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(54) **TIN ALLOY PLATING SOLUTION**

(57) A tin alloy plating solution comprising a soluble tin salt, a soluble salt of a metal nobler than tin, and a sulfide compound represented by general formula (I). In formula (I), n is 1 to 3. The metal nobler than tin is preferably silver, copper, gold, or bismuth.

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## Description

### TECHNICAL FIELD

**[0001]** The present invention relates to a tin alloy plating solution for forming a tin alloy plating film by electroplating method. More specifically, it relates to a tin alloy plating solution suitable for forming solder bumps for semiconductor wafers and printed circuit boards. This international application claims priorities based on Japanese Patent Application No. 15219 (Japanese Patent Application No. 2017-15219) filed on January 31, 2017 and Japanese Patent Application No. 222433 (Japanese Patent Application No. 2017-222433) filed on November 20, 2017, and the entire contents of Japanese Patent Application No. 2017-15219 and Japanese Patent Application No. 2017-222433 are incorporated into this international application.

### BACKGROUND ART

**[0002]** In a tin alloy plating bath (liquid) to be used for forming a tin alloy plating film, for example, a tin-silver alloy plating film on a conductive object, when oxidation reduction potentials of tin ions and other metal ions (for example, silver ions) in the bath are significantly different from each other, it has been known that metal ions nobler than tin tend to form an insoluble salt or a metal simple substance and precipitate in the plating bath, whereby making it difficult to stably maintain the plating bath. Therefore, for example, a plating solution containing a cyan compound has conventionally been used as a tin-silver alloy plating solution. However, this bath contains a toxic cyan compound, so that it is extremely high toxic and causes various problems in handling.

**[0003]** As a tin alloy plating bath containing no cyan compound, various plating baths (liquids) have conventionally been proposed (for example, see Patent Documents 1 to 4.). Patent Document 1 shows a non-cyanide type stable silver and silver alloy plating bath, and the silver and silver alloy plating bath comprises (A) a soluble salt comprising any of a silver salt, and a mixture of a silver salt and a salt of a metal such as tin, bismuth, indium, lead and the like, (B) a specific sulfide-based compound having 1 or more basic nitrogen atoms in the molecule such as 2,2'-dipyridylsulfide, 2,2'-dipiperadinyldisulfide and the like, or a specific thiocrown ether compound such as 1-aza-7-oxa-4,10-dithiacyclododecane and the like. Due to inclusion of these specific compounds, this plating bath is said to be excellent in temporal stability of the plating bath, coprecipitation of silver with various metals, appearance of the electrodeposited film and the like, as compared with the bath containing other sulfur-based compound such as thioglycolic acid and the like.

**[0004]** Patent Document 2 shows a non-cyanide type stable silver and silver alloy plating bath, and this silver and silver alloy plating bath comprises (A) a soluble salt comprising any of a silver salt, and a mixture of a silver salt and a salt of a metal such as tin, bismuth, indium, lead and the like, (B) a specific aliphatic sulfide-based compound which contains one or more ethereal oxygen atom(s), 1-hydroxypropyl group(s) or hydroxypropylene group(s), and does not contain a basic nitrogen atom in the molecule such as thiobis(diethylene glycol), dithiobis(triglycerol), 3,3'-thiodipropanol, thiodiglycerin and the like. According to this plating bath, due to inclusion of these specific compounds, it is said to be excellent in temporal stability of the plating bath, coprecipitation of silver with various metals, appearance of the electrodeposited film and the like, as compared with the bath containing thiodiglycolic acid or β-thiodiglycol which is an aliphatic monosulfide compound containing no ethereal oxygen atom(s), a 1-hydroxypropyl group nor a hydroxypropylene group.

**[0005]** Patent Document 3 shows a non-cyanide type tin-silver alloy plating bath, and the tin-silver alloy plating bath contains (a) at least one kind of an aliphatic amino acid and a nitrogen-containing aromatic carboxylic acid, and (b) at least one kind of an aliphatic sulfide and an aliphatic mercaptan. As the (a) aliphatic amino acid, glycine and the like may be mentioned, as the (a) nitrogen-containing aromatic carboxylic acid, picolinic acid, 3-aminopyrazine-2-carboxylic acid and the like may be mentioned, as the (b) aliphatic sulfide, 4,7-dithiadecane-1,10-diol and the like may be mentioned, and as the aliphatic mercaptan, thioglycol and the like may be mentioned. In this plating bath, the sulfur compound of the component (b) is used as a stabilizer for silver, and further, by using the component (a) such as glycine, picolinic acid and the like in combination, it is said that solder wettability and appearance of the tin-silver alloy film can be well improved.

**[0006]** Patent Document 4 shows a silver-based plating bath containing no cyanide, and the plating bath contains a soluble salt including a silver salt, and one kind or more of sulfide-based compounds selected from the group consisting of compounds represented by a specific general formula. According to the plating bath, it is said that stability of silver ions in the bath is improved, a sufficient complexing power can be obtained, the production cost can be reduced, and practicality is excellent.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

**[0007]**

Patent Document 1: JP Hei.11-269691A (Abstract)
Patent Document 2: JP 2000-192279A (Abstract)
Patent Document 3: JP 2006-265572A (Abstract)
Patent Document 4: JP 2007-046142A (Abstract)

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

**[0008]** In the plating baths of the above-mentioned Patent Documents 1 to 4, various kinds of complexing agents for complexing silver are contained for stability of silver ions in a plating bath or temporal stability of the plating bath. However, the complexing agents shown in Patent Documents 1 to 4 involve the problems that these are decomposed when the plating bath is used for a long term or the plating solution is stored for a long period of time, and silver tends to precipitate. Further, when the complexing agent exhibits high stability in the plating bath, it exerted bad influences on appearance of a plating film and uniformity of a film thickness in some cases.

**[0009]** An object of the present invention is to provide a tin alloy plating solution which is excellent in electrolytic stability and temporal stability, and appearance of a plating film and uniformity of a film thickness are good.

MEANS TO SOLVE THE PROBLEMS

**[0010]** The present inventors have conducted intensive studies to solve the above-mentioned problems, and as a result, they have found that when a specific sulfide compound is contained in a tin alloy plating solution, a complex of a metal nobler than tin in the plating bath is stabilized without decomposition both during use and during storage, and good appearance of a plating film and uniformity of a film thickness can be obtained, whereby reached the present invention.

**[0011]** A first aspect of the present invention is a tin alloy plating solution containing a soluble tin salt, a soluble salt of a metal nobler than tin, and a sulfide compound represented by the following formula (1). In the formula (1), n is 1 to 3.
[Formula 1]

$$HO\text{-}CH_2CH_2\text{-}S\text{-}(CH_2CH_2\text{-}O\text{-}CH_2CH_2\text{-}S)_n\text{-}CH_2CH_2\text{-}OH \qquad (1)$$

**[0012]** A second aspect of the present invention is the invention according to the first aspect, which is the tin alloy plating solution further comprising at least one kind or two or more kinds of surfactants selected from an anionic surfactant, a cationic surfactant, a nonionic surfactant and an amphoteric surfactant.

**[0013]** A third aspect of the present invention is the invention according to the first or second aspect, which is the tin alloy plating solution wherein the metal nobler than tin is at least one kind or two or more kinds of metals selected from silver, copper, gold and bismuth.

**[0014]** A fourth aspect of the present invention is the invention according to any one of the first to third aspects, which is the tin alloy plating solution further comprising an antioxidant.

**[0015]** A fifth aspect of the present invention is the invention according to any one of the first to fourth aspects, which is the tin alloy plating solution further comprising a complexing agent for tin.

**[0016]** A sixth aspect of the present invention is the invention according to any one of the first to fifth aspects, which is the tin alloy plating solution further comprising a pH adjusting agent.

**[0017]** A seventh aspect of the present invention is the invention according to any one of the first to sixth aspects, which is the tin alloy plating solution further comprising a glossing agent.

EFFECTS OF THE INVENTION

**[0018]** In the tin alloy plating solution of the first aspect of the present invention, the sulfide compound contains an oxygen atom "-O-" in the molecule in the above-mentioned general formula (1), so that there is an effect of increasing water-solubility by the hydrogen bond with water. In addition, by presenting an ether bond "CO-C" between S atoms, it is excellent in stability of the compound itself, and by containing 2 to 4 S atoms, the S atom sufficiently complexes a

metal ion nobler than tin in the plating bath and stabilized. According to this constitution, the tin alloy plating solution is excellent in electrolytic stability and temporal stability during use and storage over a long period of time. In addition, since adsorption of the sulfide compound on the surface of the plating electrode is appropriately performed, when a surfactant is used in combination as a smoothening agent, the action of the surfactant is not inhibited, and appearance of a plating film and uniformity of a film thickness are good.

**[0019]** In the tin alloy plating solution according to the second aspect of the present invention, it further contains a surfactant such as an anionic surfactant, a cationic surfactant, a nonionic surfactant, an amphoteric surfactant, and the like, so that there is an effect of making the appearance of a plating film and uniformity of a film thickness better.

**[0020]** In the tin alloy plating solution according to the third aspect of the present invention, a metal nobler than tin is at least one kind or two or more kinds selected from silver, copper, gold and bismuth, so that there are effects that it is excellent in solder wettability, mounting strength, bendability and reflowability, whisker is difficultly formed, and the like.

**[0021]** In the tin alloy plating solution according to the fourth aspect of the present invention, it further contains an antioxidant, so that there is an effect of preventing oxidation of $Sn^{2+}$ in the tin alloy plating solution.

**[0022]** In the tin alloy plating solution according to the fifth aspect of the present invention, it further contains a complexing agent for tin, so that when the tin alloy plating solution is applied to the tin plating bath near neutrality, there is an effect of stabilizing $Sn^{2+}$ ions.

**[0023]** In the tin alloy plating solution according to the sixth aspect of the present invention, it further contains a pH adjusting agent, so that there is an effect of adjusting the tin alloy plating solution to an arbitrary pH range such as acidic, weakly acidic, neutral and the like.

**[0024]** In the tin alloy plating solution according to the seventh aspect of the present invention, it further contains a glossing agent, so that there is an effect of making the crystal grains of the tin alloy in tin alloy plating film fine.

## EMBODIMENTS TO CARRY OUT THE INVENTION

**[0025]** In the following, a tin alloy plating solution according to an embodiment of the present invention will be described. The tin alloy plating solution is utilized as a material for forming a plating film of a tin alloy used as a solder bump for a semiconductor substrate (wafer), a printed circuit board, or the like.

**[0026]** The tin alloy plating solution of the present embodiment contains a soluble tin salt, a soluble salt of a metal nobler than tin, and a sulfide compound represented by the following formula (1). In the formula (1), n is 1 to 3.

[Formula 2]

$$HO\text{-}CH_2CH_2\text{-}S\text{-}(CH_2CH_2\text{-}O\text{-}CH_2CH_2\text{-}S)_n\text{-}CH_2OH_2\text{-}OH \qquad (1)$$

[Tin alloy]

**[0027]** A tin alloy produced by the tin alloy plating solution of the present embodiment is an alloy of tin (Sn), and a predetermined metal selected from silver (Ag), copper (Cu), gold (Au) and bismuth (Bi), and include, for example, a binary alloy such as an SnAg alloy, an SnCu alloy, an SnAu alloy, an SnBi alloy and the like, and a ternary alloy such as an SnCuAg alloy and the like.

[Soluble tin salt]

**[0028]** A soluble tin salt used in the tin alloy plating solution of the present embodiment is a salt that forms divalent tin ions by dissolving in water. Examples of the soluble tin salt include halides, sulfates, oxides, alkane sulfonates, aryl sulfonates and alkanol sulfonates. Specific examples of the alkane sulfonates include methane sulfonate and ethane sulfonate. Specific examples of the aryl sulfonate include benzene sulfonate, phenol sulfonate, cresol sulfonate and toluene sulfonate. Specific examples of the alkanol sulfonates include isethionate.

**[0029]** The soluble tin salt may be used one kind alone or in combination of two or more kinds. A content of the soluble tin salt in the tin alloy plating solution of the present embodiment is preferably in the range of 5 g/L or more and 200 g/L or less, and more preferably in the range of 20 g/L or more and 100 g/L or less in terms of tin. If the content of the soluble tin salt is excessively little, precipitation of tin does not normally occur in the range of 1 to 20 ASD (amperes per square decimator) generally used in bump plating, and there is a fear that formation of good bump cannot be performed. On the other hand, if the content of the soluble tin salt is excessively high, formation of bump becomes difficult due to increase in the viscosity of the plating solution, and tin is contained more than necessary, so that there is a fear that the cost of the plating bath becomes high.

[Soluble salt of metal nobler than tin]

**[0030]** The soluble salt of a metal nobler than tin to be used in the tin alloy plating solution of the present embodiment is a salt soluble in water. Examples of the metal nobler than tin include at least one kind or two or more kinds of metals selected from silver, copper, gold and bismuth. Examples of the soluble salt of these metals are the same as the examples of the soluble tin salt. Among these metals, silver or copper is preferably contained. An alloy of tin and silver (SnAg alloy) has a low melting point as a melting point at a eutectic composition (Sn-3.5 wt% Ag) of 221°C, and an alloy of tin and copper (SnCu alloy) has a low melting point as a melting point at a eutectic composition (Sn-1.7 wt% Cu) of 227°C, so that these have advantages such as excellent in solder wettability, mounting strength, bendability and reflowability, and whisker is difficultly formed and the like. The soluble salt of the metal nobler than tin may be used one kind alone or in combination of two or more kinds. A content of the soluble salt of the metal nobler than tin in the plating solution of the present embodiment is preferably in the range of 0.01 g/L or more and 10 g/L or less, and more preferably in the range of 0.1 g/L or more and 2 g/L or less in terms of the amount of the metal. If the content of the soluble salt of the metal nobler than tin is excessively little or excessively high, the composition of the deposited solder alloy cannot be made a eutectic composition, and the characteristics as a solder alloy cannot be obtained.

[Sulfide compound]

**[0031]** The sulfide compound to be used in the tin alloy plating solution of the present embodiment is represented by the above-mentioned general formula (1), and can be obtained by subjecting to dehydration condensation of thiodiethanol (n=0) in a strong acid having a dehydrating action such as concentrated sulfuric acid, alkylsulfonic acid and the like. By changing the reaction temperature, reaction time and purification conditions at this time, the value of n in the general formula (1) can be controlled. If the n exceeds 3, the sulfide compound is not water soluble and becomes hydrophobic. In order to dissolve the sulfide compound in an aqueous solution, n is required to be 3 or less. As described above, since the sulfide compound contains an oxygen atom "-O-" in the molecule in the general formula (1) described above, there is an effect of increasing water solubility by the hydrogen bond with water. In addition, by being present an ether bond "C-O-C" between S atoms, stability of the compound itself is excellent, and by containing 2 to 4 S atoms in one molecule, the S atoms can be sufficiently complexing the metal ions nobler than tin in the plating bath and stabilized. The structure of the sulfide compound can be analyzed by using analytical instruments such as high performance liquid chromatography (HPLC), high performance liquid chromatography mass spectrometer (LC-MS), Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance apparatus (NMR), and the like, in combination.

[Additive]

**[0032]** The tin alloy plating solution of the present embodiment may further contain an additive such as an acid electrolyte (free acid), a surfactant, an antioxidant, a complexing agent for tin, a pH adjusting agent, a glossing agent and the like.

(Acid electrolyte)

**[0033]** As the acid electrolyte, hydrogen chloride, hydrogen bromide, sulfuric acid, an alkanesulfonic acid, an arylsulfonic acid or an alkanolsulfonic acid can be mentioned. Specific examples of the alkanesulfonic acid include methanesulfonic acid or ethanesulfonic acid. Specific examples of the arylsulfonic acid include benzenesulfonic acid, phenolsulfonic acid, cresol sulfonic acid or toluenesulfonic acid. Specific examples of the alkanol sulfonic acid include isethionic acid. The acid electrolyte has the effect of enhancing conductivity of the tin alloy plating solution.

**[0034]** The acid electrolyte may be used one kind alone or in combination of two or more kinds. A content of the acid electrolyte in the tin alloy plating solution of the present embodiment is preferably in the range of 5 g/L or more and 500 g/L or less, and more preferably in the range of 30 g/L or more and 300 g/L or less.

(Surfactant)

**[0035]** The tin alloy plating solution of the present embodiment preferably contains a surfactant. The surfactant has a function of enhancing affinity between the tin alloy plating solution and the object to be plated, and functions of improving appearance of a plating film, improving adhesiveness with the object to be plated, and making the film thickness uniform and the like by adsorbing to the surface of the plating film at the time of forming the tin alloy plating film, thereby suppressing crystal growth of the tin alloy in the plating film and making the crystals fine. As the surfactant, various kinds of the surfactants such as an anionic surfactant, a cationic surfactant, a nonionic surfactant and an amphoteric surfactant, and the like can be used.

**[0036]** Specific examples of the anionic surfactant include alkyl sulfate, polyoxyethylene alkyl ether sulfate, polyoxyethylene alkyl phenyl ether sulfate, alkyl benzene sulfonate, alkyl naphthalene sulfonate and the like. Specific examples of the cationic surfactant include mono- to trialkylamine salts, dimethyldialkyl ammonium salts, trimethylalkyl ammonium salts and the like. Specific examples of the nonionic activating agent include materials in which 2 to 300 mol of ethylene oxide (EO) and/or propylene oxide (PO) is subjected to addition condensation to alkanols having 1 to 20 carbon atoms, phenol, naphthol, bisphenols, alkylphenols having 1 to 25 carbon atoms, arylalkylphenols, alkylnaphthols having 1 to 25 carbon atoms, alkoxyl phosphoric acids (salts) having 1 to 25 carbon atoms, sorbitan esters, polyalkylene glycols, aliphatic amides having 1 to 22 carbon atoms, and the like. Specific examples of the amphoteric surfactant include carboxybetaine, imidazoline betaine, aminocarboxylic acid, and the like.

**[0037]** The surfactant may be used one kind alone or in combination of two or more kinds. An amount of the surfactant to be added in the tin alloy plating solution of the present embodiment is generally in the range of 0.01 g/L or more and 50 g/L or less, preferably in the range of 0.1 g/L or more and 20 g/L or less, and more preferably in the range of 1 g/L or more and 10 g/L or less.

(Antioxidant)

**[0038]** The tin alloy plating solution of the present embodiment may contain an antioxidant, if necessary. The antioxidant is intended to prevent oxidation of $Sn^{2+}$ in the tin alloy plating solution. Examples of the antioxidant include ascorbic acid or a salt thereof, pyrogallol, hydroquinone, phloroglucinol, trihydroxy-benzene, catechol, cresol sulfonic acid or a salt thereof, catechol sulfonic acid or a salt thereof, hydroquinone sulfonic acid or a salt thereof or the like. For example, in an acidic bath, hydroquinone sulfonic acid or a salt thereof are preferable, and in a neutral bath, ascorbic acid or a salt thereof, and the like are preferable.

**[0039]** The antioxidant may be used one kind alone or in combination of two or more kinds. An amount to be added of the antioxidant in the tin alloy plating solution of the present embodiment is generally in the range of 0.01 g/L or more and 20 g/L or less, preferably in the range of 0.1 g/L or more and 10 g/L or less, and more preferably in the range of 0.1 g/L or more and 5 g/L or less.

(Complexing agent for tin)

**[0040]** The tin alloy plating solution of the present embodiment can be applied to a tin alloy plating bath in an optional pH range such as acidic, weakly acidic, neutral, and the like. $Sn^{2+}$ ions are stable at strong acidity (pH: <1), but tend to form white precipitates from acidity to near neutrality (pH: 1 to 7). For this reason, when the tin alloy plating solution of the present embodiment is applied to the tin plating bath near neutrality, it is preferable to add a complexing agent for tin for the purpose of stabilizing the $Sn^{2+}$ ions.

**[0041]** As the complexing agent for tin, oxycarboxylic acids, polycarboxylic acids and monocarboxylic acids can be used. Specific examples thereof include gluconic acid, citric acid, glucoheptonic acid, gluconolactone, acetic acid, propionic acid, butyric acid, ascorbic acid, oxalic acid, malonic acid, succinic acid, glycolic acid, malic acid, tartaric acid, or salts thereof, and the like. It is preferably gluconic acid, citric acid, glucoheptonic acid, gluconolactone, glucoheptolactone, or salts thereof, and the like. In addition, it is also effective as a complexing agent such as polyamines including ethylenediamine, ethylenediamine tetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), iminodipropionic acid (IDP), hydroxyethylethylene-diaminetriacetic acid (HEDTA), triethylenetetramine hexaacetic acid (TTHA), ethylenedioxybis(ethylamine)-N,N,N',N'-tetraacetic acid, mercaptotriazoles, mercaptotetrazoles, glycines, nitrilotrimethylphosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid, or salts thereof, and the like, or aminocarboxylic acids.

**[0042]** The complexing agent for tin may be used one kind alone or in combination of two or more kinds. An amount to be added of the complexing agent for tin in the tin alloy plating solution of the present embodiment is generally in the range of 0.001 mol or more and 10 mol or less, preferably in the range of 0.01 mol or more and 5 mol or less, and more preferably in the range of 0.5 mol or more and 2 mol or less based on 1 mol of tin in the soluble tin salt compound contained in the tin alloy plating solution.

(pH adjusting agent)

**[0043]** The tin alloy plating solution of the present embodiment can contain a pH adjusting agent, if necessary. Examples of the pH adjusting agent include various kinds of acids such as hydrochloric acid, sulfuric acid, and the like, and various kinds of bases such as aqueous ammonia, potassium hydroxide, sodium hydroxide, sodium hydrogen carbonate, and the like. In addition, as the pH adjusting agent, it is also effective including monocarboxylic acids such as acetic acid, propionic acid, and the like, boric acids, phosphoric acids, dicarboxylic acids such as oxalic acid, succinic acid, and the like, and oxycarboxylic acids such as lactic acid, tartaric acid, and the like.

(Glossing agent)

**[0044]** The tin alloy plating solution of the present embodiment can contain a glossing agent, if necessary. As the glossing agent, an aromatic carbonyl compound is effective. The aromatic carbonyl compound has a function of refining the crystal particles of the tin alloy in the tin alloy plating film. The aromatic carbonyl compound is a compound in which a carbonyl group (-CO-X: wherein X means a hydrogen atom, a hydroxyl group, an alkyl group having a number of the carbon atoms in the range of 1 to 6 or an alkoxy group having a number of the carbon atoms in the range of 1 to 6) is bonded to the carbon atom of the aromatic hydrocarbon. The aromatic hydrocarbons include a benzene ring, a naphthalene ring and an anthracene ring. The aromatic hydrocarbons may have a substituent(s). Examples of the substituent(s) include a halogen atom, a hydroxyl group, an alkyl group having a number of the carbon atoms in the range of 1 to 6 or an alkoxy group having a number of the carbon atoms in the range of 1 to 6. The carbonyl group may be directly bonded to the aromatic hydrocarbon, or may be bonded via an alkylene group having a number of the carbon atoms in the range of 1 or more and 6 or less. The aromatic carbonyl compound includes benzalacetone, cinnamic acid, cinnamaldehyde and benzaldehyde.

**[0045]** The aromatic carbonyl compound may be used one kind alone or in combination of two or more kinds. An amount to be added of the aromatic carbonyl compound in the tin alloy plating solution of the present embodiment is generally in the range of 0.01 mg/L or more and 500 mg/L, preferably in the range of 0.1 mg/L or more and 100 mg/L or less, and more preferably in the range of 1 mg/L or more and 50 mg/L or less.

**[0046]** The tin alloy plating solution of the present embodiment can be prepared by, for example, mixing a soluble tin salt, a soluble salt of a metal nobler than tin, the sulfide compound represented by the general formula (1) described above and other components with water. In order to suppress oxidation of $Sn^{2+}$ ions and reduction reaction of a metal ion nobler than tin, it is preferable that the soluble salt of a metal nobler than tin is mixed after introducing the sulfide compound.

**[0047]** As a method of forming a plating film using the plating solution of the present embodiment, electroplating is used as described above. A current density at the time of forming a plating film by electroplating is in the range of 0.1 $A/dm^2$ or more and 100 $A/dm^2$ or less, and preferably in the range of 0.5 $A/dm^2$ or more and 20 $A/dm^2$ or less. The liquid temperature is in the range of 10°C or higher and 50°C or lower, and more preferably in the range of 20°C or higher and 40°C or lower.

EXAMPLES

**[0048]** Next, Examples of the present invention will be described in detail along with Comparative Examples.

(Bath preparation of SnAg plating solution)

<Example 1>

**[0049]** With an aqueous tin methanesulfonate solution were mixed methanesulfonic acid as a free acid, a sulfide compound wherein n=1 of the general formula (1) as a complexing agent, and a nonionic surfactant (polyoxyethylene and polyoxypropylene were added to ethylenediamine with a ratio of 50: 50) and dissolved, and a silver methanesulfonate liquid was further added and mixed. And finally, ion exchange water was added to prepare a bath of an SnAg plating solution having the following composition. Incidentally, the aqueous tin methanesulfonate solution was prepared by electrolyzing a metal tin plate and the aqueous silver methanesulfonate solution was prepared by electrolyzing a metal silver plate, both in an aqueous methanesulfonic acid solution, respectively.

(Composition of SnAg plating solution)

**[0050]** Tin methanesulfonate (as $Sn^{2+}$): 50 g/L
Silver methanesulfonate (as $Ag^{+}$): 0.5 g/L
Methanesulfonic acid (as free acid): 150 g/L
Sulfide compound (n=1): 5 g/L
Nonionic surfactant: 5 g/L
Ion exchange water: balance

<Example 2>

**[0051]** An SnAg plating solution was prepared as a bath in the same manner as in Example 1 except that a sulfide compound wherein n=2 of the general formula (1) was used as a complexing agent.

<Example 3>

**[0052]** An SnAg plating solution was prepared as a bath in the same manner as in Example 1 except that a sulfide compound wherein n=3 of the general formula (1) was used as a complexing agent.

<Example 4>

**[0053]** An aqueous tin methanesulfonate solution was mixed with methanesulfonic acid as a free acid and a sulfide compound wherein n=2 of the general formula (1) as a complexing agent and dissolved, and an aqueous copper methanesulfonate solution was further added and mixed. After making the solution uniform by mixing, a nonionic surfactant was further added thereto. And finally, ion exchange water was added to the mixture to prepare a bath of an SnCu plating solution having the following composition. Incidentally, the aqueous tin methanesulfonate solution was prepared by electrolyzing a metal tin plate, and the aqueous copper methanesulfonate solution was prepared by electrolyzing a metal copper plate in an aqueous methanesulfonic acid solution, respectively.

(Composition of SnCu plating solution)

**[0054]** Tin methanesulfonate (as $Sn^{2+}$): 50 g/L
Copper methanesulfonate (as $Cu^{2+}$): 0.3 g/L
Methanesulfonic acid (as free acid): 150 g/L
Sulfide compound (n=2): 5 g/L
Nonionic surfactant: 5 g/L
Ion exchange water: balance

<Example 5>

**[0055]** An aqueous tin methanesulfonate solution was mixed with methanesulfonic acid as a free acid, a sulfide compound wherein n=1 of the general formula (1) as a complexing agent and a nonionic surfactant (20 mol of polyoxyethylene was added to 1 mol of bisphenol A) to dissolve these materials, then, sodium gluconate as a complexing agent of tin and mercaptotetrazole were added, and benzalacetone was mixed as a glossing agent. Further, a silver methanesulfonate solution was added and mixed. And finally, ion exchange water was added to prepare a bath of an SnAg plating solution having the following composition.

(Composition of SnAg plating solution)

**[0056]** Tin methanesulfonate (as $Sn^{2+}$) : 80 g/L
Silver methanesulfonate (as $Ag^{+}$): 1.0 g/L
Methanesulfonic acid (as free acid): 100 g/L
Sulfide compound (n=1): 3 g/L
Nonionic surfactant: 8 g/L
Sodium gluconate: 10 g/L
Mercaptotetrazole: 1 g/L
Benzalacetone: 0.01 mg/L
Ion exchange water: balance

<Comparative Example 1>

**[0057]** An SnAg plating solution was prepared as a bath in the same manner as in Example 1 except that a sulfide compound wherein n=0 of the general formula (1) was used as a complexing agent.

<Comparative Example 2>

**[0058]** An SnAg plating solution was prepared as a bath in the same manner as in Example 1 except that a sulfide compound wherein n=4 of the general formula (1) was used as a complexing agent.

<Comparative Example 3>

**[0059]** An SnAg plating solution was prepared as a bath in the same manner as in Example 1 except that 3, 6-dithia-

1,8-octanediol was used as a complexing agent.

<Comparative Example 4>

**[0060]** An SnAg plating solution was prepared as a bath in the same manner as in Example 5 except that a sulfide compound wherein n=4 of the general formula (1) was used as a complexing agent.

<Comparative test and evaluation>

**[0061]** By using nine kinds of the prepared baths of the plating solutions in Examples 1 to 5 and Comparative Examples 1 to 4, stability and plating performance of the tin alloy plating solution were evaluated. Stability of the tin alloy plating solution was evaluated by performing an electrolytic stability test and a temporal stability test. The plating performance was evaluated by performing Hull cell test and a plating test.

(a) Electrolytic stability test

**[0062]** Nine kinds of the prepared baths of the tin alloy plating solutions were used as an electrolyte, a copper plate was located as a cathode and a platinum plate as an anode in the electrolyte, nine kinds of the prepared baths of the tin alloy plating solutions were performed to electroplating each separately at a bath temperature of 25°C and a cathode current density of 10 ASD. Since metal components in the plating solution were consumed by electroplating, while powders of stannous oxide (SnO) and silver oxide ($Ag_2O$) were added to, mixed with and dissolved in the plating solution every 5 Ah/L of electroplating to supply the metal components to the plating bath, electroplating was performed up to 200 Ah/L. A concentration of the sulfide compound which is a complexing agent remaining in the tin alloy plating solution after electroplating was quantitatively analyzed by the following HPLC (High Performance Liquid Chromatography) method. The tin alloy plating solution was filtered with a disposable syringe, and analysis was performed using L-Column ODS kept at 40°C using an HPLC apparatus (Model No.: Prominence) manufactured by Shimadzu Corporation and making a mobile phase MeOH (methanol). The concentration of the complexing agent immediately after preparation of the bath was made 100%, and a remaining ratio (%) of the complexing agent after electroplating was evaluated as the remaining amount of the complexing agent.

(b) Temporal stability test

**[0063]** Nine kinds of the prepared baths of the tin alloy plating solutions were separately charged in a sealed bottle made of a glass, and stored in a clean oven manufactured by Panasonic Corporation at 50°C for 6 months. Using an ICP Automatic Emission Spectrometer (ICP-AES, Model No.: ICPE-9800) manufactured by Shimadzu Corporation, metal concentrations other than Sn in the tin alloy plating solution immediately after preparation of the bath, that is, in the case of the SnAg alloy plating solution, the Ag concentration, and in the case of the SnCu plating solution, the Cu concentration was made 100%, respectively, and metal concentrations other than Sn remained after storage of 6 months, that is, in the case of the SnAg alloy plating solution, the Ag concentration, and in the case of the SnCu plating solution, the Cu concentration was measured and the remaining ratio (%) thereof was each calculated.

(c) Hull cell test

**[0064]** Nine kinds of the prepared baths of the tin alloy plating solutions were each separately placed in a hull cell tank manufactured by Yamamoto-MS Co., Ltd., and a hull cell plate made of copper was arranged in the liquid as a cathode and a platinum plate as an anode, respectively, to perform the Hull cell test. The plating conditions were such that the liquid temperature was 25°C, the applied current was 3 A, and the plating processing time was 5 minutes. During the plating processing, the plating solution was stirred by a cathode rocker. The hull cell evaluation was performed by observing the film appearance of a plating film on the hull cell plate subjected to plating treatment confirming with naked eyes using a current density quick reference plate, and evaluated with three judgement criteria that the film with gloss or semi-gloss was regarded as "good", the film without gloss or cloudy was regarded as "acceptable" and the film with scorching or burning was regarded as "poor".

(d) Plating test

**[0065]** Nine kinds of the prepared baths of the tin alloy plating solutions were used as electrolytes and a plating test was carried out separately. The electrolyte was adjusted to a liquid temperature of 25°C, and a substrate made of copper (10 cm in length, 10 cm in width and 0.3 mm in thickness) was immersed in the electrolyte and subjected to 10 minutes

at a current density of 5 A/dm$^2$. The film thickness of ten portions of the obtained plating film was measured by a fluorescent X-ray film thickness measuring device (manufactured by Hitachi High-Technologies Corporation). The maximum value ($T_{max}$), the minimum value ($T_{min}$) and the average value ($T_{average}$) of the film thickness at the 10 portions were obtained, and uniformity of a film thickness was calculated by the following equation (2) to evaluate whether electrodeposition was uniformly performed or not. The test results as above are shown in Table 1.

$$\text{Uniformity of film thickness} = (T_{max}-T_{min})/(2\times T_{average}) \times 100(\%) \quad (2)$$

[Table 1]

| | Tin alloy plating solution | | | Stability of plating solution | | Plating characteristics of plating solution | |
|---|---|---|---|---|---|---|---|
| | Complexing agent | | Metal other than Sn | Electrolytic stability test | Temporal stability test | Hull cell test (plating film appearance) | Plating test (film thickness uniformity) |
| | Sulfide compound | Compound other than sulfide compound | | | | | |
| Example 1 | n=1 | - | Ag | 90% | 93% | Good | 2.1% |
| Example 2 | n=2 | - | Ag | 92% | 84% | Good | 3.3% |
| Example 3 | n=3 | - | Ag | 95% | 97% | Acceptable | 4.0% |
| Example 4 | n=2 | - | Cu | 88% | 89% | Good | 3.2% |
| Example 5 | n=1 | - | Ag | 91% | 92% | Good | 4.2% |
| Comparative Example 1 | n=0 | - | Ag | 86% | 27% | Good | 2.7% |
| Comparative Example 2 | n=4 | - | Ag | 98% | 98% | Poor | 15.8% |
| Comparative Example 3 | - | 3, 6-Di-thia-1,8-octanediol | Ag | 21% | 9% | Good | 3.1% |
| Compara-tive Example 4 | n=4 | - | Ag | 93% | 92% | Poor | 24.6% |

**[0066]** As clearly seen from Table 1, in the case of Examples 1 to 5 using the sulfide compound represented by n=0 to 3 in the general formula (1), even after electrolytic plating, the complexing agent remained with a high ratio as 90% to 95% in the SnAg plating solution and as 88% in the SnCu plating solution, and even after lapse of time, the remaining ratio of Ag or Cu in the solution was as high as 84% to 97% in the SnAg plating solution, and 89% in the SnCu plating solution, and in the plating performance, appearance of the film was good and uniformity of a film thickness was as good as 2.1% to 4.2% in the SnAg plating solution and 3.2% in the SnCu plating solution. On the other hand, in Comparative Example 1, while electrolytic stability and plating performance were good, the residual ratio of Ag decreased after lapse of time. This is considered that the compound of n=0 used in Comparative Example 1 has one S atom in one molecule, so that an ability of forming a complex with Ag ion is not sufficient, and Ag was reduced and deposited. Also, in Comparative Example 2 and Comparative Example 4, while stability of the plating solution was good, the plating performance worsened. This is presumed that the compound of n=4 has high hydrophobicity and is strong in adsorbing power to the surface of the electrode, so that it interfered with the smoothening action of the surfactant used in combination. Further, in Comparative Example 3, while the plating performance was good, the sulfide compound of the present invention as a complexing agent was not contained in the tin alloy plating solution, so that a concentration of the complexing agent was lowered after the electrolytic plating.

UTILIZABILITY IN INDUSTRY

**[0067]** The plating solution of the present invention can be utilized for forming a part of an electronic component such as a bump electrode of a semiconductor wafer or a printed circuit board.

## Claims

1. A tin alloy plating solution which comprises a soluble tin salt, a soluble salt of a metal nobler than tin, and a sulfide compound represented by the following formula (1). In the formula (1), n is 1 to 3.

$$HO\text{-}CH_2CH_2\text{-}S\text{-}(CH_2CH_2\text{-}O\text{-}CH_2CH_2\text{-}S)_n\text{-}CH_2CH_2\text{-}OH \qquad (1)$$

2. The tin alloy plating solution according to Claim 1, which further comprises at least one kind or two or more kinds of surfactants selected from an anionic surfactant, a cationic surfactant, a nonionic surfactant and an amphoteric surfactant.

3. The tin alloy plating solution according to Claim 1 or Claim 2, wherein the metal nobler than tin is at least one kind or two or more kinds of metals selected from silver, copper, gold and bismuth.

4. The tin alloy plating solution according to any one of Claim 1 to Claim 3, which further comprises an antioxidant.

5. The tin alloy plating solution according to any one of Claim 1 to Claim 4, which further comprises a complexing agent for tin.

6. The tin alloy plating solution according to any one of Claim 1 to Claim 5, which further comprises a pH adjusting agent.

7. The tin alloy plating solution according to any one of Claim 1 to Claim 6, which further comprises a glossing agent.

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2017/044668

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C25D3/60(2006.01)i, C25D3/56(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C25D3/60, C25D3/56

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

| | |
|---|---|
| Published examined utility model applications of Japan | 1922–1996 |
| Published unexamined utility model applications of Japan | 1971–2018 |
| Registered utility model specifications of Japan | 1996–2018 |
| Published registered utility model applications of Japan | 1994–2018 |

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | JP 2006-265572 A (ISHIHARA CHEM CO., LTD.) 05 October 2006, claims, paragraphs [0010], [0018] (Family: none) | 1-7 |
| A | JP 2016-183409 A (MITSUBISHI MATERIALS CORP.) 20 October 2016, claims, paragraph [0063] & WO 2016/152983 A1 & TW 201704545 A | 1-7 |
| A | JP 2001-164396 A (ISHIHARA CHEM CO., LTD.) 19 June 2001, claims & US 6607653 B1, claims & TW 589411 B & KR 10-2001-0030495 A | 1-7 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
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## REFERENCES CITED IN THE DESCRIPTION

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