(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 156 522 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
19.04.2017 Bulletin 2017/16

(21) Application number: **15807050.8**

(22) Date of filing: **04.06.2015**

(51) Int Cl.:
C25D 3/32 (2006.01) ***C25D 7/00*** (2006.01)

(86) International application number:
PCT/JP2015/066187

(87) International publication number:
WO 2015/190390 (17.12.2015 Gazette 2015/50)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA

(30) Priority: **11.06.2014 JP 2014120714**

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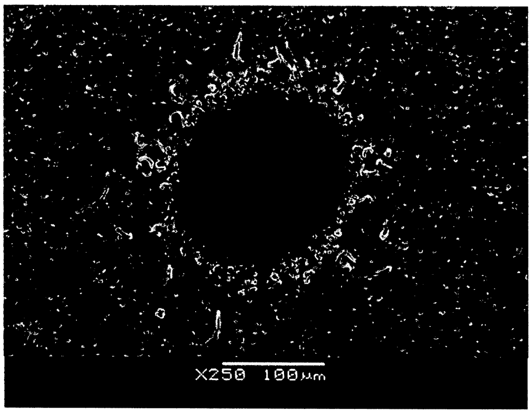
(54) TIN ELECTROPLATING BATH AND TIN PLATING FILM

(57) Provided is a tin electroplating bath for obtaining a tin plating film for which the occurrence of tin whiskers when an external stress is applied on the tin plating film is limited. The tin electroplating bath is characterized in comprising at least one kind of compound selected from a group consisting of flavonoid compounds and glycosides thereof, compounds having a xanthene skeleton and glycosides thereof, and compounds having an acridine skeleton and glycosides thereof.

[FIG. 1]



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Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The invention relates to a tin electroplating bath and a tin plating film. In particular, the invention relates to a tin plating film in which the formation of tin whiskers when an external (mechanical) stress is applied on the tin plating film is inhibited, and a tin electroplating bath used for forming the tin plating film.

BACKGROUND ART

[0002] Coating films of tin plating, tin alloy plating or the like have been formed on electronic device components such as connectors, terminals, IC chips, and the like in terms of soldering, corrosion prevention, and the like. As methods of forming such tin or tin alloy plating films, various methods have been heretofore proposed. For example, Patent Document 1 discloses a surface treatment method of a plated material obtained by plating a metallic material with tin or tin-lead alloy, in which the plated material is dipped as an anode in a surface treatment solution containing one or two or more selected from the group consisting of benzotriazole compounds, mercaptobenzothiazole compounds, and triazine compounds specified as an inhibitor to conduct an electrolysis. It is described that the tin or tin-lead alloy plated material that has been surface-treated by this method exhibits less deterioration of solderability and has excellent corrosion resistance.

[0003] Patent Document 2 proposes a tin or tin/lead alloy plating liquid capable of forming bright plating over a wide current density region. As the plating liquid, an aqueous solution for tin or tin/lead alloy electroplating is disclosed, the aqueous solution containing an alkanesulfonic acid as an acid, a divalent tin salt or both of a divalent tin salt and a divalent lead salt of the alkanesulfonic acid as metal salts, one or two or more kinds of polyoxyethylene alkyl phenyl ethers and polyoxyethylene naphthyl ethers as dispersants, and chlorobenzaldehyde, naphthaldehyde and picolinic acid as brightening agents.

[0004] Patent Document 3 proposes a plating bath that gives an electrodeposited film having excellent reflow properties, leveling properties and soldering properties and that has superior aging stability, enabling bright plating over a wide range from a low-current density region to a high-current density region. Specifically, as the plating bath, disclosed is a plating bath obtaining by adding at least one kind of surfactants, at least one kind of aromatic aldehydes, and at least one kind of N-substituted unsaturated fatty acid amide compounds to a main plating bath containing an alkanesulfonic acid and/or an alkanolsulfonic acid and divalent tin salts thereof and/or divalent lead salts thereof.

[0005] Furthermore, Patent Document 4 discloses an aqueous plating bath which is free of fluorides or fluoroborates and which deposits smooth, level and bright coatings of tin or the like. As the aqueous plating bath, disclosed is a plating bath containing (A) a bath-soluble metal salt such as a stannous salt, (B) at least one of alkanesulfonic acids and alkanolsulfonic acids, (C) at least one of nonionic, cationic, or amphoteric surfactants, (D) one or more primary brightening agents of aromatic aldehydes, acetophenones and carbonyl compounds having a specified group, and (E) one or more secondary brightening agents of lower aliphatic aldehydes and specified substituted olefins.

[0006] Incidentally, it is known that if tin or tin alloy plating films have an internal stress therein, whiskers are formed. These whiskers develop a problem such as short-circuiting. Since the formation of whiskers is greatly inhibited by adding lead to the above plating film, the formation of whiskers had never been regarded as a problem in the period when tin-lead alloy plating films were mainstream. However, with the trend toward lead-free plating due to the enforcement of the RoHS (Restriction of Hazardous Substance) directive, improvement measures have been again required. Therefore, various methods, such as improvements of the plating solution, for reducing an internal stress in a tin plating film or tin alloy plating film have been proposed. However, even if the internal stress is reduced and the film itself hardly produces whiskers, there is a problem that when an external stress is applied on the film, whiskers due to the external stress are formed. For example, in a connector, a lead is plugged into a connector pin on which a tin or tin alloy plating film is formed, and an external load is applied on a contact section with the lead in the connector pin. That is, an external stress is applied on the tin or tin alloy plating film formed on the surface of the connector pin (hereinafter, this state may be referred to as "contact pressure"), and this state is the same as a state where the above internal stress is generated. As a result, tin whiskers easily form. Hereinafter, such tin whiskers due to the external stress are sometimes referred to as "contact pressure whiskers".

[0007] In the methods for forming a tin or tin alloy plating disclosed in the above-mentioned Patent Documents 1 to 4, no study was made about the inhibition of the formation of the above contact pressure whiskers. As methods for preventing the formation of the above contact pressure whiskers, methods for forming a tin alloy plating film using a plating solution containing elements effective for preventing the formation of the above contact pressure whiskers together with tin have so far been given. For example, Patent Document 5 discloses that a connector in which a silver plating is formed as a bismuth segregation inhibiting layer on a base material, and a surface layer composed of a tin-bismuth alloy is provided thereon makes it possible to effectively inhibit the formation and growth of whiskers. Patent Document 6 discloses that a gold plating is formed as a base material layer and then a tin-containing material layer is formed thereon, followed by conducting a heat treatment to form an intermetallic compound of tin and gold, thereby suppressing the formation of whiskers.

[0008] However, the methods of the above-mentioned Patent Documents 5 and 6 entail high cost, and in addition, if two or more metal elements are indispensable, the control of alloy ratios of a plating bath and a plating film is necessary. In particular, when using a tin-silver alloy plating bath or the tin-bismuth alloy plating bath as described in the above-mentioned Patent Document 5, the following problems may occur. That is, a substantial difference in potential exists between two metal elements in the plating bath, and if a tin anode surface and a plated workpiece are left immersed in the plating bath while no current is applied, they may become useless because the displacement and deposition of silver or bismuth occurs on the surface of the above tin anode and plated workpiece. Moreover, there is also a problem of increased costs compared with tin plating as described above.

[0009] As another method for preventing the formation of contact pressure whiskers, a treatment method of melting a tin film at a temperature equal to or higher than the melting point, namely a reflow treatment method can be given. In this method, the formation of contact pressure whiskers is inhibited but cannot be completely prevented, resulting in another problem such as deteriorated solderability.

[0010] Furthermore, in the case of a connector with a narrow space between connector pins, a gold plating treatment may be performed. When the gold plating treatment is performed, the above-mentioned contact pressure whiskers are not formed as a matter of course, but there is a problem of greatly increased costs.

RELATED-ART DOCUMENTS

PATENT DOCUMENTS

[0011]

Patent Document 1: JP-A-Hei-07-173676
Patent Document 2: JP-A-Hei-10-036994
Patent Document 3: Japanese Patent No.2856857
Patent Document 4: JP-A-Sho-61-223193
Patent Document 5: JP-A-2011-001630
Patent Document 6: Japanese Patent No.5215305

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0012] The present invention has been made by focusing on the above situation, and an object of thereof is to achieve a tin electroplating bath that makes it possible to, without increasing costs, form a tin plating film wherein the formation of tin whiskers when an external stress is applied on the tin plating film is inhibited.

MEANS FOR SOLVING THE PROBLEMS

[0013] A tin electroplating bath according to the present invention, which can solve the problems as described above, is characterized by comprising one or more compounds (hereinafter referred to as the compounds X) selected from the group consisting of flavonoid compounds and glycosides thereof, compounds having a xanthene skeleton and glycosides thereof, and compounds having an acridine skeleton and glycosides thereof. Hereinafter, the tin electroplating bath according to the present invention may often be referred to as the "electroplating bath" or the "plating bath".

[0014] It is preferred that one or more compounds selected from the group consisting of the flavonoid compounds and glycosides thereof be used as the compounds X.

[0015] It is preferred that the compounds X is contained at a concentration of 0.0001 g/L or higher and 5 g/L or lower in the tin electroplating bath.

[0016] The present invention also includes a tin plating film obtained by using the above-mentioned tin electroplating bath, wherein a Vickers hardness at a position of t/2 in a cross section in a film thickness (t) direction of the tin plating film is 10 or lower.

EFFECTS OF THE INVENTION

[0017] In the tin plating film obtained by using the tin electroplating bath according to the present invention, even when an external stress is applied on the tin plating film, the formation of whiskers due to the above external stress is inhibited.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

FIG. 1 is a photograph showing an example of the overall image of an indentation in the evaluation of whisker inhibiting effect in Example;
FIG. 2 is an enlarged photograph of a part of FIG. 1, showing an example of the measurement of whisker length; and
FIG. 3 is a view illustrating measurement positions of the whisker length and diameter in Example.

MODE FOR CARRYING OUT THE INVENTION

[0019] The present inventors have intensively studied an electroplating method for forming a tin plating film without increasing costs, wherein the formation of tin whiskers when an external stress is applied on the tin plating film is inhibited, by focusing on a tin electroplating bath used for forming the tin plating film. As a result, the present inventors found that by adding one or more compounds (hereinafter may be referred to as the "compounds X") selected from the group consisting of flavonoid compounds and glycosides thereof, compounds having a xanthene skeleton and glycosides thereof, and compounds having an acridine skeleton and glycosides thereof to the tin electroplating bath as essential components, the predetermined object can be achieved. Thus, the present invention has been made based on this findings.

[0020] A mechanism that contact pressure whiskers are inhibited by adding the above compounds X to the plating bath has not been fully clarified yet, but is considered to be as follows. That is, it is considered that the crystal size of Sn constituting the plating increases due to the presence of the above compounds X in the tin electroplating bath, resulting in a decrease in hardness of the plating film. Then, it is assumed that by decreasing in hardness of the plating film, even if an external stress is applied on the plating film, the stress is dispersed and relaxed in the plating film, in other words, the external stress is not locally accumulated, and hence the formation of contact pressure whiskers is inhibited.

[0021] Examples of the above-mentioned flavonoid compounds and glycosides thereof include flavones such as chrysin, luteolin, apigenin, apiin that is a glycoside of apigenin, and the like; flavonols such as galangin, kaempferol, myricetin, morin, quercetin, rutin and quercitrin that are glycosides of quercetin, and the like; isoflavones such as genistin, daidzein, daidzin that is a glycoside of daidzein, and the like; flavanols (catechins) such as catechin, epicatechin, epigallocatechin, epicatechin gallate, epigallocatechin gallate, theaflavin, and the like; flavanones such as naringenin, naringin that is a glycoside of naringenin, hesperetin, hesperidin that is a glycoside of hesperetin, and the like; chalcones such as carthamindin, carthamin that is a glycoside of carthamindin, and the like; anthocyanidins such as cyanidin, cyanine that is a glycoside of cyanidin, delphinidin, delfin that is a glycoside of delphinidin, pelargonidin, pelargonin, that is a glycoside of pelargonidin, and the like.

[0022] Examples of the compounds having a xanthene skeleton and glycosides thereof include xanthylium, 3,6-bis(ethylamino)-9-[2-(ethoxycarbonyl)phenyl]-2,7-dimethylxanthylium chloride, 3,6-diamino-9-(2-carboxyphenyl)xanthylium, 3,6-bis(diethylamino)xanthylium chloride, fluorescein, calcein, uranine, tetraiodofluorescein, fluorescein-4-isothiocyanate, and the like.

[0023] Examples of the compounds having an acridine skeleton and glycosides thereof include acridine, 3,6-dimethylamino acridine, acriflavine, 9(10H)acridone, 9-aminoacridine, acrinol, 9-phenylacridine, proflavine, and the like.

[0024] Of the above-mentioned compounds X, the flavonoid compounds and glycosides thereof are particularly preferable. Of these, flavonols and glycosides thereof are more preferable.

[0025] In order to satisfactorily produce a plating film so as to effectively exhibit the above effects and suppress burnt deposit at high current densities, a preferable content of the above compounds X (the content of a single compound in the case where a compound is contained singly, and the total content of two or more compounds in the case where two or more compounds are contained) in the electroplating bath is preferably 0.0001 g/L or higher, more preferably 0.001 g/L or higher, further preferably 0.005 g/L or higher. On the other hand, a too high content of the above compounds X not only does not provide sufficient whisker inhibiting effects but also provides reduced cathode current efficiency. Therefore, the content of the above compounds X is preferably 5 g/L or lower, more preferably 2 g/L or lower, further preferably 1 g/L or lower.

[0026] The present invention is characterized in that the above compounds X are used in the tin electroplating bath, and the following components typically used for forming tin electroplating films may be contained as other components in the tin electroplating bath.

[Tin salt]

[0027] A tin salt is an essential component to the construction of a plating film. The form of the tin salt used in the present invention is not particularly limited as long as it is usually used in the field of an electroplating bath. The tin salt can be either a stannous salt or a stannic salt.

[0028] Examples of the stannous salt (tin(II) salt) include tin(II) organosulfonates, for example, tin(II) alkanesulfonates such as tin(II) methanesulfonate, and tin(II) alkanolsulfonates such as tin(II) isethionate; and inorganic tin compounds such as tin(II) sulfate, tin(II) borofluoride, tin(II) chloride, tin(II) bromide, tin(II) iodide, tin(II) oxide, tin(II) phosphate, tin(II) pyrophosphate, tin(II) acetate, tin(II) citrate, tin(II) gluconate, tin(II) tartrate, tin(II) lactate, tin(II) succinate, tin(II) sulfamate, tin(II) borofluoride, tin(II) formate, tin(II) silicofluoride, and the like. Examples of the stannic salt (tin(IV) salt) include sodium stannate, potassium stannate, and the like.

[0029] As the tin salts, in particular, the above tin(II) organosulfonates, for example, tin(II) alkanesulfonates such as tin(II) methanesulfonate, and tin(II) alkanolsulfonates such as tin(II) isethionates are preferred.

[0030] The concentration of tin (Sn^{2+} ions or Sn^{4+} ions) in the electroplating bath of the present invention is not particularly limited as long as it is controlled so that a desired tin plating is carried out. The concentration of the tin can be, for example, within a range of 5 to 100 g/L, preferably within a range of 10 to 70 g/L.

[0031] In the tin electroplating bath of the present invention, when a strongly acidic plating bath is used, a complexing agent may be added thereto since the above tin(IV) salt is insoluble under a strong acid. The complexing agent is not particularly limited, and for example, sodium sulfite, potassium sulfite, ammonium sulfite, sodium cyanide, potassium cyanide, sodium thiosulfate, potassium thiosulfate, ammonium thiosulfate, phosphoric acid, boric acid, citric acid, gluconic acid, tartaric acid, lactic acid, malic acid, ethylenediamine, triethanolamine, glycine, alanine, hydroxyethylethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), cyclohexanediaminetetraacetic acid, diethylenetriaminepentaacetic acid (DTPA), triethylenetriaminehexaacetic acid (TTHA), hydroxyethyliminodiacetic acid (HIMDA), dihydroxyethyliminoacetic acid (DHEIMA), dihydroxyethylethylenediaminediacetic acid (DHEDDA), glycine, iminoacetic acid, nitrilotriacetic acid (NTA), aminotrimethylenephosphonic acid, 1-hydroxyethylidene-1, 1-diphosphonic acid, ethylenediaminetetramethylenephosphonic acid, diethylene triamine penta (methylene phosphonic acid), and the like may be used. These complexing agents may be used singly or in combination of two or more.

[0032] The content of the complexing agent is not particularly limited, but is preferably about 1 to 500 g/L, more preferably about 10 to 300 g/L. If the content of the complexing agent is too low, tin may be deposited in the plating bath, leading to a deterioration in bath stability. On the other hand, if the content of the complexing agent is too high, the formation of complexes with Sn^{2+} may excessively proceed, and the deposition rate may reduce, whereby it becomes impossible to form a plating film having a desired film thickness. Furthermore, it becomes difficult to dissolve the complexing agent, and this would be also uneconomical.

[0033] As described above, the plating bath of the present invention does not necessarily require an alloy element. However, an alloy element may be contained as long as it does not exert harmful effects on deposition of plating, film hardness, productivity, and costs. As examples of the alloy element, In and the like capable of suppressing film hardness can be given. However, bismuth and silver are not preferable as the alloy element because the problems of potential difference as described above may occur. Moreover, it is not preferred that copper be used as the alloy element because the film hardness tends to become high, and hence the formation of whiskers is facilitated. Furthermore, lead is not preferred from the viewpoint of a lead-free trend as described above.

[Inorganic acid, organic acid and water-soluble salt thereof]

[0034] Inorganic acids, organic acids and water-soluble salts thereof serve to adjust a pH and the like and act on stability of a plating bath. Furthermore, they also act on electrical conductivity (voltage).

[0035] The inorganic acids and organic acids used in the present invention are not particularly limited as long as they are usually used for plating films. Examples of the inorganic acids include sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, sulfamic acid, and the like. Examples of the organic acids include organic sulfonic acids (alkanesulfonic acids such as methanesulfonic acid, and alkanolsulfonic acids such as isethionic acid), carboxylic acids (aromatic carboxylic acids, saturated aliphatic carboxylic acids, and aminocarboxylic acids), and the like. In view of solution stability and the like, organic sulfonic acids are preferable, and methanesulfonic acid is more preferable.

[0036] These acids may exist as free forms and may exist as water-soluble salts such as water-soluble salts of inorganic acids and water-soluble salts of organic acids. The kinds of the above salts are not particularly limited as long as they are in the form of water-soluble salts, and for example, potassium salts, sodium salts, ammonium salts, magnesium salts, and the like can be given.

[0037] In the present invention, the above inorganic acids, organic acids, and water-soluble salts thereof may be used singly or in combination of two or more. If a preferable content of the above components (the content of a single component in the case where a component is contained singly, and the total content of two or more components in the case where two or more components are contained) in the electroplating bath is too low, stability of the plating bath may degrade, and settlings tend to easily occur. Therefore, the above content is preferably 50 g/L or higher, more preferably 100 g/L or higher. On the other hand, excessive addition of the above components is wasteful because the effect of addition is saturated, and therefore the content is preferably 500 g/L or lower, more preferably 300 g/L or lower.

[Nonionic surfactant]

[0038] Nonionic surfactants serve to improve wettability of a plating bath against a base material.

[0039] As the above nonionic surfactants, alkylene oxide nonionic surfactants are suitably used. Specifically, usable examples thereof include polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene alkylamines, polyoxyethylene alkylamides, polyoxyethylene fatty acid esters, polyoxyethylene polyhydric alcohol ethers, ethylene oxide-propylene oxide block copolymer surfactants, ethylene oxide-propylene oxide random copolymer surfactants, propylene oxide polymer surfactants, and the like. Of these, polyoxyethylene alkylphenyl ethers are particularly preferred.

[0040] In the present invention, the above nonionic surfactants may be used singly or in combination of two or more. A preferable content of the above nonionic surfactants (the content of a single nonionic surfactant in the case where a nonionic surfactant is contained singly, and the total content of two or more nonionic surfactants in the case where two or more nonionic surfactants are contained) in the electroplating bath is preferably 0.05 g/L or higher, more preferably 1 g/L or higher, because a too low content may cause burnt deposit at high current densities. On the other hand, an excessively high content of the above nonionic surfactant may result in such a defect that the resulting plating film becomes darker or irregular in color. Therefore, the above content is preferably 100 g/L or lower, more preferably 50 g/L or lower.

[Antioxidant]

[0041] When using tin(II) salts, antioxidants serve to prevent oxidation of divalent Sn ions and other bath components in the bath and stabilize the bath. Furthermore, when using tin(IV) salts, antioxidants contribute to stability of a Sn complex. As the above antioxidants, cathecol, hydroquinone, 4-methoxyphenol (p-methoxyphenol), and the like can be used.

[0042] These antioxidants may be used singly or in combination of two or more. A preferable content of the above antioxidants (the content of a single antioxidant in the case where an antioxidant is contained singly, and the total content of two or more antioxidants in the case where two or more antioxidants are contained) in the electroplating bath is preferably 0.1 g/L or higher, more preferably 0.2 g/L or higher, because a too low content may not bring about sufficient anti-oxidation effects. On the other hand, a too high content of the above antioxidants may result in a reduction in current efficiency or the like (occurrence of burnt deposit) and a deterioration in physical properties (deterioration of viscosity and defoaming property) of the plating bath due to decomposed matters. Therefore, the above content is preferably 10 g/L or lower, more preferably 5 g/L or lower. The above-mentioned concentration of the antioxidants is the same even in the case of tin(II) salts and in the case of tin(IV) salts.

[Organic solvent]

[0043] Organic solvents are used for the purpose of dissolving the above compounds X in the plating bath. Organic solvents are used also for the purpose of improving stability in the plating bath. Examples of the organic solvents include at least one of monohydric alcohols such as methanol, 2-propanol (isopropyl alcohol), and the like; and dihydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, and the like.

[0044] These organic solvents may be used singly or in combination of two or more. If a preferable content of the above organic solvents (the content of a single organic solvent in the case where an organic solvent is contained singly, and the total content of two or more organic solvents in the case where two or more organic solvents are contained) in the electroplating bath is too low, sufficient solubility cannot be obtained, and hence turbidity and/or settlings may be formed. Therefore, the above content is preferably 5 g/L or higher. On the other hand, a too high content of the organic solvent may result in a reduction in current efficiency or the like (occurrence of burnt deposit) and a deterioration of physical properties (viscosity and defoaming property) of the plating bath due to decomposed matters. Therefore, the above content is preferably 100 g/L or lower, more preferably 70 g/L or lower, further preferably 50 g/L or lower, and still further preferably 20 g/L or lower.

[0045] It is preferred that the tin electroplating bath have a pH of 10 or lower. In particular, when using a tin(II) salt, if the pH is too high, tetravalent tin may be easily generated. Therefore, it is preferred to adjust to pH 3 or lower. On the other hand, when using a tin(IV) salt, if the plating bath has a too high pH or too low pH, complexs cannot be formed, thereby degrading stability of the plating bath. Therefore, it is preferred to adjust to pH 3 to pH 10. For this adjustment of pH, it is preferred to use the same acid as a free acid contained in the tin salt used, and for example, when tin methanesulfonate is used, it is preferred to use methanesulfonic acid for adjusting a pH.

[0046] As for conditions such as bath temperature, current density, plating bath immersion time, and the like for performing electroplating using the tin electroplating bath of the present invention, methods and conditions that are conventionally carried out in tin electroplating can be adopted.

[0047] In the tin plating film obtained by electroplating using the tin electroplating bath defined in the present invention, a Vickers hardness at a position of t/2 in a cross section in a film thickness (t) direction is reduced to 10 or lower. The Vickers hardness is preferably lower than 9.0, more preferably 8.5 or lower. Note that the lower limit of the Vickers hardness is around 4 taking into consideration a function as a protective film of the tin plating film.

[0048] This application claims the benefits of priority to Japanese Patent Application No. 2014-120714 filed on June 11, 2014. The entire content of the specification of Japanese Patent Application No. 2014-120714 filed on June 11, 2014 is incorporated herein by reference.

EXAMPLES

[0049] Below, by way of examples, the present invention will be more specifically described. However, the present invention is not limited by the following examples. It is naturally understood that modifications may be properly made and practiced within the scope adaptable to the gists described above and below. All of these are included in the technical scope of the present invention.

[0050] To examine usefulness of the compounds X defined in the present invention, first, tin electroplating baths containing various components (water-soluble tin salt, acid, surfactant, compounds X, antioxidant, and organic solvent) shown in the following Tables 1A to 1D were prepared. Blanks in Tables 1A to 1D indicate that the component was not added. Note that all the plating baths shown in Tables 1A to 1D had a pH of 1 or lower. Using each of the plating baths, a tin electroplating film was formed on the surface of a base material made of a phosphor bronze material as the following plating step, so as to have a thickness of 2 μm for samples to be used in the following evaluation of whisker inhibiting effects and have a thickness of 30 μm for samples to be used in the following measurement of film hardness, thereby obtaining samples on which a tin plating film was formed.

(Plating step)

[0051] Electrolytic degreasing (two minutes) → water rinsing (30 seconds) → pickling (30 seconds) → water rinsing (30 seconds) → nickel under-plating (thickness: 1.5 μm, conditions indicated below) → water rinsing (30 seconds) →pickling (30 seconds) → water rinsing (30 seconds) → tin plating (conditions indicated below) → water rinsing (30 seconds) → rinsing with ion exchanged water → drying

[0052] In the nickel under-plating in the above step, a nickel sulfamate plating bath (compositions: nickel sulfamate: 300 g/L, nickel chloride: 15 g/L, boric acid: 30 g/L) was used as a plating bath to perform electroplating under the following conditions.

(Nickel plating conditions)

[0053]

Cathode current density: 8 A/dm^2
Liquid temperature: 50°C
Plating time: 60 seconds
pH: 4.0

[0054] In the tin plating in the above step, electroplating was performed under the following conditions.

(Tin plating conditions)

[0055]

Cathode current density: 20 A/dm^2
Liquid temperature: 50°C

[0056] Plating time: the case of a sample for evaluation of whisker inhibiting effects: 12 seconds; the case of a sample for measurement of film hardness: 180 seconds

[0057] Using the samples obtained as above, the evaluation of the whisker inhibiting effects and the measurement of the film hardness were conducted as follows.

[Evaluation of whisker inhibiting effects]

[0058] Using the above samples for evaluation, the evaluation of the whisker inhibiting effects was conducted. In the evaluation, a load test and a whisker measurement were conducted in accordance with Whisker test methods for electronic connectors specified by Japan Electronics and Information Technology Industries Association (JEITA RC-5241). Specifically, using a loading tester, in accordance with a sphere indentation method, a load of 200 g was locally applied on the tin plating film with a zirconia ball indenter having a diameter of 1 mm and left for 120 hours. Then, the load was removed from the tin plating film, an indentation formed on the tin plating film was observed at a magnification of 2,000 times by a scanning electron microscope (SEM). Using the SEM image, the lengths of whiskers generated from a peripheral region of the indentation were measured. An example of the SEM image of the above indentation is shown in FIG. 1. Furthermore, a part of the SEM image of FIG. 1 is enlarged, an example of the measurement of whisker length is shown in FIG. 2.

[0059] In this Example, "whiskers" having an aspect ratio (length/diameter) of 2 or more were regarded as measurement objects, and the length and the number of the whiskers were measured. The measurement method of the whisker length was in conformity with in JEITA ET-7410 Annex 2. The measurement positions of the length and diameter of whisker in a columnar shape are shown in FIG. 3, and the measurement positions of the length of whisker in a wire shape is as shown in FIG. 2. When the whisker was bent as shown in FIG. 2, the longest portion in linear distance of the whisker was measured.

[0060] Whiskers having a length of 1 μm or longer, which can be visually observed, were chosen as measurement objects, and the number of whiskers having a length of 1 μm or longer and 10 μm or shorter and the number of whiskers having a length of longer than 10 μm were respectively counted. This measurement was conducted at one indentation per sample or at a plurality of indentations per sample. When the plurality of indentations were formed, the number of whiskers having a length of 1 μm or longer and 10 μm or shorter and the number of whiskers having a length of longer than 10 μm were determined from the average value of whiskers per indentation. The evaluation was conducted according to the following criteria. In the following criteria, the cases of A and B were judged as acceptable, in particular the case of A was judged as superior, and the case of C was judged as unacceptable.

(Evaluation Criteria)

[0061]

A: Whiskers having a length of longer than 10 μm were not observed, and five or less whiskers having a length of 1 μm or longer and 10 μm or shorter were observed;
B: Whiskers having a length of longer than 10 μm were not observed, and six or more whiskers having a length of 1 μm or longer and 10 μm or shorter were observed; and
C: One or more whiskers having a length of longer than 10 μm were observed.

[Measurement of tin plating film hardness]

[0062] The above samples for evaluation were embedded in a resin to measure a Vickers hardness at a position of t/2 in a cross section in a film thickness (t) direction of the tin-plating film. The measurement conditions are as follows. The Vickers hardnesses are shown in the "film hardness [Hv]" in Table 1A to Table ID.

(Measurement conditions of film hardness)

[0063] Measurement equipment: Microhardness tester HM-124 manufactured by Akashi Corporation

Load: 0.0010 kg (0.0098 N)
Retaining time: 15 seconds
Application rate: 10 μm/sec

[0064] These results are shown in Table 1A to Table 1D.

[TABLE1A]

		Example1	Example2	Example3	Example4	Example5	Example6	Example7	Example8	Example9
Water-soluble tin salt [g/L] (as Sn^{2+} ion)	Tin(II) sulfate	50	50	50						
	Tin(II) methanesulfonate				50	50	50			
	Tin(II) isethionate							60	60	60
Inorganic acid or organic acid [g/L]	Sulfuric acid	100	100	100						
	Methanesulfonic acid				150	150	150			100
	Isethionic acid						100	150	150	150
Nonionic surfactant [g/L]	Polyoxyethylene styrenated phenyl ether (EO addition molar number 12.5)	20								
	Polyoxyethylene para-cumyl ether (EO addition molar number 10)		20					50		
	Polyoxyethylene bisphenol A ether (EO addition molar number 17.5)			20						
	Polyoxyethylene tallow amine (EO addition molar number 10)					5				50
	Polyoxyethylene β-naphthyl ether (EO addition molar number 10)						5			
	Polyoxyethylene polyoxypropylene lauryl ether (average molecular weight 600, EO/PO=75/25)								50	

(continued)

		Example1	Example2	Example3	Example4	Example5	Example6	Example7	Example8	Example9
Flavonoid compounds and glycosides thereof [g/L]	quercetin	0.1						0.2		
	apiin		0.05						0.1	
	rutin			0.5						0.7
	hesperetin				0.01					
	naringin					0.05				
	cyanine						0.02			
Antioxidant [g/L]	Cathecol	1.2				1.5				
	Hydroquinone		0.5		0.2				3	
	p-Methoxyphenol			2.5			1			
Organic solvent [g/L]	Ethylene glycol	50	50	50						
	Diethylene glycol				30	30	30			
	Isopropyl alcohol							20	30	20
Film hardness [Hv]		8.5	8.5	8.8	8.9	9.2	8.3	8.8	9.2	9.1
Whisker evaluation		A	A	A	A	B	A	A	B	B

[TABLE1B]

		Example10	Example11	Example12	Example13	Example14	Example15	Example16	Example17	Example18
Water-soluble tin salt [g/L] (as Sn^{2+} ion)	Tin(II) sulfate							50	50	50
	Tin(II) methanesulfonate	70	70	70						
	Tin(II) isethionate				70	70	70			
Inorganic acid or organic acid [g/L]	Sulfuric acid							130	130	130
	Methanesulfonic acid	300	200	200						
	Isethionic acid		100	100	100	200	300			
Nonionic surfactant [g/L]	Polyoxyethylene styrenated phenyl ether (EO addition molar number 12.5)	30	30	30	20	20	20			
	Polyoxyethylene para-cumyl ether (EO addition molar number 10)				10	10	10			
	Polyoxyethylene bisphenol A ether (EO addition molar number 17.5)							40		
	Polyoxyethylene tallow amine (EO addition molar number 10)								40	
	Polyoxyethylene β-naphthyl ether (EO addition molar number 10)									40

(continued)

		Example10	Example11	Example12	Example13	Example14	Example15	Example16	Example17	Example18
Flavonoid compounds and glycosides thereof [g/L]	naringin	1					1			
	catechin		0.05					0.05		
	morin			0.2					0.5	
	chrysin				0.005					0.7
	hesperidin					0.5				
Antioxidant [g/L]	Cathecol	1.2				1.5				
	Hydroquinone		0.5		0.2					3
	p-Methoxyphenol			2.5				1		
Organic solvent [g/L]	Ethylene glycol	50	50	50				50		
	Diethylene glycol				30	30	30			
	Isopropyl alcohol								70	70
Film hardness [Hv]		8.2	8.4	8.7	8.5	9.3	8.8	9.1	8.9	8.6
Whisker evaluation		A	B	A	A	B	A	B	A	A

[TABLE1C]

		Example19	Example20	Example21	Example22	Example23	Example24	Example25	Example26	Example27
Water-soluble tin salt [g/L] (as Sn^{2+}ion)	Tin(II) sulfate	50	50	50						
	Tin(II) methanesulfonate				50	50	50			
	Tin(II) isethionate							60	60	60
Inorganic acid or organic acid [g/L]	Sulfuric acid	100	100	100						
	Methanesulfonic acid				150	150	150			100
	Isethionic acid						100	150	150	150

(continued)

		Example19	Example20	Example21	Example22	Example23	Example24	Example25	Example26	Example27
Nonionic surfactant [g/L]	Polyoxyethylene styrenated phenyl ether (EO addition molar number 12.5)	30	30	30	20	20	20			
	Polyoxyethylene para-cumyl ether (EO addition molar number 10)				10	10	10			
	Polyoxyethylene bisphenol A ether (EO addition molar number 17.5)							40		
	Polyoxyethylene tallow amine (EO addition molar number 10)								40	
	Polyoxyethylene (β-naphthyl ether (EO addition molar number 10)									40

(continued)

		Example19	Example20	Example21	Example22	Example23	Example24	Example25	Example26	Example27
Compound having xanthene skeleton or acridine skeleton or glycosides thereof [g/L]	fluorescein	1					1			
	uranine		0.05					0.05		
	3,6-bis(ethylamino)-9-[2-(ethoxycarbonyl)phenyl]-2,7-dimethylxanthylium chloride			0.2					0.5	
	9(10H)acridone				0.005					0.7
	acrinol					0.5				
Antioxidant [g/L]	Cathecol	1.2				1.5				
	Hydroquinone		0.5		0.2					3
	p-Methoxyphenol			2.5				1		
Organic solvent [g/L]	Ethylene glycol	50	50	50				50		
	Diethylene glycol				30	30	30			
	Isopropyl alcohol								70	70
Film hardness [Hv]		8.5	8.8	8.5	9.1	9.1	8.5	9.0	8.8	8.9
Whisker evaluation		B	B	B	B	B	B	B	B	B

[TABLE1D]

		Comparative Example1	Comparative Example2	Comparative Example3	Comparative Example4	Comparative Example5	Comparative Example6
Water-soluble tin salt [g/L] (as Sn^{2+}ion)	Tin(II) sulfate	20					60
	Tin(II) methanesulfonate		50		30		
	Tin(II) isethionate			50		30	
Inorganic acid or organic acid [g/L]	Sulfuric acid	100					100
	Methanesulfonic acid		100		150		
	Isethionic acid			150		100	
Nonionic surfactant [g/L]	Polyoxyethylene styrenated phenyl ether (EO addition molar number 12.5)	20					
	Polyoxyethylene para-cumyl ether (EO addition molar number 10)		10				
	Polyoxyethylene bisphenol A ether (EO addition molar number 17.5)						
	Polyoxyethylene tallow amine (EO addition molar number 10)						
	Polyoxyethylene β-naphthyl ether (EO addition molar number 10)				10	10	10
	Polyoxyethylene polyoxypropylene lauryl ether (average molecular weight 600, EO/PO=75/25)			30			
Leveling agent [g/L]	Benzothiazole		5				
	2-Mercaptobenzothiazole	1					
	2-Mercaptobenzoxazole			5			
	2-Mercaptobenzimidazole				10		
	Methacrylic acid					2.4	2.4
	1-Naphthaldehyde						0.5

(continued)

		Comparative Example1	Comparative Example2	Comparative Example3	Comparative Example4	Comparative Example5	Comparative Example6
Antioxidant [g/L]	Cathecol	1.2				1.5	
	Hydroquinone		0.5		0.2		
	p-Methoxyphenol			2.5			1
Organic solvent [g/L]	Ethylene glycol	30			40		
	Diethylene glycol			20			
	Isopropyl alcohol		50			70	70
Film hardness [Hv]		11.8	11.4	10.8	12.9	17.6	23.3
Whisker evaluation		C	C	C	C	C	C

[0065] In Tables 1A to 1D, Examples 1 to 27 are inventive examples which satisfy the requirements of the present invention. In these examples, since the plating bath containing the defined compounds X was used to form tin plating films, the formation of whiskers was inhibited even if an external stress was applied on the resulting tin plating film. On the other hand, Comparative Examples 1 to 6 do not contain the defined compounds X, Comparative Example 1 is an example containing 2-mercaptobenzothiazole disclosed in Patent Document 1, Comparative Example 5 is an example containing methacrylic acid disclosed in Patent Document 3, and Comparative Example 6 is an example containing methacrylic acid disclosed in Patent Document 3 and naphthaldehyde disclosed in Patent Documents 2 and 4. In all of these Comparative Examples, long whiskers were formed.

[0066] Furthermore, when the film hardnesses of Examples 1 to 27 and the film hardnesses of Comparative Examples 1 to 6 are compared, the film hardnesses of Examples 1 to 27 are lower than those of Comparative Examples 1 to 6. In Examples 1 to 27, it can be considered that since the tin plating film was formed using the compounds X as described above, the resulting tin plating film had a lower film hardness, and when an external stress was applied, the external stress was relaxed, and hence the formation of whiskers was inhibited.

[0067] In particular, as Examples 1 to 4, 6, 7, 10, 12, 13, 15, 17 and 18 obtain the whisker evaluation results of A, it is revealed that in the case where flavonoids or glycosides thereof are used as the compounds X, the formation of whiskers can be sufficiently inhibited. Furthermore, it is revealed that in the case where flavonoids or glycosides thereof are used, the formation of whiskers can be sufficiently inhibited when the film hardness is lower than 9.0.

Claims

1. A tin electroplating bath comprising one or more compounds (hereinafter referred to as the compounds X) selected from the group consisting of flavonoid compounds and glycosides thereof, compounds having a xanthene skeleton and glycosides thereof, and compounds having an acridine skeleton and glycosides thereof.

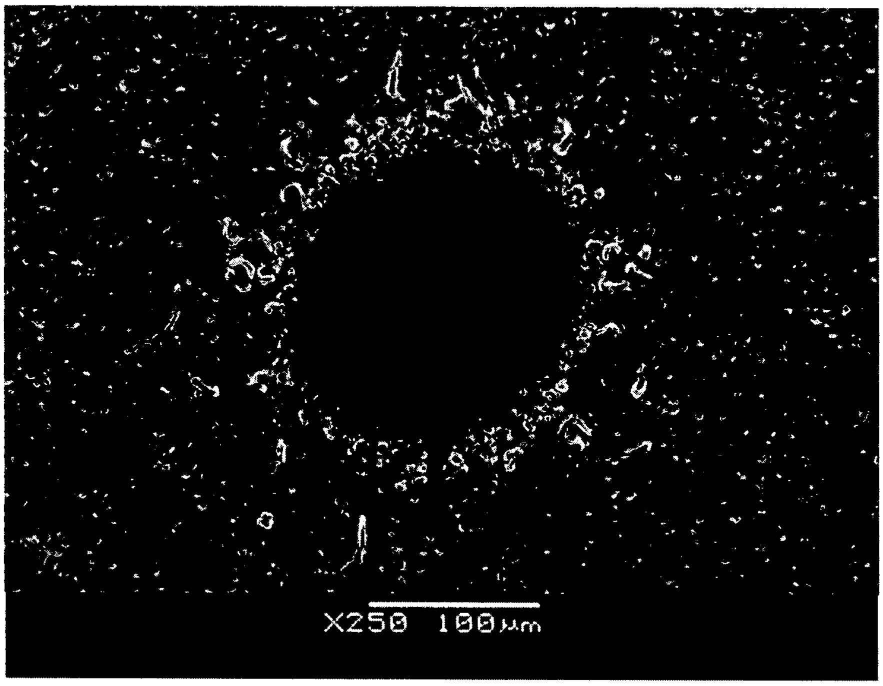
2. The tin electroplating bath according to claim 1, wherein one or more compounds selected from the group consisting of the flavonoid compounds and glycosides thereof are used as the compounds X.

3. The tin electroplating bath according to claim 1 or 2, wherein the compounds X are contained at a concentration of 0.0001 g/L or higher and 5 g/L or lower in the tin electroplating bath.

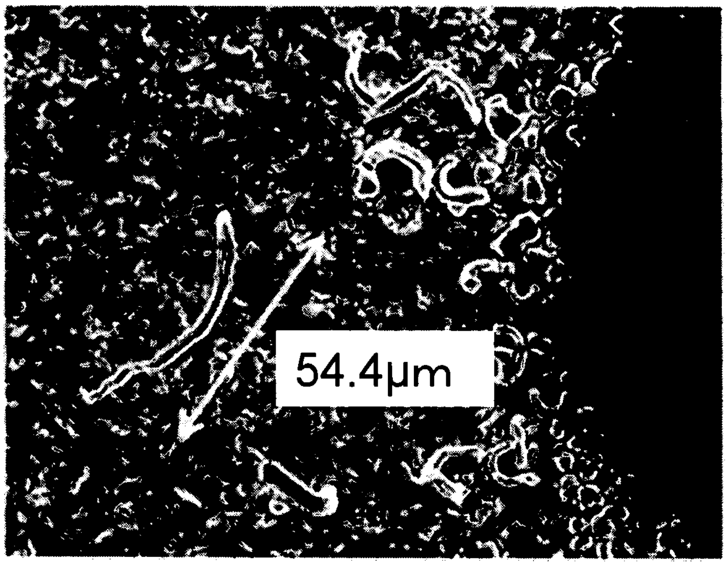
4. A tin plating film obtained by using the tin electroplating bath according to claim 1 or 2, wherein a Vickers hardness at a position of t/2 in a cross section in a film thickness (t) direction of the tin plating film is 10 or lower.

5. A tin plating film obtained by using the tin electroplating bath according to claim 3, wherein a Vickers hardness at a position of t/2 in a cross section in a film thickness (t) direction of the tin plating film is 10 or lower.

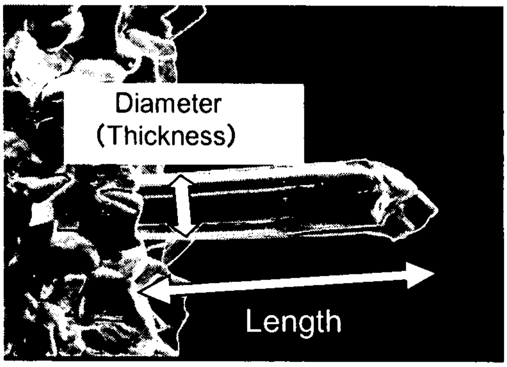
[FIG. 1]



[FIG. 2]



[FIG. 3]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/066187

A. CLASSIFICATION OF SUBJECT MATTER
C25D3/32(2006.01)i, *C25D7/00*(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)
C25D3/32, C25D7/00

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2015
Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

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.
X	JP 10-060682 A (Atotech Deutschland GmbH), 03 March 1998 (03.03.1998), claims; paragraphs [0011], [0023] & EP 810303 A1 & DE 19623274 A	1-5
X	JP 2010-174373 A (Rohm and Haas Electronic Materials L.L.C.), 12 August 2010 (12.08.2010), claims; paragraphs [0001], [0050] & US 2010/0216302 A1 & EP 2221396 A1 & KR 10-2010-0080481 A & CN 102051645 A & TW 201037103 A	1-5

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

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"&" document member of the same patent family

Date of the actual completion of the international search 17 August 2015 (17.08.15)	Date of mailing of the international search report 25 August 2015 (25.08.15)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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