

DESCRIPTION

TITLE OF INVENTION: METHOD AND APPARATUS FOR REGENERATION
OF PLATING COMPOSITION

5 TECHNICAL FIELD

[0001] The present invention relates to a method of regenerating a plating composition, and an apparatus for regenerating a plating composition.

10 BACKGROUND ART

[0002] Relating to plating compositions used for metal plating, Japanese Unexamined Patent Application Publication (Translation of PCT Application) No. 2004-534151 proposes a method of regenerating a plating solution, in which tin
15 (IV) ions are reduced to tin (II) ions using electrolytically deposited tin. Further, Japanese Unexamined Patent Application Publication (Translation of PCT Application) No. 2015-518923 proposes a method of regenerating a plating composition by oxidizing and
20 reducing two kinds of metal components contained in the plating composition with the use of an apparatus provided with a working electrode compartment, a counter electrode compartment, and an ion exchange membrane separating these compartments.

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0003] An object of one aspect of the present invention is to provide a method of regenerating a plating composition, by which metal ions in a high oxidation state that are contained in a plating composition can be efficiently reduced to metal ions in a low oxidation state.

SOLUTION TO PROBLEM

10 [0004] A first aspect is a method of regenerating a plating composition, the method including: removing at least a portion of a surfactant from a plating composition containing tin (IV) ions and the surfactant; introducing the plating composition, from which at least a portion of the surfactant has been removed, to a working electrode compartment which includes a working electrode and is separated from a counter electrode compartment including a counter electrode by a membrane selected from the group consisting of an ion exchange membrane, a reverse osmosis membrane, and a nanofiltration membrane, so as to reduce at least a portion of the tin (IV) ions in the introduced plating composition to metallic tin using the working electrode as a cathode; and oxidizing at least a portion of the thus reduced metallic tin to tin (II) ions using the working electrode as an anode.

[0005] A second aspect is an apparatus for regenerating a plating composition, the apparatus including: a surfactant removing means; a working electrode compartment including a working electrode; a counter electrode compartment including a counter electrode; and a membrane which separates the working electrode compartment and the counter electrode compartment and is selected from the group consisting of an ion exchange membrane, a reverse osmosis membrane, and a nanofiltration membrane.

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ADVANTAGEOUS EFFECTS OF INVENTION

[0006] According to one aspect of the present invention, a method of regenerating a plating composition, by which metal ions in a high oxidation state that are contained in a plating composition can be efficiently reduced to metal ions in a low oxidation state, can be provided.

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DESCRIPTION OF EMBODIMENTS

[0007] The term "step" as used herein encompasses not only an independent step but also a step not clearly distinguishable from another step as long as the intended purpose of the step is achieved. If multiple substances correspond to a component in a composition, the content of the component in the composition means the total amount of the multiple substances present in the composition unless

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otherwise specified. Further, upper limit and lower limit values that are described for a numerical range in the present specification can be arbitrarily selected and combined. Embodiments of the present invention will now be described in detail. The embodiments described below are exemplifications of a method and apparatus for regeneration of plating composition for embodying the technical ideas of the present invention, and the present invention is not limited to the method and apparatus for regeneration of plating composition described below.

Method of Regenerating Plating Composition

[0008] The method of regenerating a plating composition includes: the first step of removing at least a portion of a surfactant from a plating composition containing tin (IV) ions and the surfactant; the second step of introducing the plating composition, from which at least a portion of the surfactant has been removed, to a working electrode compartment which includes a working electrode and is separated from a counter electrode compartment including a counter electrode by a membrane selected from the group consisting of an ion exchange membrane, a reverse osmosis membrane, and a nanofiltration membrane, so as to reduce at least a portion of the tin (IV) ions in the introduced plating composition to metallic tin using the working

electrode as a cathode; and the third step of oxidizing at least a portion of the thus reduced metallic tin to tin (II) ions using the working electrode as an anode.

[0009] By removing at least a portion of the surfactant from the plating composition and then electrochemically reducing the tin (IV) ions using an electrochemical apparatus provided with a counter electrode compartment and a working electrode compartment that are separated by a membrane through which tin ions hardly pass, such as an ion exchange membrane, the tin (IV) ions may be efficiently reduced to metallic tin. The reason for this is believed to be, for example, as follows. It is believed that, by the removal of at least a portion of the surfactant contained in the plating composition, the inhibition of reduction of the tin (IV) ions by an interaction between the surfactant and a cathode may be suppressed, as a result of which the reduction efficiency of the tin (IV) ions on the cathode may be improved.

[0010] In the first step, from a plating composition containing tin (IV) ions and a surfactant, at least a portion of the surfactant is removed. The plating composition may be an electrolytic plating solution or an electroless plating solution. The plating composition may be preferably an electrolytic plating solution or an electrolytic tin plating solution, more preferably a used

electrolytic tin plating solution. In the plating composition, at least the tin (IV) ions and the surfactant may be dissolved in a liquid medium. The liquid medium constituting the plating composition may be any liquid medium containing at least water and, if necessary, the liquid medium may further contain a water-soluble organic solvent and the like in addition to water.

[0011] The surfactant contained in the plating composition may be any of a nonionic surfactant, a cationic surfactant, an anionic surfactant, an amphoteric surfactant, and the like. In the plating composition, the surfactant may function as a so-called gloss agent, leveler, or the like. From the standpoint of the reduction efficiency of the tin (IV) ions, the surfactant may contain at least one selected from the group consisting of a nonionic surfactant, a cationic surfactant, and an amphoteric surfactant. In the plating composition, the surfactant may be contained singly, or in combination of two or more kinds thereof.

[0012] Examples of the nonionic surfactant include: ester-type surfactants in which a polyhydric alcohol, such as glycerin, sorbitol, or sucrose, and a fatty acid are ester-bonded; ether-type surfactants that are formed by an addition of ethylene oxide, propylene oxide, or the like to a hydroxy group-containing compound such as a higher

alcohol or an alkylphenol; and ester-ether-type surfactants that are formed by an addition of ethylene oxide, propylene oxide, or the like to an ester-type surfactant. Specific examples of the nonionic surfactant include polyethylene glycol, polypropylene glycol, polyoxyethylene octylphenol, polyoxyethylene β -naphthyl ether, polyoxyethylene alkylamines, polyoxyethylene alkyl ethers, polyoxyethylene polyoxypropylene alkyl ethers, glycerin fatty acid esters and ethylene oxide adducts thereof, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, fatty acid monoethanolamides and ethylene oxide adducts thereof, fatty acid-*N*-methyl monoethanolamides and ethylene oxide adducts thereof, fatty acid diethanolamides and ethylene oxide adducts thereof, sucrose fatty acid esters, alkyl (poly)glycerol ethers, polyglycerin fatty acid esters, polyethylene glycol fatty acid esters, fatty acid methyl ester ethoxylates, and *N*-long-chain alkyldimethylamine oxides. These nonionic surfactants may contain a fluorine atom as a substituent in their structures.

[0013] Examples of the cationic surfactant include amine salt-type surfactants and quaternary ammonium salt-type surfactants. Specific examples of the cationic surfactant include alkyl (or alkenyl) trimethyl ammonium salts, alkyl (or alkenyl) triethyl ammonium salts, dialkyl (or alkenyl) dimethyl ammonium salts, alkyl (or alkenyl) quaternary

ammonium salts, mono- or di-alkyl (or alkenyl) quaternary ammonium salts containing an ether group, an ester group, or an amide group, alkyl (or alkenyl) pyridinium salts, alkyl (or alkenyl) dimethylbenzyl ammonium salts, alkyl (or alkenyl) isoquinolinium salts, dialkyl (or alkenyl) morphonium salts, polyoxyethylene alkyl (or alkenyl) amines, alkyl (or alkenyl) amine salts, polyamine fatty acid derivatives, amyl alcohol fatty acid derivatives, benzalkonium chloride, and benzethonium chloride. These cationic surfactants may contain a fluorine atom as a substituent in their structures.

[0014] The amphoteric surfactant exhibits the properties of an anionic surfactant in the alkaline range but the properties of a cationic surfactant in the acidic range. Examples of the amphoteric surfactant include carboxylates and sulfonates, and the amphoteric surfactant may be any of amino acid-type amphoteric surfactants, betaine-type amphoteric surfactants, and the like. Specific examples of the amphoteric surfactant include alkyl dimethyl aminoacetic acid betaine, alkyl dimethyl acetic acid betaine, alkyldimethylcarboxybetaine, alkyldimethylcarboxymethylene ammonium betaine, alkyldimethyl ammonioacetate, fatty acid amide propyldimethyl amino acid betaine, alkyloylamide propyl dimethyl glycine, 2-alkyl-1-(2-hydroxyethyl)imidazolium-1-

acetate, alkyldiaminoethylglycine,
dialkyldiaminoethylglycine, and alkyldimethylamine oxide.

[0015] Examples of the anionic surfactant include
carboxylates, sulfonates, sulfates, and phosphates.

5 [0016] The content of the surfactant in the plating
composition may be, for example, 0.01 g/L to 10 g/L,
preferably 0.1 g/L or more, or 5 g/L or less. The content
of the surfactant in the plating composition after the
removal in the first step may be, for example, 0.005 g/L or
10 more. The content of the surfactant can be measured using
the surface tension as an index. Specifically, the content
of the surfactant can be measured using a stalagmometer.

[0017] The tin (IV) ions contained in the plating
composition may be, for example, derived from a water-
15 soluble tin (IV) salt, or generated by oxidation of tin
(II) ions constituting the plating composition before use.
Further, the tin (IV) ions contained in the plating
composition may be simple metal ions or complex ions.

Examples of a complexing agent forming the complex ions
20 include: carboxylic acids such as gluconic acid (including
gluconolactone), citric acid, glutaric acid, succinic acid,
malic acid, tartaric acid, and lactic acid, and salts and
derivatives thereof; phosphoric acids such as
tripolyphosphoric acid and hydroxyethane diphosphonic acid,
25 and salts thereof; saccharides such as sorbitol and

mannitol, and salts thereof; amino acids such as phenylalanine, glutamic acid, aspartic acid, alanine, and glycine, and salts thereof; HEDTA; and EDTA. The complexing agent may contain at least one selected from the group consisting of the above-exemplified compounds, and may contain at least gluconic acid. The complexing agent may be used singly, or in combination of two or more kinds thereof. When the tin (IV) ions are complex ions, the pH of the plating composition may be set to be weakly acidic to weakly alkaline, so that the corrosion of a plated material that is weak against a strong acid or a strong alkali (e.g., a material in which an oxide is used as a member, such as a ceramic capacitor) may be inhibited.

[0018] The content of the tin (IV) ions in the plating composition may be, for example, 0.1 g/L to 100 g/L, preferably 1 g/L or more. Further, the content of the complexing agent in the plating composition may be, for example, equimolar to 20 times by mole, preferably 10 times by mole or less, of tin ions. The content of the tin (IV) ions in the plating composition is measured by, for example, high-frequency inductively-coupled plasma emission spectroscopy (ICP-AES), or redox titration with potassium iodate that is performed after reduction with iron powder.

[0019] The plating composition may contain tin (II) ions in addition to the tin (IV) ions. The tin (II) ions may be

simple metal ions or complex ions. A complexing agent forming the complex ions is the same as that of the tin (IV) ions. When the plating composition contains tin (II) ions, the content of the tin (II) ions in the plating composition may be, for example, 100 g/L or less, preferably 20 g/L or less. The content of the tin (II) ions in the plating composition is measured in the same manner as that of the tin (IV) ions.

[0020] The tin (II) ions may be derived from a water-

soluble tin (II) salt. Specific examples of the water-soluble tin (II) salt include stannous sulfate, stannous chloride, tin fluoroborate, tin (II) alkanesulfonates, tin (II) alkanolsulfonates, and tin (II) aromatic sulfonates.

The water-soluble tin (II) salt may contain at least one

selected from the group consisting of the above-exemplified salts, and may contain at least a tin (II) alkanesulfonate.

Examples of the alkanesulfonic acid in the tin (II)

alkanesulfonate include alkanesulfonic acids having 1 to 3 carbon atoms, specifically methanesulfonic acid,

ethanesulfonic acid, propanesulfonic acid, and 2-propanesulfonic acid.

[0021] The plating composition may further contain other metal ions in addition to the tin ions. Examples of the other metal ions include salts of a lead ion, a copper ion,

a silver ion, a bismuth ion, a cobalt ion, a nickel ion,

and the like.

[0022] The plating composition may further contain alkali metal ions, ammonium ions, or the like. When the plating composition contains alkali metal ions, ammonium ions, or the like, the electric conductivity of the plating composition is improved, so that not only the heat generation due to a fluid resistance is inhibited during electrolytic plating, but also the throwing power tends to be improved. Examples of the alkali metal ions include a lithium ion, a sodium ion, a potassium ion, a rubidium ion, and a cesium ion. The alkali metal ions, ammonium ions, or the like may be added to the plating composition in the form of, for example, a salt with an acid component. When the plating composition contains an acid component, for example, the stability of the plating composition is further improved. Examples of the acid component include sulfuric acid, hydrochloric acid, alkanesulfonic acids, alkanolsulfonic acids, aromatic sulfonic acids, phosphoric acid, alkyl carboxylic acids, and arylcarboxylic acids, and the acid component may contain at least one selected from the group consisting of these acids. These acids may be used singly, or in combination of two or more kinds thereof.

[0023] The plating composition may have a pH of, for example, 1 to 13, preferably 3 or higher, or 4 or higher,

but preferably 11 or lower, or 9 or lower. When the pH of the plating composition is in this range, the tin (IV) ions tend to be reduced more efficiently. The pH of the plating composition may be adjusted to be in a desired range with, for example, a pH modifier. Examples of the pH modifier include alkali metal hydroxides and ammonia, in addition to the above-exemplified acid components.

[0024] The plating composition may further contain an

antioxidant. When the plating composition contains an antioxidant, for example, the stability of the plating composition is improved, so that the bath life can be extended. Examples of the antioxidant include

hydroquinone, ascorbic acid, catechol, hypophosphorous acid, and erythorbic acid. When the plating composition

contains an antioxidant, the content of the antioxidant in the plating composition may be, for example, 0.01 g/L to 20 g/L, preferably 0.1 g/L or more, or 5 g/L or less.

[0025] When the plating composition contains an

antioxidant, the first step may include removing at least a portion of the antioxidant. The antioxidant may be removed by an activated carbon treatment.

[0026] Examples of a method of removing the surfactant

in the first step include an activated carbon treatment and a gel filtration treatment. The method of removing the

surfactant in the first step may preferably include an

activated carbon treatment. The method of removing the surfactant based on an activated carbon treatment may include, for example, bringing the plating composition into contact with an activated carbon. By using an activated carbon, at least a portion of the surfactant may be removed from the plating composition more efficiently. In the first step, a method of electrostatically adsorbing the surfactant (e.g., a method of bringing the surfactant into contact with an ion exchange resin) and an activated carbon treatment may be employed in combination.

[0027] The activated carbon is a porous substance which contains carbon as a main component and has been subjected to a chemical or physical activation treatment. The activated carbon used in the activated carbon treatment may be a chemically activated carbon or a gas-activated carbon. Further, the activated carbon may be a powder activated carbon, a granular activated carbon, or a combination thereof.

[0028] The activated carbon may have a specific surface area of, for example, 200 m²/g to 1,500 m²/g, preferably 300 m²/g or more, or 700 m²/g or less. The specific surface area is measured using nitrogen gas after heat-treating the activated carbon at 200°C for 6 hours as a pretreatment, based on the Brunauer-Emmett-Teller (BET) theory. Further, the activated carbon may have an average

pore size of, for example, 1.5 nm to 3.5 nm, preferably 2.0 nm to 3.0 nm. As for the shape of mesopores of the activated carbon, the average pore width on the adsorption side, which is determined by the INNES method, may be, for example, 2 nm to 30 nm, preferably 4 nm to 10 nm. The average pore width on the desorption side, which is determined by the INNES method, may be, for example, 2 nm to 5 nm, preferably 2 nm to 3.5 nm.

[0029] The amount of the activated carbon to be used for the contact with the plating composition may be selected as appropriate in accordance with the type of the activated carbon. The amount of the activated carbon to be used may be any amount with which at least a portion of the surfactant contained in the plating composition can be removed, and it may be an amount that is sufficient for removing preferably 50% by mass or more, 70% by mass or more, or 90% by mass or more, of the surfactant. The amount of the activated carbon to be used may also be selected in accordance with the method of bringing the plating composition into contact with the activated carbon. For example, when the plating composition is brought into contact in a single pass, the required amount of the activated carbon may be greater as compared to a case where the plating composition is circulated and thereby brought into contact.

[0030] A contact between the plating composition and the activated carbon may be made by, for example, mixing the plating composition and the activated carbon and subsequently performing solid-liquid separation, or passing the plating composition through the activated carbon maintained in a filtration device, a cartridge, or the like. The temperature of the contact between the plating composition and the activated carbon may be, for example, 0°C or higher, or 70°C or lower.

[0031] In the second step, the plating composition, from which at least a portion of the surfactant has been removed, is introduced into a working electrode compartment of an electrochemical device which is provided with the working electrode compartment including a working electrode and a counter electrode compartment including a counter electrode, and in which the working electrode compartment and the counter electrode compartment are separated by a membrane selected from the group consisting of an ion exchange membrane, a reverse osmosis membrane, and a nanofiltration membrane; and at least a portion of the tin (IV) ions in the thus introduced plating composition are reduced to metallic tin using the working electrode as a cathode. In the counter electrode compartment of the electrochemical device, a conductive ion-containing aqueous solution may be arranged. When a conductive ion-containing

aqueous solution is arranged in the counter electrode compartment, the tin (IV) ions may be reduced more efficiently.

[0032] Examples of a material of the working electrode
5 provided in the working electrode compartment include gold, platinum, platinum-coated titanium, silver, nickel, graphite, tin, titanium, and iridium oxide. Examples of a material of the counter electrode include platinum, platinum-coated titanium, gold, nickel, iridium oxide,
10 titanium, graphite, and palladium. The working electrode compartment and the counter electrode compartment are separated by an ion exchange membrane. By this, the tin (IV) ions may be reduced more efficiently. The ion exchange membrane may be a cation exchange membrane, an
15 anion exchange membrane, or a combination thereof. The ion exchange membrane may be selected as appropriate from commercially available ion exchange membranes. From the standpoint of the reduction efficiency of the tin (IV) ions, the ion exchange membrane may include at least a
20 cation exchange membrane. The cation exchange membrane may contain, for example, a copolymer of a fluorine resin based on sulfonated tetrafluoroethylene. Alternatively, for example, a membrane which tin ions hardly pass through, such as a reverse osmosis membrane (RO membrane) or a
25 nanofiltration membrane (NF membrane or loose RO membrane),

may be used in place of the ion exchange membrane.

[0033] When a conductive ion-containing aqueous solution is arranged in the counter electrode compartment, the conductive ion-containing aqueous solution may contain at least water and a water-soluble metal salt. The water-soluble metal salt may contain, for example, an alkali metal ion or an alkaline earth metal ion as a metal ion. Further, the water-soluble metal salt may contain, for example, a sulfate ion, a nitrate ion, or a phosphate ion, as an anion.

[0034] In the second step, at least a portion of the tin (IV) ions in the plating composition introduced to the working electrode compartment are subjected to a first electrolysis treatment using the working electrode as a cathode, whereby the tin (IV) ions are reduced to metallic tin. This metallic tin generated by reduction may be deposited on, for example, the working electrode. The current density in the electrolysis of the tin (IV) ions may be, for example, 0.05 A/dm² to 1 A/dm², preferably 0.1 A/dm² or higher, or 0.5 A/dm² or lower. The temperature during the electrolysis may be, for example, 30°C to 80°C, preferably 35°C or higher, or 75°C or lower. The time required for the electrolysis may be, for example, 10 minutes to 200 hours.

[0035] In the third step, at least a portion of the

metallic tin generated by reduction in the second step is subjected to a second electrolysis treatment using a working electrode as an anode, whereby the metallic tin is oxidized to tin (II) ions. In the third step, the metallic tin deposited on the working electrode in the second step may be electrolyzed and thereby oxidized to tin (II) ions using the working electrode as an anode. In other words, the third step may be performed following the reduction of the tin (IV) ions in the second step, using the same electrochemical device.

[0036] The current density in the electrolysis of the metallic tin may be, for example, 0.5 A/dm² to 100 A/dm². Further, the temperature during the electrolysis of the metallic tin may be, for example, 10°C to 80°C, preferably 15°C or higher, or 75°C or lower. The time required for the electrolysis may be, for example, 0.2 hours to 10 hours.

[0037] The method of regenerating a plating composition may further include the step of adding a surfactant to the plating composition after the third step. By using the surfactant-added plating composition, a plating having a more favorable surface can be formed. The surfactant to be added may be of the same kind as the surfactant removed in the first step. Further, the amount of the surfactant to be added may be equivalent to the amount of the surfactant

removed in the first step.

Apparatus for Regenerating Plating Composition

[0038] The apparatus for regenerating a plating

5 composition includes: a surfactant removing means; a
working electrode compartment including a working
electrode; a counter electrode compartment including a
counter electrode; and a membrane which separates the
working electrode compartment and the counter electrode
10 compartment and is selected from the group consisting of an
ion exchange membrane, a reverse osmosis membrane, and a
nanofiltration membrane. The apparatus for regenerating a
plating composition may be used for the above-described
method of regenerating a plating composition.

15 [0039] Examples of the surfactant removing means

provided in the apparatus include an activated carbon
treatment and a gel filtration treatment. The surfactant
removing means may preferably include an activated carbon
treatment. The removal of the surfactant by the activated
20 carbon treatment may include, for example, bringing the
plating composition into contact with an activated carbon.
By using an activated carbon, the surfactant can be removed
from the plating composition more efficiently. A contact
between the plating composition and the activated carbon
25 may be made by, for example, passing the plating

composition through the activated carbon maintained in a cartridge or the like. In other words, the apparatus may also include a cartridge configured such that an activated carbon is filled therein and the plating composition may be passed therethrough.

[0040] The apparatus may include an electrochemical device including: a working electrode compartment; a counter electrode compartment; and a membrane that separates the working electrode compartment and the counter electrode compartment and is selected from the group consisting of an ion exchange membrane, a reverse osmosis membrane, and a nanofiltration membrane, which electrochemical device is configured such that it can perform an electrolysis treatment. The apparatus may further include a power supply device, a control device, a temperature control device, and the like that enable the electrolysis treatment.

[0041] The present invention may include the following embodiments:

<1> A method of regenerating a plating composition, the method comprising: removing at least a portion of a surfactant from a plating composition comprising tin (IV) ions and the surfactant; introducing the plating composition, from which at least a portion of the surfactant has been removed, to a working electrode

compartment which comprises a working electrode and is separated from a counter electrode compartment comprising a counter electrode by a membrane selected from the group consisting of an ion exchange membrane, a reverse osmosis membrane, and a nanofiltration membrane, so as to reduce at least a portion of the tin (IV) ions in the introduced plating composition to metallic tin using the working electrode as a cathode; and oxidizing at least a portion of the thus reduced metallic tin to tin (II) ions using the working electrode as an anode.

[0042] <2> The method according to <1>, wherein the at least a portion of the tin (IV) ions form tin (IV) gluconate complexes.

[0043] <3> The method according to <1> or <2>, wherein the ion exchange membrane is a cation exchange membrane.

[0044] <4> The method according to any one of <1> to <3>, wherein the working electrode compartment has a pH of 1 to 13.

[0045] <5> The method according to any one of <1> to <4>, wherein a conductive ion-containing aqueous solution is arranged in the counter electrode compartment.

[0046] <6> The method according to any one of claims <1> to <5>, wherein the process of removing at least a portion of the surfactant from the plating composition comprises bringing the plating composition into contact with an

activated carbon.

[0047] <7> The method according to any one of <1> to <6>, wherein the surfactant comprises at least one selected from the group consisting of a nonionic surfactant, a cationic surfactant, and an amphoteric surfactant.

[0048] <8> The method according to any one of <1> to <7>, wherein the plating composition comprises an antioxidant.

[0049] <9> An apparatus for regenerating a plating composition, the apparatus comprising: a surfactant removing means; a working electrode compartment comprising a working electrode; a counter electrode compartment comprising a counter electrode; and a membrane which separates the working electrode compartment and the counter electrode compartment and is selected from the group consisting of an ion exchange membrane, a reverse osmosis membrane, and a nanofiltration membrane.

[0050] <10> An apparatus for regenerating a plating composition for use in the method for regenerating a plating composition according to any one of <1> to <8>, the apparatus comprising: a surfactant removing means; a working electrode compartment comprising a working electrode; a counter electrode compartment comprising a counter electrode; and a membrane which separates the working electrode compartment and the counter electrode

compartment and is selected from the group consisting of an ion exchange membrane, a reverse osmosis membrane, and a nanofiltration membrane.

5 EXAMPLES

[0051] The present invention will now be described more concretely by way of Examples; however, the present invention is not limited to the below-described Examples.

10 Reference Example

Preparation of Plating Composition

[0052] A plating composition having the following formulation was prepared using purified water, potassium stannate (IV) as a tin (IV) ion source, tin (II)

15 methanesulfonate as a tin (II) ion source, gluconic acid, a cationic surfactant containing decyltrimethylammonium chloride, hydroquinone, and sodium methanesulfonate.

[0053]

 Tin (IV) ion: 0.16 mol/L

20 Tin (II) ion: 0.04 mol/L

 Gluconic acid: 0.8 mol/L

 Methanesulfonic acid: 1.2 mol/L

 Surfactant: 1 g/L

 Hydroquinone: 1 g/L

25 Sodium ion: 1.4 mol/L

Example 1

[0054] The thus prepared plating composition in an amount of 2 L was passed through an activated carbon cartridge (MX, manufactured by Kankyo Technos Co., Ltd.) attached to a filter at room temperature (25°C), and then introduced to a working electrode compartment of an electrochemical device. This electrochemical device was equipped with platinum-coated titanium electrodes as a working electrode and a counter electrode, and the working electrode compartment and a counter electrode compartment were separated by a cation exchange membrane (NOAFION^(TM) 424). A 10-g/L aqueous sodium sulfate solution was added to the counter electrode compartment of the electrochemical device and, using the working electrode as a cathode, a 1-hour electrolysis treatment was performed at a solution temperature of 40°C to 70°C, a current density of 0.1 A/dm² to 0.5 A/dm², and a current value of 36.1 A. Subsequently, using the working electrode as an anode, a 0.5-hour electrolysis treatment was performed at a solution temperature of 20°C to 70°C, a current density of 1 A/dm² to 80 A/dm², and a current value of 34.3 A, whereby a regenerated plating composition was obtained as a treated plating composition.

[0055] For this regenerated plating composition, the

concentration of tin (IV) ions and that of tin (II) ions were evaluated by a combination of redox titration and high-frequency inductively-coupled plasma emission spectroscopy (ICP-AES). Specifically, redox titration was performed with an iodine standard solution in 2 M hydrochloride acid using starch as an indicator to calculate the concentration of tin (II) ions. Further, the total concentration of tin ions was determined by ICP-AES, and the concentration of tin (II) ions was subtracted from the thus determined total concentration to calculate the concentration of tin (IV) ions.

[0056] As a result, in the regenerated plating composition, the concentration of tin (IV) ions and that of tin (II) ions were found to be 0.04 mol/L and 0.16 mol/L, respectively. From this result, the reduction efficiency of tin (IV) ions is evaluated to be 95%. The reduction efficiency is calculated by dividing an integrated current value in the third step by one-half of an integrated current value in the second step.

[0057] In this case, the activated carbon contained in the activated carbon cartridge (MX) had a specific surface area of 437 m²/g and an average pore size of 2.4 nm as determined by the BET method. As for the shape of mesopores, the average pore width on the adsorption side and the average pore width on the desorption side were 6.0

nm and 2.1 nm, respectively, as determined by the INNES method.

[0058] It is noted here that the same results were also obtained when the activated carbon cartridge was changed to
5 YCC-R manufactured by Nihon Filter Co., Ltd.

[0059] In this case, the activated carbon contained in the activated carbon cartridge (YCC-R) had a specific surface area of 1,237 m²/g and an average pore size of 1.8 nm as determined by the BET method. As for the shape of
10 mesopores, the average pore width on the adsorption side and the average pore width on the desorption side were 2.5 nm and 4.0 nm, respectively, as determined by the INNES method.

15 Comparative Example 1

[0060] A treated plating composition was obtained by performing an electrolysis treatment twice in the same manner as in Example 1, except that the plating composition was directly introduced to the working electrode
20 compartment without being passed through the activated carbon cartridge.

[0061] When the concentration of tin (IV) ions and that of tin (II) ions were evaluated for the thus obtained treated plating composition in the same manner as described
25 above, the concentration of tin (IV) ions and that of tin

(II) ions were found to be 0.19 mol/L and 0.01 mol/L, respectively. From this result, the reduction efficiency of tin (IV) ions is evaluated to be 0%.

5 Comparative Example 2

[0062] A treated plating composition was obtained by performing an electrolysis treatment twice in the same manner as in Example 1, except that an electrolysis device in which a working electrode compartment and a counter
10 electrode compartment were not separated by a cation exchange membrane and were thus in a state where a liquid can flow between these compartments was used.

[0063] When the concentration of tin (IV) ions and that of tin (II) ions were evaluated for the thus obtained
15 treated plating composition in the same manner as described above, the concentration of tin (IV) ions and that of tin (II) ions were found to be 0.20 mol/L and 0.0 mol/L, respectively. From this result, the reduction efficiency of tin (IV) ions is evaluated to be 0%.

20 [0064] The disclosure of Japanese Patent Application No. 2022-189216 (filing date: November 28, 2022) is incorporated herein by reference in its entirety. All documents, patent applications, and technical standards cited in the present description are incorporated herein by
25 reference to the same extent as in cases where the

individual documents, patent applications, and technical standards are specifically and individually described to be incorporated by reference.

CLAIMS

[Claim 1] A method of regenerating a plating composition, the method comprising:

removing at least a portion of a surfactant from a plating composition comprising tin (IV) ions and the surfactant;

introducing the plating composition, from which at least a portion of the surfactant has been removed, to a working electrode compartment which comprises a working electrode and is separated from a counter electrode compartment comprising a counter electrode by a membrane selected from the group consisting of an ion exchange membrane, a reverse osmosis membrane, and a nanofiltration membrane, so as to reduce at least a portion of the tin (IV) ions in the introduced plating composition to metallic tin using the working electrode as a cathode; and

oxidizing at least a portion of the thus reduced metallic tin to tin (II) ions using the working electrode as an anode.

[Claim 2] The method according to claim 1, wherein the at least a portion of the tin (IV) ions form tin (IV) gluconate complexes.

[Claim 3] The method according to claim 1 or 2, wherein the ion exchange membrane is a cation exchange membrane.

[Claim 4] The method according to any one of claims 1 to

3, wherein the working electrode compartment has a pH of 1 to 13.

[Claim 5] The method according to any one of claims 1 to 4, wherein a conductive ion-containing aqueous solution is arranged in the counter electrode compartment.

[Claim 6] The method according to any one of claims 1 to 5, wherein the process of removing at least a portion of the surfactant from the plating composition comprises bringing the plating composition into contact with an activated carbon.

[Claim 7] The method according to any one of claims 1 to 6, wherein the surfactant comprises at least one selected from the group consisting of a nonionic surfactant, a cationic surfactant, and an amphoteric surfactant.

[Claim 8] The method according to any one of claims 1 to 7, wherein the plating composition comprises an antioxidant.

[Claim 9] An apparatus for regenerating a plating composition, the apparatus comprising:

- 20 a surfactant removing means;
- a working electrode compartment comprising a working electrode;
- a counter electrode compartment comprising a counter electrode; and
- 25 a membrane which separates the working electrode

compartment and the counter electrode compartment and is selected from the group consisting of an ion exchange membrane, a reverse osmosis membrane, and a nanofiltration membrane.