.

Silver strike plating bath	
silver isethionate (as silver)	3 g/L
tris(3-hydroxypropyl)phosphine	15 g/L
isethionic acid	40 g/L
temperature	25 degrees C.
electric current density	2.5 A/dm ²
plating time	60 sec

Silver plating bath	
silver isethionate (as silver)	30 g/L
isethionic acid	80 g/L
polyethylene-imine	0.1 g/L
3-amino pyrazole	1 g/L
5-amino-1,2,4-triazole-3-carboxylic acid	0.05 g/L
temperature	25 degrees C.
electric current density	1 A/dm ²
plating time	5 min

[0081] Neither cracking nor peeling of the plating film was observed in the bending test, showing a good flexibility and adhesiveness. No sign of resist dissolution and peeling was observed in the test piece having a simulated pattern.

Example 4

[0082] Acid degreasing, silver strike plating, silver plating and drying were applied to a 42 alloy substrate in this order. Washing was conducted between each step. The silver plating bath contained displacement prevention agent. The composition of the treatment bath used in each step is as follows.

Silver strike plating bath	
silver methanesulfonate (as silver)	3 g/L
tris(3-hydroxypropyl)phosphine	15 g/L
methanesulfonic acid	40 g/L
3-amino rhodanine	0.05 g/L
temperature	25 degrees C.
electric current density	2.5 A/dm ²
plating time	60 sec

Silver plating bath	
silver methanesulfonate (as silver)	30 g/L
methanesulfonic acid	80 g/L
alkylamineoxide-based surfactant	0.1 g/L
thiophene-2-carboxylic acid	0.5 g/L
temperature	25 degrees C.
electric current density	1 A/dm ²
plating time	5 min

[0083] Neither cracking nor peeling of the plating film was observed in the bending test, showing a good flexibility and adhesiveness. No sign of resist dissolution and peeling was observed in the test piece having a simulated pattern.

Example 5

[0084] Acid degreasing, copper strike plating, displacement prevention treatment, acid dipping, silver plating and drying were applied to a 42 alloy substrate in this order. Washing was conducted between each step. The composition of the treatment bath used in each step is as follows.

Copper strike plating bath	
copper methanesulfonate (as copper)	10 g/L
tris(3-hydroxypropyl)phosphine	15 g/L
methanesulfonic acid	10 g/L
sulfuric acid	50 g/L
temperature	50 degrees C.
electric current density	5 A/dm ²
plating time	10 sec

Displacement prevention treatment bath	
dipotassium hydrogenphosphate	5 g/L
2-mercaptobenzimidazole	0.03 g/L
amino piperazine	1 ml/L
temperature	20 degrees C.
dipping time	10 sec

Acid dipping	
Methanesulfonic acid	50 g/L

Silver plating bath	
silver methanesulfonate (as silver)	30 g/L
methanesulfonic acid	80 g/L
tris(3-hydroxypropyl)phosphine	150 g/L
1,2,4-triazole	4 g/L
2-mercapto-benzothiazole	0.05 g/L
4-amino-1,2,4-triazole	3 g/L
temperature	25 degrees C.
electric current density	1 A/dm ²
plating time	5 min

[0085] Neither cracking nor peeling of the plating film was observed in the bending test, showing a good flexibility and adhesiveness. No sign of resist dissolution and peeling was observed in the test piece having a simulated pattern.

Example 6

[0086] Acid degreasing, copper strike plating, silver strike plating, silver plating and drying were applied to a 42 alloy substrate in this order. Washing was conducted between each step. The composition of the treatment bath used in each step is as follows.

Copper strike plating bath	
copper methanesulfonate (as copper)	10 g/L
tris(3-hydroxypropyl)phosphine	15 g/L
methanesulfonic acid	10 g/L
sulfuric acid	50 g/L
temperature	50 degrees C.
electric current density	5 A/dm ²
plating time	10 sec

Silver strike plating bath	
silver methanesulfonate (as silver)	3 g/L
tris(3-hydroxypropyl)phosphine	15 g/L
methanesulfonic acid	40 g/L
aminopiperazine	1 ml/L
temperature	25 degrees C.
electric current density	2.5 A/dm ²
plating time	60 sec

Silver plating bath	
silver methanesulfonate (as silver)	30 g/L
methanesulfonic acid	80 g/L
3-mercapto-1,2,4-triazole	10 g/L
1,2,4-triazole	1 g/L
2-mercapto-benzothiazole	0.05 g/L
temperature	25 degrees C.
electric current density	1 A/dm ²
plating time	5 min

[0087] Neither cracking nor peeling of the plating film was observed in the bending test, showing a good flexibility and adhesiveness. No sign of resist dissolution and peeling was observed in the test piece having a simulated pattern.

What is claimed is:

1. A method for silver plating onto a substrate, comprising conducting strike plating onto a substrate using a non-cyanide acid strike plating bath and subsequently conducting silver plating onto the substrate using a non-cyanide acid silver plating bath.

2. The method according to claim 1, wherein both the non-cyanide acid silver plating bath and the non-cyanide acid strike plating bath have a pH of less than 3.

3. The method according to claim 1, wherein the non-cyanide acid strike plating bath is an acid silver strike plating bath or an acid copper strike plating bath.

4. The method according to claim 1, wherein either or both of the non-cyanide acid silver plating bath and the non-cyanide acid strike plating bath contain at least a sulfonate ion.

5. The method according to claim 1, wherein either or both of the non-cyanide acid silver plating bath and the non-cyanide acid strike plating bath contain at least an aliphatic phosphine.

6. The method according to claim 3, wherein the acid copper strike plating bath is used and contains at least a sulfate ion.

7. The method according to claim 4, wherein either or both of the non-cyanide acid silver plating bath and the non-cyanide acid strike plating bath further contain an azole compound and/or a thiophene compound.

8. The method according to claim 5, wherein either or both of the non-cyanide acid silver plating bath and the non-cyanide acid strike plating bath further contain an azole compound and/or a thiophene compound.

9. The method according to claim 6, wherein either or both of the non-cyanide acid silver plating bath and the non-cyanide acid strike plating bath further contain an azole compound and/or a thiophene compound.

10. The method according to claim 4, wherein either or both of the non-cyanide acid silver plating bath and the non-cyanide acid strike plating bath further contain a surfactant or a surface-active polymer compound.

11. The method according to claim 5, wherein either or both of the non-cyanide acid silver plating bath and the non-cyanide acid strike plating bath further contain a surfactant or a surface-active polymer compound.

12. The method according to claim 6, wherein either or both of the non-cyanide acid silver plating bath and the non-cyanide acid strike plating bath further contain a surfactant or a surface-active polymer compound.

13. The method according to claim 3, wherein the method further comprises the step of conducting displacement deposition prevention treatment to the substrate between the strike plating and the silver plating and wherein the strike plating is conducted using the acid copper strike plating bath.

14. The method according to claim 1, wherein the method further comprises the step of conducting pretreatment using an acid degreasing bath prior to the strike plating.

15. The method according to claim 1, wherein either or both of the non-cyanide acid silver plating bath and the non-cyanide acid strike plating bath comprises an ion-exchange membrane therein to separate an anode and a cathode.

* * * * *