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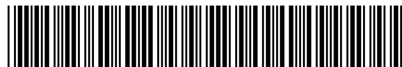

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(54) **COPPER-TIN ALLOY PLATING BATH**

KUPFER-ZINN-LEGIERUNGSPLATTIERUNGSBAD

BAIN DE PLACAGE D'ALLIAGE DE CUIVRE-ÉTAIN

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(56) References cited:
EP-A1- 1 591 563 **JP-A- 2001 026 898**
JP-A- 2004 244 719 **JP-A- 2004 510 053**
JP-A- 2008 537 017 **JP-A- 2010 174 373**
US-A1- 2004 035 714 **US-A1- 2005 263 403**
US-A1- 2010 216 302

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EP 3 178 969 B1

Description

[0001] The present invention relates to a copper-tin alloy plating bath.

[0002] Nickel plating has been widely used in electroplating. However, there are indications that nickel plating has a nickel allergy problem such that the metallic element (nickel) contained in the plating film causes skin rashes or inflammation. There is thus a need for a technique that replaces nickel plating.

[0003] Meanwhile, copper-tin alloys are known to have a white appearance and film properties that are comparable to those of nickel. For this reason, copper-tin alloy plating is drawing attention as an alternative to nickel plating.

[0004] Cyanide ion-containing plating baths (cyanide baths) have been used for copper-tin alloy plating, but are problematic in terms of the work environment and wastewater treatment regulations. In recent years, pyrophosphate baths (e.g., Patent Literature 1 to 3), acidic baths (e.g., Patent Literature 4 and 5), and the like have been proposed as cyanide-ion-free (hereinafter may be referred to as "non-cyanide"), copper-tin alloy baths. However, when a pyrophosphate bath is used, compared with the case in which a cyanide bath is used, the formed plating film has high internal stress, and therefore, cracks are generated during plating, thus making it difficult to thicken the plating film. In acidic baths, the deposition potentials of copper and tin are not adjusted; therefore, when an acidic bath is used for barrel plating with a large variation in the current density, copper is preferentially deposited, resulting in a large variation in the alloy composition.

US 2010/216302 A1 describes electrolyte compositions including tin ions, ions of one or more alloying metals, a flavone compound and a dihydroxy bis-sulfide, wherein the electrolyte compositions are free of lead and cyanide.

US 2005/263403 A1 discloses a method for electrodeposition of bronzes, with which the substrate to be coated is plated in an acid electrolyte that contains at least tin and copper ions, an alkylsulfonic acid and a wetting agent, and the preparation of such an electrolyte.

US 2004/035714 A1 relates to an electrolyte and a method for depositing tin-copper alloy layers.

EP 1 591 563 A1 describes a tin-containing plating bath.

[0005] There is thus a demand for a plating bath that enables thickening of a plating film as in the case of a cyanide bath, and that can also be applied to barrel plating.

PTL 1: JPH10-102278A

PTL 2: JP2001-295092A

PTL 3: JP2004-035980A

PTL 4: JP2009-161804A

PTL 5: JP2010-189753A

[0006] The present invention has been accomplished in view of the above-described problems of the conventional techniques. A primary object of the present invention is to provide a copper-tin alloy plating bath that allows for film thickening without using cyanide ions, and that can also be applied to barrel plating.

[0007] The present inventors conducted extensive research to achieve the above object, and found that a copper-tin alloy plating bath that allows for film thickening without using cyanide ions and that can also be applied to barrel plating can be obtained by using a specific sulfur-containing compound and a specific hydroxyl group-containing aromatic compound. The present invention has been accomplished through further research based on this finding.

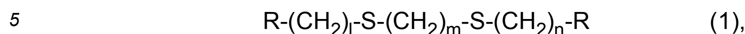
[0008] More specifically, the present invention and embodiments thereof are defined in the claims.

[0009] Since a specific sulfur-containing compound and a specific hydroxyl group-containing aromatic compound are used in combination in the copper-tin alloy plating bath of the present invention, an alloy film containing copper and tin at any ratio can be obtained. In addition, since a specific sulfur-containing compound is used as a complexing agent in the copper-tin alloy plating bath of the present invention, cracking is less likely to occur compared with the case in which hitherto known pyrophosphate baths are used, and the plating film can be thickened without using a cyanide bath. Further, since, regarding the copper-tin alloy plating bath of the present invention, the current density has a small influence on the alloy ratio compared with the case in which hitherto known acidic baths are used, the copper-tin alloy plating bath of the present invention can also be applied to barrel plating with a large variation in the current density. Moreover, a plating film having an excellent bright appearance can be obtained by a nonionic surfactant, and an aromatic ketone or an aromatic aldehyde comprised in the aqueous solution of the copper-tin alloy plating bath.

[0010] Fig. 1 is a diagram showing the relationship between the current density of a copper-tin alloy plating bath and the copper content of a plating film.

[0011] The copper-tin alloy plating bath of the present invention is described in detail below.

[0012] The copper-tin alloy plating bath of the present invention comprises an aqueous solution containing a water-soluble copper compound and a water-soluble divalent tin compound as metal sources, a sulfur-containing compound represented by formula (1):



$$R\text{-}(CH_2)_l\text{-}S\text{-}(CH_2)_m\text{-}S\text{-}(CH_2)_n\text{-}R \quad (1),$$

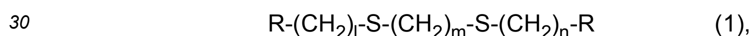
wherein R is H, OH, or SO_3Na, and l, m, and n are each independently an integer of 0 to 3, as a complexing agent, and a hydroxyl group-containing aromatic compound.

[0013] The water-soluble copper compound, which is a copper ion source, is not particularly limited as long as it is a water-soluble compound containing divalent copper as a copper component. Specific examples of water-soluble copper compounds include copper(II) chloride, copper(II) sulfate, copper(II) nitrate, copper(II) carbonate, copper(II) oxide, copper(II) acetate, copper(II) methanesulfonate, copper(II) sulfamate, copper(II) fluoride, copper(II) 2-hydroxyethanesulfonate, copper(II) 2-hydroxypropanesulfonate, copper(II) pyrophosphate, and the like. Among these copper compounds, copper(II) sulfate is preferable. These water-soluble copper compounds can generally be used singly, or in a combination of two or more. The concentration of the water-soluble copper compound is such that the copper ion concentration is 1 to 60 g/L, and preferably 10 to 40 g/L.

[0014] The water-soluble divalent tin compound, which is a tin ion source, is not particularly limited as long as it is a water-soluble compound containing divalent tin as a tin component. Specific examples of water-soluble divalent tin compounds include stannous chloride, stannous sulfate, stannous acetate, stannous pyrophosphate, stannous methanesulfonate, stannous sulfamate, stannous gluconate, stannous tartrate, stannous oxide, stannous fluoroborate, stannous 2-hydroxyethanesulfonate, stannous 2-hydroxypropanesulfonate, and the like. Among these tin compounds, stannous sulfate is preferable. These water-soluble divalent tin compounds can generally be used singly, or in a combination of two or more. The concentration of the water-soluble divalent tin compound is such that the divalent tin ion concentration is 5 to 40 g/L, and preferably 5 to 25 g/L.

[0015] The proportions of the water-soluble copper compound and the water-soluble divalent tin compound are preferably such that the copper:tin ratio (metal component molar ratio) is 1:0.1 to 0.6, and more preferably such that the copper:tin ratio (metal component molar ratio) is 1:0.1 to 0.3.

[0016] A significant feature of the present invention is that a sulfur-containing compound represented by formula (1):



$$R\text{-}(CH_2)_l\text{-}S\text{-}(CH_2)_m\text{-}S\text{-}(CH_2)_n\text{-}R \quad (1),$$

wherein R is H, OH, or SO_3Na, and l, m, and n are each independently an integer of 0 to 3
is used as a complexing agent. Specific examples of sulfur-containing compounds represented by formula (1) include methanedithiol, 1,2-ethanedithiol, 1,3-propanedithiol, 3,6-dithia-1,8-octanediol, bis-(sodium sulfopropyl)-disulfide, and the like. Among these compounds, for example, 3,6-dithia-1,8-octanediol and bis-(sodium sulfopropyl)-disulfide, both of which have little odor, are preferable from the viewpoint of the work environment, and 3,6-dithia-1,8-octanediol is more preferable. These sulfur-containing compounds can generally be used singly, or in a combination of two or more. The concentration of the complexing agent is 5 to 500 g/L, and preferably 80 to 320 g/L.

[0017] In the present invention, a hydroxyl group-containing aromatic compound is used. Examples of hydroxyl group-containing aromatic compounds include compounds in which a benzene ring or a furan ring is substituted with one or more hydroxyl groups. Compounds having a benzene ring are preferable from the viewpoint of the work environment and solution stability. Specific examples of hydroxyl group-containing aromatic compounds include phenol, catechol, hydroquinone, resorcinol, pyrogallol, *p*-cresolsulfonic acid, ascorbic acid, erythorbic acid; alkali metal salts thereof; and the like. Examples of alkali metals include sodium, potassium, and the like. Preferred hydroxyl group-containing aromatic compounds are phenol, catechol, hydroquinone, resorcinol, pyrogallol, *p*-cresolsulfonic acid, sodium ascorbate, and sodium erythorbate. These hydroxyl group-containing aromatic compounds are considered to have the action of reducing divalent copper ions (Cu^{2+}) to monovalent copper ions (Cu^{1+}), and are considered to aid copper ions and the complexing agent in forming a complex. These hydroxyl group-containing aromatic compounds can generally be used singly, or in a combination of two or more. The concentration of the hydroxyl group-containing aromatic compound is 1 to 50 g/L, and preferably 5 to 30 g/L.

[0018] The amounts of the complexing agent and the hydroxyl group-containing aromatic compound are such that relative to 1 mol/L of copper, the amount of the complexing agent is preferably 2 mol/L or more, and the amount of the hydroxyl group-containing aromatic compound is preferably 1 mol/L or more.

[0019] Examples of acids constituting the base of the copper-tin alloy plating bath include a wide variety of known organic acids and inorganic acids. Specific examples of organic acids include methanesulfonic acid, ethanesulfonic acid, 2-propanolsulfonic acid, 2-sulfoacetic acid, 2-sulfopropionic acid, 3-sulfopropionic acid, sulfosuccinic acid, sulfomethylsuccinic acid, sulfofumaric acid, sulfomaleic acid, 2-sulfobenzoic acid, 3-sulfobenzoic acid, 4-sulfobenzoic acid, 5-sulfosalicylic acid, 4-sulfophthalic acid, 5-sulfoisophthalic acid, 2-sulfoterephthalic acid, phenolsulfonic acid, and the like.

Specific examples of inorganic acids include sulfuric acid, hydrochloric acid, sulfamic acid, and the like. Among these, sulfuric acid, methanesulfonic acid, sulfosuccinic acid, and the like are preferable. These acids can generally be used singly, or in a combination of two or more. The concentration of the acid is 10 to 400 g/L, and preferably 150 to 200 g/L.

[0020] The copper-tin alloy plating bath is generally in a weakly acidic to strongly acidic pH range. More specifically, the pH of the solution of the plating bath is adjusted to 4.5 or less. An overly high pH is not preferable because if the pH is overly high, the obtained plating film will have insufficient smoothness. Examples of usable pH adjusting agents include various acids, such as hydrochloric acid and sulfuric acid; various bases, such as ammonium hydroxide, sodium hydroxide, and potassium hydroxide; and the like. In addition, a pH buffer may be added to reduce variation in the pH of the plating bath. As the pH buffer, a known pH buffer can be used. Examples of pH buffers include sodium or potassium acetate, sodium, potassium, or ammonium borate, sodium or potassium formate, sodium or potassium tartrate, sodium, potassium, or ammonium dihydrogen phosphate, and the like. These pH adjusting agents and pH buffers can generally be used singly, or in a combination of two or more.

[0021] The plating bath contains a surfactant, and a leveler. Further, the plating bath may contain additives, such as high molecular compounds, if necessary.

[0022] Examples of high molecular compounds include polyethylene glycol and the like.

[0023] The surfactant is at least one nonionic surfactant selected from the group consisting of polyoxyethylene alkylamines, polyoxyalkylene phenyl ethers, and polyoxyalkylene naphthyl ethers.

[0024] When a high molecular compound is added to the plating bath, the concentration of the high molecular compound can be in the range of 0.01 to 100 g/L, and preferably 0.1 to 40 g/L. The surfactant is present in an amount of 0.1 to 40 g/L.

[0025] Levelers are additives that improve smoothness and brightness. The leveler is at least one aromatic ketone or aromatic aldehyde selected from the group consisting of benzalacetone, cinnamaldehyde, α-methylcinnamaldehyde, α-hexylcinnamaldehyde, α-amylcinnamaldehyde, cuminaldehyde, benzaldehyde, and anisaldehyde. These levelers can be used singly, or in a combination of two or more.

[0026] The leveler is present in the plating bath in a concentration of 0.01 to 10 g/L.

[0027] In the present invention, a surfactant and a leveler are used in combination. The combined use of a surfactant and a leveler can expand the current-density region in which a bright plating film is obtained. This enables a plating film obtained from the plating bath of the present invention to have more excellent smoothness and higher brightness. As a combination of a surfactant and a leveler, a combination of a nonionic surfactant, and an aromatic ketone or an aromatic aldehyde is used. The nonionic surfactant is preferably a polyoxyethylene alkylamine. A plating film having excellent bright appearance can be obtained by the nonionic surfactant, and the aromatic ketone or the aromatic aldehyde comprised in the aqueous solution of the plating bath.

[0028] In the present invention, a surfactant and a leveler are used in combination, wherein the concentration of the surfactant is 0.1 to 40 g/L, the concentration of the leveler is 0.01 to 10 g/L, and the surfactant:leveler ratio is 1:1 to 100:1.

[0029] Additives other than the additives mentioned above, such as stress-reducing agents, conductive auxiliary agents, antifoaming agents, and brighteners, may be suitably selected and added to the plating bath, if necessary.

[0030] Examples of stress-reducing agents include naphtholsulfonic acid, saccharin, sodium 1,5-naphthalenedisulfonate, and the like. These can be used singly, or in a combination of two or more. Examples of conductive auxiliary agents include hydrochloric acid, sulfuric acid, acetic acid, nitric acid, sulfamic acid, pyrophosphoric acid, boric acid, and like acids; ammonium salts, sodium salts, potassium salts, and organic amine salts thereof; and the like. These can be used singly, or in a combination of two or more. As antifoaming agents and brighteners, commercially available antifoaming agents and brighteners for copper plating, tin plating, copper-tin alloy plating, and general plating can be suitably selected and used.

[0031] The bath preparation method for the plating bath of the present invention is not particularly limited. For example, the target plating solution can be obtained by dissolving a water-soluble copper compound and a water-soluble divalent tin compound in an aqueous solution in which an acid such as sulfuric acid is dissolved; adding a complexing agent and a reducing agent thereto; adding additives of the present invention thereto and, if necessary, adding other additives thereto; and, finally, adjusting the pH to a predetermined pH.

[0032] There is no particular limitation on the plating method in which the plating bath of the present invention is used. The plating bath of the present invention can be used in known plating methods, and can also be applied to barrel plating, in which the variation in current density is large.

[0033] When the bath temperature during plating is low, throwing power increases, but the film formation speed tends to decrease. Conversely, when the bath temperature is high, the film formation speed increases, but throwing power onto low-current-density regions tends to decrease. Taking this point into consideration, an appropriate bath temperature can be determined. The bath temperature is preferably in the range of 5 to 40°C.

[0034] The cathode current density can also be appropriately determined according to the plating solution used, type of object to be plated, etc. A cathode current density of 0.1 to 3 A/dm^2 is preferable.

[0035] The anode may be any known anode that can be used for copper-tin alloy plating, such as a soluble anode (e.g., a tin anode, a phosphorus-containing copper anode, an oxygen-free copper anode, or a copper-tin alloy anode)

or an insoluble anode (e.g., a stainless anode, a carbon anode, a lead anode, a lead-tin alloy anode, a lead-antimony alloy anode, a platinum anode, a titanium anode, a titanium-platinum anode, or an oxide coated anode, such as an iridium-oxide-coated titanium electrode). The cathode is an object to be plated that is described below. Thus, it can be said that the method for copper-tin alloy plating of the present invention is a method in which electrolysis is performed using an object to be plated as a cathode in the copper-tin alloy plating bath described above.

[0036] The copper-tin alloy plating film described above is formed on the surface of an article to be plated by the above plating method. The alloy composition of the obtained film is such that the Cu:Sn weight ratio is 95:5 to 5:95, and the alloy composition can be easily changed by varying the Cu concentration or the Sn concentration in the plating solution. The article to be plated is not particularly limited as long as the surface is conductive and smooth. Examples of such articles include home appliances, faucet fittings, sundry articles, decorations, clothing accessories, and the like.

[0037] The copper-tin alloy plating bath of the present invention can be suitably used for plating for clothing accessories or decorations; and plating for, for example, electronic or electric components. However, this does not limit applications to other purposes.

Examples

[0038] The present invention is described below in more detail with reference to Reference Examples and Comparative Examples.

[0039] Plating treatment was performed using plating baths having the compositions shown in Tables 1 to 6 below under the following conditions to individually form plating films on objects to be plated.

Object to be plated: iron plate (5 cm × 5 cm)

Plating method:

Anode: pure tin plate (10 cm × 5 cm, two plates)
Amount of solution: 1.5 L (a plastic container having a size of 14 cm × 8 cm × 18 cm was used)
Stirring: shaking with a cathode rocker

Plating conditions:

Temperature: 18 to 20°C
Current density: 1 A/dm^2
Electrolytic time: 25 minutes

[0040] Tables 1 to 6 show the state of each plating solution, wherein the examples are reference examples, and the properties of each of the plating films formed as described above. The evaluation methods for the properties are as follows. Solution state: The state of each solution was visually confirmed. Solution stability: After being allowed to stand for 24 hours, each plating solution was visually confirmed.
Plating appearance and occurrence of cracking: Plating appearance and occurrence of cracking were observed with a digital microscope.
Cu:Sn ratio: The Cu:Sn ratio was evaluated with a fluorescent X-ray film thickness measurement apparatus.

[0041] In addition, in the plating baths of Example 3, which is a reference example, and Comparative Examples 11 and 12, plating treatment was performed at current densities of 0.01, 0.1, 0.5, 1, 2, and 3 A/dm^2, and the copper content of the formed plating films was determined. Fig. 1 shows the results.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
98% sulfuric acid (g/L)	185	185	185	–	–	185	185	185	185	185	185	185	185	185
Methanesulfonic acid (g/L)	–	–	–	150	–	–	–	–	–	–	–	–	–	–
Sulfosuccinic acid (g/L)	–	–	–	–	150	–	–	–	–	–	–	–	–	–
Copper sulfate pentahydrate (g/L)	30	45	60	60	60	60	60	60	60	60	60	60	60	60
Stannous sulfate (g/L)	10	10	10	10	10	10	10	10	10	10	10	10	10	10
3,6-dithia-1,8-octanediol (g/L)	60	90	120	120	120	–	–	–	–	–	120	–	–	–
Bis-(sodium sulfopropyl)-disulfide (g/L)	–	–	–	–	–	180	–	–	–	–	–	–	–	–
Methanedithiol (g/L)	–	–	–	–	–	–	50	–	–	–	–	–	–	–
1,2-ethanedithiol (g/L)	–	–	–	–	–	–	–	60	–	–	–	–	–	–
1,3-propanedithiol (g/L)	–	–	–	–	–	–	–	–	70	–	–	–	–	–
Thiourea (g/L)	–	–	–	–	–	–	–	–	–	–	–	50	–	–
Sodium 3-mercapto-1-propanesulfonate (g/L)	–	–	–	–	–	–	–	–	–	–	–	–	100	–
Thioglycolic acid (g/L)	–	–	–	–	–	–	–	–	–	–	–	–	–	60
Catechol (g/L)	7	10	15	15	15	15	15	15	15	15	–	15	15	15
pH	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.2 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less
Solution state	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	Bad odor	Bad odor	Bad odor	Precipitates	No precipitates	Precipitates	Bad odor	Precipitates
Solution stability	Good	Good	Good	Good	Good	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor
Plating appearance (1 A/dm^2)	Gray Dull	White Dull	White Dull	White Dull	White Dull	White Dull	Gray Dull	Gray Dull	Gray Dull	Plating was not performed.				
Presence or absence of cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks					
Cu:Sn ratio (wt%)	43:57	51:49	64:36	63 : 37	66 : 34	59:41	65:35	61:39	66:34					

Table 2

	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10
98% sulfuric acid (g/L)	185	185	185	185	185	185	185	185	185	185	185	185
Copper sulfate pentahydrate (g/L)	60	60	60	60	60	60	60	60	60	60	60	60
Stannous sulfate (g/L)	10	10	10	10	10	10	10	10	10	10	10	10
3,6-dithia-1,8-octanediol (g/L)	120	120	120	120	120	120	120	120	120	120	120	120
Hydroquinone (g/L)	15	–	–	–	–	–	–	–	–	–	–	–
Resorcinol (g/L)	–	15	–	–	–	–	–	–	–	–	–	–
Phenol (g/L)	–	–	15	–	–	–	–	–	–	–	–	–
p-cresolsulfonic acid (g/L)	–	–	–	30	–	–	–	–	–	–	–	–
Pyrogallol (g/L)	–	–	–	–	20							
Sodium ascorbate (g/L)	–	–	–	–	–	30	–	–	–	–	–	–
Sodium erythorbate (g/L)	–	–	–	–	–	–	30	–	–	–	–	–
Sodium hypophosphite (g/L)	–	–	–	–	–	–	–	15	–	–	–	–
Sodium sulfite (g/L)	–	–	–	–	–	–	–	–	20	–	–	–
Sodium hydrogen sulfite (g/L)	–	–	–	–	–	–	–	–	–	20	–	–
Ammonium sulfite (g/L)	–	–	–	–	–	–	–	–	–	–	20	–
Sodium thiosulfate (g/L)	–	–	–	–	–	–	–	–	–	–	–	25
pH	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.2 or less	0.1 or less	0.1 or less	0.1 or less
Solution state	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	Bad odor	Bad odor	Bad odor	Precipitates
Solution stability	Good	Good	Good	Good	Good	Good	Good	Poor	Good	Good	Good	Poor
Plating appearance (1 A/dm^2)	Gray Dull	Gray Dull	Gray Dull	White Dull	Black Dull	White Dull	Gray Dull	Gray Dull	Plating was not performed.			
Presence or absence of cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	Cracks				
Cu:Sn ratio (wt%)	62:38	61:39	65:35	59:41	61:39	62:38	63:37	62:38				

Table 3

	Example 17	Example 18	Example 19	Example 20	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26	Example 27	Example 28
98% sulfuric acid (g/L)	185	185	185	185	185	185	185	185	185	185	185	185
Copper sulfate pentahydrate (g/L)	60	60	60	60	60	60	60	60	60	60	60	60
Stannous sulfate (g/L)	10	10	10	10	10	10	10	10	10	10	10	10
3,6-dithia-1,8-octanediol (g/L)	120	120	120	120	120	120	120	120	120	120	120	120
Polyoxyethylene alkylamine (g/L)	10	–	–	–	–	–	–	–	–	–	–	–
Polyethylene glycol (g/L)	–	5	–	–	–	–	–	–	–	–	–	–
Polyoxyalkylene phenyl ether (g/L)	–	–	20	–	–	–	–	–	–	–	–	–
Polyoxyalkylene naphthyl ether (g/L)	–	–	–	10	–	–	–	–	–	–	–	–
Tetra-lower-alkylammonium halide (g/L)	–	–	–	–	0.5	–	–	–	–	–	–	–
Alkylamine hydrochloride (g/L)	–	–	–	–	–	1	–	–	–	–	–	–
Alkylaminoethylglycine (g/L)	–	–	–	–	–	–	1	–	–	–	–	–
Alkyl-β-naphthalenesulfonic acid (g/L)	–	–	–	–	–	–	–	30	–	–	–	–
Fatty acid soap-based surfactants (g/L)	–	–	–	–	–	–	–	–	10	–	–	–
Phenol ether sulfuric acid ester salt (g/L)	–	–	–	–	–	–	–	–	–	5	–	–
Sulfobetaine (g/L)	–	–	–	–	–	–	–	–	–	–	5	–
Dimethylalkylbetaine (g/L)	–	–	–	–	–	–	–	–	–	–	–	10
pH	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less
Solution state	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates
Solution stability	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
Plating appearance (1 A/dm^2)	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright
Presence or absence of cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks
Cu:Sn ratio (wt%)	61:39	58:42	63:37	59:41	60:40	57:43	63:37	53:37	58:42	59:41	56:44	63:37

Table 4

	Example 29	Example 30	Example 31	Example 32	Example 33	Example 34	Example 35	Example 36	Example 37	Example 38	Example 39
98% sulfuric acid (g/L)	185	185	185	185	185	185	185	185	185	185	185
Copper sulfate pentahydrate (g/L)	60	60	60	60	60	60	60	60	60	60	60
Stannous sulfate (g/L)	10	10	10	10	10	10	10	10	10	10	10
3,6-dithia-1,8-octanediol (g/L)	120	120	120	120	120	120	120	120	120	120	120
Benzalacetone (g/L)	1	–	–	–	–	–	–	–	–	–	–
Cinnamaldehyde (g/L)	–	1	–	–	–	–	–	–	–	–	–
α-methylcinnamaldehyde (g/L)	–	–	3	–	–	–	–	–	–	–	–
α-hexylcinnamaldehyde (g/L)	–	–	–	5	–	–	–	–	–	–	–
α-amylcinnamaldehyde (g/L)	–	–	–	–	5	–	–	–	–	–	–
Cuminaldehyde (g/L)	–	–	–	–	–	1	–	–	–	–	–
Benzaldehyde (g/L)	–	–	–	–	–	–	1	–	–	–	–
Anisaldehyde (g/L)	–	–	–	–	–	–	–	3	–	–	–
Propionaldehyde (g/L)	–	–	–	–	–	–	–	–	3	–	–
Acetaldehyde (g/L)	–	–	–	–	–	–	–	–	–	0.5	–
Formaldehyde (g/L)	–	–	–	–	–	–	–	–	–	–	0.5
pH	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less
Solution state	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates
Solution stability	Good	Good	Good	Poor	Poor	Good	Good	Good	Good	Good	Good
Plating appearance (1 A/dm^2)	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright	White Semi-bright
Presence or absence of cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks
Cu:Sn ratio (wt%)	57:43	58:42	60:40	58:42	57:43	61:39	58:42	61:39	59:41	63:37	64:36

Table 5

	Example 40	Example 41	Example 42	Example 43	Example 44	Example 45	Example 46	Example 47	Example 48	Example 49	Example 50
98% sulfuric acid (g/L)	185	185	185	185	185	185	185	185	185	185	185
Copper sulfate pentahydrate (g/L)	60	60	60	60	60	60	60	60	60	60	60
Stannous sulfate (g/L)	10	10	10	10	10	10	10	10	10	10	10
3,6-dithia-1,8-octanediol (g/L)	120	120	120	120	120	120	120	120	120	120	120
Polyoxyethylene alkylamine (g/L)	10	10	10	10	10	10	10	10	10	10	10
Benzalacetone (g/L)	1	–	–	–	–	–	–	–	–	–	–
Cinnamaldehyde (g/L)	–	1	–	–	–	–	–	–	–	–	–
α-methylcinnamaldehyde (g/L)	–	–	3	–	–	–	–	–	–	–	–
α-hexylcinnamaldehyde (g/L)	–	–	–	5	–	–	–	–	–	–	–
α-amylcinnamaldehyde (g/L)	–	–	–	–	5	–	–	–	–	–	–
Cuminaldehyde (g/L)	–	–	–	–	–	1	–	–	–	–	–
Benzaldehyde (g/L)	–	–	–	–	–	–	1	–	–	–	–
Anisaldehyde (g/L)	–	–	–	–	–	–	–	3	–	–	–
Propionaldehyde (g/L)	–	–	–	–	–	–	–	–	3	–	–
Acetaldehyde (g/L)	–	–	–	–	–	–	–	–	–	0.5	–
Formaldehyde (g/L)	–	–	–	–	–	–	–	–	–	–	0.5
pH	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less	0.1 or less
Solution state	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates	No precipitates
Solution stability	Good	Good	Good	Poor	Poor	Good	Good	Good	Good	Good	Good
Plating appearance (1 A/dm^2)	White Bright	White Bright	White Bright	White Bright	White Bright	White Bright	White Bright	White Bright	White Bright	White Bright	White Bright
Presence or absence of cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks	No cracks
Cu:Sn ratio (wt%)	59:41	58:42	61:39	57:43	62:38	58:42	58:42	62:38	59:41	59:41	62:38

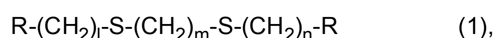
Table 6

	Comparative Example 11	Comparative Example 12
Potassium pyrophosphate (g/L)	200	-
Copper pyrophosphate (g/L)	20	-
Stannous sulfate (g/L)	10	-
Organic sulfonic acid (g/L)	-	100
Stannous sulfate (g/L)	-	36
Copper sulfate pentahydrate (g/L)	-	12
Brightener	Appropriate amount	Appropriate amount
pH	7 to 8	0.5
Solution state	No precipitates	No precipitates
Solution stability	Good	Poor
Plating appearance (1 A/dm^2)	White	White
Presence or absence of cracks	Cracks	No cracks
Cu:Sn ratio (wt%)	58:42	53:47

[0042] The results of Tables 1 to 5 reveal that no precipitates were formed in the plating baths of Examples 1 to 50 which are reference examples; that the solution state was stable, especially in the plating baths of Examples 1 to 5, 10 to 31, 34 to 42, and 45 to 50 which are reference examples; and that crack-free plating films were obtained by plating. As is clear from the results of Examples 1 to 5, which are reference examples, in Table 1, a copper-tin alloy plating film having any ratio can be obtained by adjusting the metal concentration in the plating solution. The results of Tables 3 to 5 show that adding a surfactant or a leveler to the plating solution improves brightness of a plating appearance, and that a plating appearance having excellent brightness can be obtained by adding both a surfactant and a leveler to the plating solution. In addition, Fig. 1 shows that in the plating bath of Example 3, which is a reference example, the current density has a small influence on the alloy ratio as compared with the case of a hitherto known acidic bath (Comparative Example 12).

Claims

1. A copper-tin alloy plating bath comprising an aqueous solution having a pH of 4.5 or less, the aqueous solution containing a water-soluble divalent copper compound, a water-soluble divalent tin compound, a sulfur-containing compound represented by formula (1) :



$$R\text{-}(CH_2)_l\text{-}S\text{-}(CH_2)_m\text{-}S\text{-}(CH_2)_n\text{-}R \qquad (1),$$

wherein R is H, OH, or SO_3Na, and l, m, and n are each independently an integer of 0 to 3,
a hydroxyl group-containing aromatic compound, a surfactant, and a leveler,

the surfactant being at least one nonionic surfactant selected from the group consisting of polyoxyethylene alkylamines, polyoxyalkylene phenyl ethers, and polyoxyalkylene naphthyl ethers,
the leveler being at least one aromatic ketone or aromatic aldehyde selected from the group consisting of benzalacetone, cinnamaldehyde, α-methylcinnamaldehyde, α-hexylcinnamaldehyde, α-amylcinnamaldehyde, cuminaldehyde, benzaldehyde, and anisaldehyde,
the water-soluble divalent copper compound being present in an amount such that the amount of divalent copper ions is 1 to 60 g/L,
the water-soluble divalent tin compound being present in an amount such that the amount of divalent tin ions is 5 to 40 g/L,
the sulfur-containing compound being present in an amount of 5 to 500 g/L,
the hydroxyl group-containing aromatic compound being present in an amount of 1 to 50 g/L,

the surfactant being present in an amount of 0.1 to 40 g/L,
the leveler being present in an amount of 0.01 to 10 g/L, and
the surfactant:leveler ratio being 1:1 to 100:1.

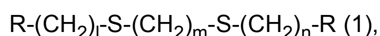
2. The copper-tin alloy plating bath according to claim 1, wherein the sulfur-containing compound is at least one member selected from the group consisting of methanedithiol, 1,2-ethanedithiol, 1,3-propanedithiol, 3,6-dithia-1,8-octanediol, and bis-(sodium sulfopropyl)-disulfide.

3. The copper-tin alloy plating bath according to claim 1 or 2, wherein the hydroxyl group-containing aromatic compound is at least one member selected from the group consisting of phenol, catechol, hydroquinone, resorcinol, pyrogallol, *p*-cresolsulfonic acid, sodium ascorbate, and sodium erythorbate.

4. A method for copper-tin alloy plating, the method comprising performing electrolysis using an object to be plated as a cathode in the copper-tin alloy plating bath according to any one of claims 1 to 3.

Patentansprüche

1. Kupfer-Zinn-Legierung-Plattierungsbad, umfassend eine wässrige Lösung mit einem pH von 4,5 oder weniger, wobei die wässrige Lösung eine wasserlösliche zweiwertige Kupferverbindung, eine wasserlösliche zweiwertige Zinnverbindung, eine schwefelhaltige Verbindung, dargestellt durch Formel (1):



$R-(CH_2)_l-S-(CH_2)_m-S-(CH_2)_n-R$ (1),

wobei R H, OH oder SO_3Na darstellt und l, m, und n jeweils unabhängig voneinander eine ganze Zahl von 0 bis 3 darstellen,
eine hydroxylgruppenhaltige aromatische Verbindung, ein grenzflächenaktives Mittel und einen Nivellierer enthält,
wobei das grenzflächenaktive Mittel mindestens ein nichtionisches grenzflächenaktives Mittel, ausgewählt aus der Gruppe, bestehend aus Polyoxyethylenalkylaminen, Polyoxyalkylenphenylethern und Polyoxyalkylennaphthylethern, ist,
wobei der Nivellierer mindestens ein aromatisches Keton oder aromatischer Aldehyd, ausgewählt aus der Gruppe, bestehend aus Benzalaceton, Zimtaldehyd, α-Methylzimtaldehyd,
α-Hexylzimtaldehyd, α-Amylzimtaldehyd, Cuminaldehyd, Benzaldehyd und Anisaldehyd, ist,
wobei die wasserlösliche zweiwertige Kupferverbindung in einer Menge vorliegt, so dass die Menge an zweiwertigen Kupferionen 1 bis 60 g/L beträgt,
wobei die wasserlösliche zweiwertige Zinnverbindung in einer Menge vorliegt, so dass die Menge an zweiwertigen Zinnionen 5 bis 40 g/L beträgt,
wobei die schwefelhaltige Verbindung in einer Menge von 5 bis 500 g/L vorliegt,
wobei die hydroxylgruppenhaltige aromatische Verbindung in einer Menge von 1 bis 50 g/L vorliegt,
wobei das grenzflächenaktive Mittel in einer Menge von 0,1 bis 40 g/L vorliegt,
wobei der Nivellierer in einer Menge von 0,01 bis 10 g/L vorliegt, und
wobei das Verhältnis grenzflächenaktives Mittel:Nivellierer 1:1 bis 100:1 beträgt.

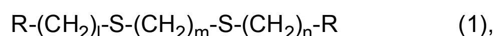
2. Kupfer-Zinn-Legierung-Plattierungsbad nach Anspruch 1, wobei die schwefelhaltige Verbindung mindestens ein Bestandteil, ausgewählt aus der Gruppe, bestehend aus Methandithiol, 1,2-Ethandithiol, 1,3-Propandithiol, 3,6-Dithia-1,8-octandiol und Bis-(natriumsulfopropyl)-disulfid, ist.

3. Kupfer-Zinn-Legierung-Plattierungsbad nach Anspruch 1 oder 2, wobei die hydroxylgruppenhaltige aromatische Verbindung mindestens ein Bestandteil, ausgewählt aus der Gruppe, bestehend aus Phenol, Catechol, Hydrochinon, Resorcin, Pyrogallol, *p*-Cresolsulfonsäure, Natriumascorbat und Natriumerythorbat, ist.

4. Verfahren zum Plattieren einer Kupfer-Zinn-Legierung, wobei das Verfahren das Durchführen von Elektrolyse unter Verwendung eines zu plattierenden Gegenstandes als eine Kathode in dem Kupfer-Zinn-Legierung-Plattierungsbad nach einem der Ansprüche 1 bis 3 umfasst.

Revendications

1. Bain de placage d'alliage de cuivre-étain, comprenant une solution aqueuse ayant un pH de 4,5 ou moins, la solution aqueuse contenant un composé du cuivre bivalent soluble dans l'eau, un composé de l'étain bivalent soluble dans l'eau, un composé soufré représenté par la formule (1) :



$$R\text{-}(CH_2)_l\text{-}S\text{-}(CH_2)_m\text{-}S\text{-}(CH_2)_n\text{-}R \qquad (1),$$

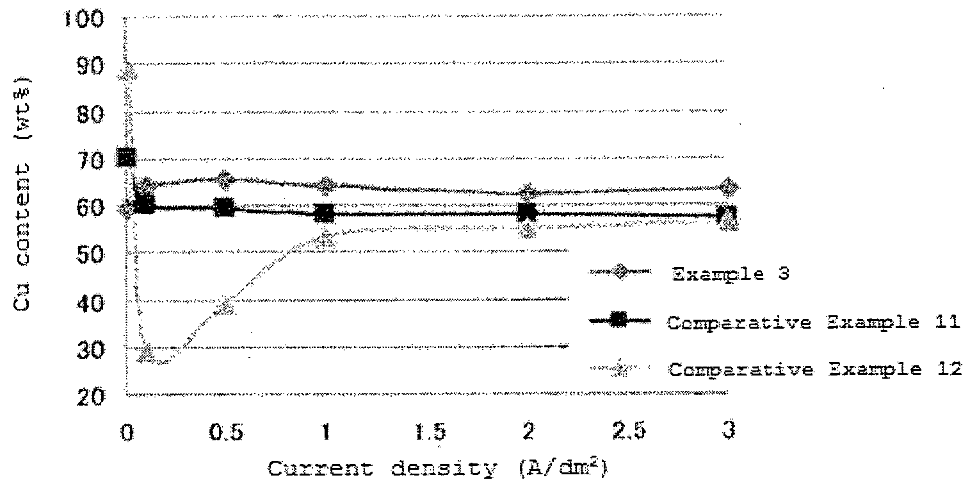
où R est H, OH ou SO_3Na, et l, m et n sont chacun indépendamment un entier allant de 0 à 3,
un composé aromatique contenant un groupe hydroxyle, un tensioactif et un agent nivelant,
le tensioactif étant au moins un tensioactif non ionique choisi parmi le groupe consistant en des polyoxyéthylène-alkylamines, des polyoxyalkylène-phényléthers et des polyoxyalkylène-naphtyléthers,
l'agent nivelant étant au moins une cétone aromatique ou un aldéhyde aromatique choisi parmi le groupe consistant en de la benzalacétone, du cinnamaldéhyde, de l'a-méthylcinnamaldéhyde, de l'a-hexylcinnamaldéhyde, de l'a-amylcinnamaldéhyde, du cuminaldéhyde, du benzaldéhyde et de l'anisaldéhyde,
le composé du cuivre bivalent soluble dans l'eau étant présent en une quantité telle que la quantité des ions cuivre bivalents se situe dans l'intervalle allant de 1 à 60 g/litre,
le composé de l'étain bivalent soluble dans l'eau étant présent en une quantité telle que la quantité des ions étain bivalents se situe dans l'intervalle allant de 5 à 40 g/litre,
le composé soufré étant présent en une quantité située dans l'intervalle allant de 5 à 500 g/litre,
le composé aromatique contenant un hydroxyle étant présent en une quantité située dans l'intervalle allant de 1 à 50 g/litre,
le tensioactif étant présent en une quantité située dans l'intervalle allant de 0,1 à 40 g/litre,
l'agent nivelant étant présent en une quantité située dans l'intervalle allant de 0,01 à 10 g/litre, et le rapport tensioactif:agent nivelant allant de 1:1 à 100:1.

2. Bain de placage d'alliage cuivre-étain selon la revendication 1, où le composé soufré est au moins un membre du groupe consistant en du méthanedithiol, du 1,2-éthane-dithiol, du 1,3-propanedithiol, du 3,6-dithia-1,8-octanediol, et du bis(sulfopropyl de sodium)disulfure.

3. Bain de placage d'alliage cuivre-étain selon la revendication 1 ou 2, où le composé aromatique contenant un groupe hydroxyle est au moins un membre du groupe consistant en du phénol, du catéchol, de l'hydroquinone, du résorcinol, du pyrogallol, de l'acide p-crésolsufonique, de l'ascorbate de sodium et de l'érythorbate de sodium.

4. Procédé de placage d'alliage cuivre-étain, le procédé comprenant la réalisation d'une électrolyse à l'aide d'un objet à plaquer comme cathode dans le bain de placage d'alliage cuivre-étain selon l'une quelconque des revendications 1 à 3.

Fig. 1



REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 2010216302 A1 **[0004]**
- US 2005263403 A1 **[0004]**
- US 2004035714 A1 **[0004]**
- EP 1591563 A1 **[0004]**
- JP 2001295092 A **[0005]**
- JP 2004035980 A **[0005]**
- JP 2009161804 A **[0005]**
- JP 2010189753 A **[0005]**