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(71) **Demandeur/Applicant:**
OKUNO CHEMICAL INDUSTRIES CO., LTD., JP
(72) **Inventeurs/Inventors:**
TSUJIMOTO, TAKAMITSU, JP;
NAGAO, TOSHIMITSU, JP;
HARA, KENJI, JP;
KATAYAMA, JUNICHI, JP;
OTSUKA, KUNIAKI, JP
(74) **Agent**: MARKS & CLERK

(54) Titre : BAIN DE PLACAGE D'ALLIAGE DE CUIVRE-ETAIN
(54) Title: COPPER-TIN ALLOY PLATING BATH

(57) Abrégé/Abstract:

The objective of the present invention is to provide a copper-tin alloy plating bath which is capable of forming a thick film without using cyanide ions, and which is able to be suited to barrel plating. The present invention relates to a copper-tin alloy plating bath which is composed of an aqueous solution that contains a water-soluble copper compound, a water-soluble divalent tin compound, a sulfur-containing compound represented by formula (1) and an aromatic compound having a hydroxyl group. $R-(CH_2)_l-S-(CH_2)_m-S-(CH_2)_n-R$ (1) (In the formula, R represents H, OH or SO_3Na; and each of l, m and n independently represents an integer of 0-3.)

ABSTRACT

An object of this 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. This invention relates to a copper-tin alloy plating bath comprising an aqueous solution containing a water-soluble copper compound, a water-soluble divalent tin compound, a sulfur-containing compound represented by formula (1):

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

wherein R is H, OH, or SO_3Na, and l, m, and n are each independently an integer of 0 to 3,

and a hydroxyl group-containing aromatic compound.

DESCRIPTION

Title of Invention: COPPER-TIN ALLOY PLATING BATH

Technical Field

[0001]

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

Background Art

[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.

[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.

Citation List

Patent Literature

[0006]

PTL 1: JPH10-102278A
PTL 2: JP2001-295092A
PTL 3: JP2004-035980A
PTL 4: JP2009-161804A
PTL 5: JP2010-189753A

Summary of Invention

Technical Problem

[0007]

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.

Solution to Problem

[0008]

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.

[0009]

More specifically, the present invention provides the following copper-tin alloy plating bath and the like.

Item 1. A copper-tin alloy plating bath comprising an aqueous solution containing a water-soluble copper compound, a water-soluble divalent tin compound, a sulfur-containing compound represented by formula (1):

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

wherein R is H, OH, or SO_3Na, and l, m, and n are each independently an integer of 0 to 3,

and a hydroxyl group-containing aromatic compound.

Item 2. The copper-tin alloy plating bath according to Item 1, wherein the water-soluble copper compound is present in an amount such that the amount of copper ions is 1 to 60 g/L, the water-soluble divalent tin compound is present in an amount such that the amount of divalent tin ions is 5 to 40 g/L, the sulfur-containing compound is present in an amount of 5 to 500 g/L, and the hydroxyl group-containing aromatic compound is present in an amount of 1 to 50 g/L.

Item 3. The copper-tin alloy plating bath according to Item 1 or 2, 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.

Item 4. The copper-tin alloy plating bath according to any one of Items 1 to 3, 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.

Item 5. The copper-tin alloy plating bath according to any one of Items 1 to 4, wherein the aqueous solution further contains a nonionic surfactant, and an aromatic ketone or an aromatic aldehyde.

Item 6. 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 Items 1 to 5.

Item 7. An article comprising a copper-tin alloy plating film formed by the method according to Item 6.

Advantageous Effects of Invention

[0010]

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 further adding a nonionic surfactant, and an aromatic ketone or an aromatic aldehyde to the copper-tin alloy plating bath.

Brief Description of Drawings

[0011]

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.

Description of Embodiments

[0012]

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

[0013]

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):

$R-(CH_2)_l-S-(CH_2)_m-S-(CH_2)_n-R$ (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.

[0014]

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, for example, such that the copper ion concentration is about 1 to 60 g/L, and preferably about 10 to 40 g/L.

[0015]

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, for example, such that the divalent tin ion concentration is about 5 to 40 g/L, and preferably about 5 to 25 g/L.

[0016]

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.

[0017]

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

$R-(CH_2)_l-S-(CH_2)_m-S-(CH_2)_n-R$ (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, for example, about 5 to 500 g/L, and preferably about 80 to 320 g/L.

[0018]

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, for example, about 1 to 50 g/L, and preferably about 5 to 30 g/L.

[0019]

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.

[0020]

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 about 10 to 400 g/L, and preferably about 150 to 200 g/L.

[0021]

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.

[0022]

The plating bath may contain additives, such as high molecular compounds, surfactants, and levelers, if necessary.

[0023]

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

[0024]

Examples of usable surfactants include known nonionic surfactants, cationic surfactants, anionic surfactants, and amphoteric surfactants. These surfactants can be used singly, or in a combination of two or more. It is preferable that at least one nonionic surfactant be contained.

[0025]

Examples of nonionic surfactants include polyoxyalkylene alkyl ethers, polyoxyalkylene phenyl ethers, polyoxyalkylene naphthyl ethers, polyoxyalkylene alkyl esters, polyoxyalkylene sorbitan fatty acid esters, polyoxyalkylene sorbit fatty acid esters, polyethylene glycol fatty acid esters, polyoxyalkylene glycerin fatty acid esters, polyoxyalkylene alkylamines, and the like. Among these, polyoxyalkylene alkylamines are preferable, and polyoxyethylene alkylamines are more preferable. Examples of cationic surfactants include tetra-lower-alkylammonium halides, alkyltrimethylammonium halides, alkylamine hydrochlorides, alkylamine oleates, alkylaminoethylglycines, and the like. Examples of anionic surfactants include alkyl-β-naphthalenesulfonic acids, fatty acid soap-based surfactants, alkyl sulfonic acid salts, alkyl sulfuric acid ester salts, polyoxyethylene alkylphenol ether sulfuric acid ester salts, and the like. Examples of amphoteric surfactants include 2-alkyl-*N*-carboxymethyl-*N*-hydroxyethyl imidazolinium betaines, dimethylalkylbetaines, sulfobetaines, *N*-alkyl-β-aminopropionic acids, and the like.

[0026]

When a high molecular compound or a surfactant is added to the plating bath, the concentration of the high molecular compound or the surfactant can be in the range of about 0.01 to 100 g/L, and preferably about 0.1 to 40 g/L.

[0027]

Levelers are additives that improve smoothness and brightness. Examples of usable levelers include ketone compounds and aldehyde compounds. As ketone compounds, a wide variety of known aromatic ketones and aliphatic ketones can be used.

Examples of aromatic ketones include acetophenone, benzophenone, benzalacetone, and the like. Examples of aliphatic ketones include acetone, diethyl ketone, and the like. As aldehyde compounds, a wide variety of known aromatic aldehydes and aliphatic aldehydes can be used. Examples of aromatic aldehydes include cinnamaldehyde, α-methylcinnamaldehyde, α-amylcinnamaldehyde, α-hexylcinnamaldehyde, cuminaldehyde, benzaldehyde, anisaldehyde, and the like. Examples of aliphatic aldehydes include formaldehyde, acetaldehyde, propionaldehyde, and the like. Among these, aromatic ketones and aromatic aldehydes are preferable. These levelers can be used singly, or in a combination of two or more.

[0028]

When a leveler is added to the plating bath, the concentration of the leveler can be in the range of about 0.01 to 30 g/L, and preferably about 0.01 to 10 g/L.

[0029]

As additives, a surfactant and a leveler are preferably used in combination. A 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 preferable. The nonionic surfactant is preferably a polyoxyethylene alkylamine. A plating film having excellent bright appearance can be obtained by further adding a nonionic surfactant, and an aromatic ketone or an aromatic aldehyde to the plating bath.

[0030]

When a surfactant and a leveler are used in combination, the concentration of the surfactant is preferably about 0.1 to 40 g/L, the concentration of the leveler is preferably about 0.01 to 10 g/L, and the surfactant:leveler ratio is preferably about 1:1 to 100:1.

[0031]

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.

[0032]

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.

[0033]

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, if necessary, other additives thereto; and, finally, adjusting the pH to a predetermined pH.

[0034]

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.

[0035]

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 about 5 to 40°C.

[0036]

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 about 0.1 to 3 A/dm^2 is preferable.

[0037]

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.

[0038]

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.

[0039]

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

[0040]

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

[0041]

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

[0042]

Tables 1 to 6 show the state of each plating solution, 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.

[0043]

In addition, in the plating baths of Example 3 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.

[0044]

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					

[0045]

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				

[0046]

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

[0047]

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

[0048]

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

[0049]

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

[0050]

The results of Tables 1 to 5 reveal that no precipitates were formed in the plating baths of Examples 1 to 50; 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; and that crack-free plating films were obtained by plating. As is clear from the results of Examples 1 to 5 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 the present invention, 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

[Claim 1]

A copper-tin alloy plating bath comprising an aqueous solution containing a water-soluble copper compound, a water-soluble divalent tin compound, a sulfur-containing compound represented by formula (1):

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

wherein R is H, OH, or SO_3Na, and l, m, and n are each independently an integer of 0 to 3,

and a hydroxyl group-containing aromatic compound.

[Claim 2]

The copper-tin alloy plating bath according to claim 1, wherein the water-soluble copper compound is present in an amount such that the amount of copper ions is 1 to 60 g/L, the water-soluble divalent tin compound is present in an amount such that the amount of divalent tin ions is 5 to 40 g/L, the sulfur-containing compound is present in an amount of 5 to 500 g/L, and the hydroxyl group-containing aromatic compound is present in an amount of 1 to 50 g/L.

[Claim 3]

The copper-tin alloy plating bath according to claim 1 or 2, 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.

[Claim 4]

The copper-tin alloy plating bath according to any one of claims 1 to 3, 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.

[Claim 5]

The copper-tin alloy plating bath according to any one of claims 1 to 4, wherein the aqueous solution further contains a nonionic surfactant, and an aromatic ketone or an aromatic aldehyde.

[Claim 6]

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 5.

[Claim 7]

An article comprising a copper-tin alloy plating film formed by the method according to claim 6.

Drawings

Fig. 1