

DESCRIPTION

Title of Invention: CHEMICAL POLISHING SOLUTION USED FOR SURFACE TREATMENT OF COPPER OR COPPER ALLOYS, AND SURFACE TREATMENT METHOD

Technical Field

[0001]

The present invention relates to a chemical polishing solution used for the surface treatment of copper or copper alloy, a surface treatment method for copper or copper alloy using the same, and a method for producing copper or copper alloy whose surface is treated.

Background Art

[0002]

In lead frames and the like used in semiconductor packages, the surface of copper or copper alloy may be plated with nickel, gold, or the like. In such plating, in general, a natural oxide film or an organic substance is present on the surface of copper or copper alloy. If the plating is carried out without removing such a natural oxide film or an organic substance, color unevenness (plating unevenness) may be generated in some cases, or the thickness of the plating may become ununiform.

Hence, in order to suppress generation of color unevenness attended with plating or in order to uniform the thickness of the plating, it is desired to appropriately remove a natural oxide film or an organic substance present on the surface of copper or copper alloy from the surface thereof. However, conventional chemical solutions (for example, Patent Literatures 1 to 3) have been problematic in that a part of such a natural oxide film or an organic substance remains without being removed, or in that color unevenness occurs after completion of the plating due to such a remaining natural oxide film or organic substance.

Citation List

Patent Literature

[0003]

Patent Literature 1: Japanese Patent Publication (Kokai) No. 9-184081 A (1997)

Patent Literature 2: Japanese Patent Publication (Kokai) No. 2017-031502 A

Patent Literature 3: Japanese Patent Publication (Kokai) No. 2017-195311 A

Summary of Invention

Technical Problem

[0004]

Under such circumstances, it is desired to provide a treatment solution for appropriately removing a natural oxide film or an organic substance existing on the surface of copper or copper alloy. When the surface of copper or copper alloy is treated, a part of the copper or the copper alloy may be dissolved in the treatment solution. It is further desired to provide a treatment solution having stable performance to remove the natural oxide film or the organic substance, regardless of the amount of the copper or the copper alloy dissolved in the treatment solution.

Solution to Problem

[0005]

The present invention relates to a chemical polishing solution, a surface treatment method, and a method for producing copper or copper alloy whose surface is treated, as described below.

[1] A chemical polishing solution used for the surface treatment of copper or copper alloy, comprising:

(A) 0.1% to 3.5% by mass of hydrogen peroxide, based on the total amount of the chemical polishing solution,

(B) 1% to 20% by mass of one or more types selected from the group consisting of sulfuric acid and nitric acid, based on the total amount of the chemical polishing solution,

(C) 0.05% to 0.8% by mass of a fluoride, as a content relative to fluorine atoms, based on the total amount of the chemical polishing solution,

(D) 0.01% to 4% by mass of one or more types selected from the group consisting of anthranilic acid, cyclohexylamine, cyclohexanol, and 1,5-pentanediol, based on the total amount of the chemical polishing solution,

(E) 0.0005% to 0.005% by mass of a fluorine-based surfactant, based on the total amount of the chemical polishing solution, and

(F) water.

[2] The chemical polishing solution according to the above [1], wherein the pH of the chemical polishing solution is 3 or less.

[3] The chemical polishing solution according to the above [1] or [2], wherein the component (C) is one or more types selected from the group consisting of potassium acid

fluoride, ammonium acid fluoride, and hydrogen fluoride.

[4] The chemical polishing solution according to any one of the above [1] to [3], wherein the component (B) is sulfuric acid.

[5] The chemical polishing solution according to any one of the above [1] to [4], wherein the component (D) comprises one or more types selected from the group consisting of cyclohexanol and cyclohexylamine.

[6] The chemical polishing solution according to any one of the above [1] to [5], wherein the component (E) comprises one or more types selected from the group consisting of a perfluoroalkyl group, a perfluoroalkenyl group, and a perfluorophenyl group.

[7] A surface treatment method for copper or copper alloy, the method comprising contacting the chemical polishing solution according to any one of the above [1] to [6] with the surface of copper or copper alloy to perform a surface treatment on the copper or the copper alloy.

[8] The surface treatment method according to the above [7], wherein the temperature of the chemical polishing solution is 25°C to 50°C upon performing the surface treatment on the copper or the copper alloy.

[9] The surface treatment method according to the above [7] or [8], wherein the time required for contacting the chemical polishing solution with the surface of the copper or the copper alloy to perform the surface treatment on the copper or the copper alloy is 1 second or more and 10 minutes or less.

[10] A method for producing copper or copper alloy whose surface is treated, the method comprising contacting the chemical polishing solution according to any one of the above [1] to [6] with the surface of copper or copper alloy to perform a surface treatment on the copper or the copper alloy.

[11] A method for producing the chemical polishing solution according to any one of the above [1] to [6], the method comprising uniformly stirring, at least, the component (A), the component (B), the component (C), the component (D), the component (E), and the component (F).

Advantageous Effects of Invention

[0006]

According to a preferred embodiment of the present invention, by treating the surface of copper or copper alloy using the chemical polishing solution of the present invention, natural oxides or organic substances present on the surface of the copper or the copper alloy can be appropriately removed, while keeping low the amount of the copper

or the copper alloy dissolved, and thus, the surface of the copper or the copper alloy, on which no color unevenness occurs or the occurrence of color unevenness is suppressed, can be obtained. According to a more preferred embodiment of the present invention, the chemical polishing solution of the present invention is also excellent in terms of storage stability. In addition, according to a further preferred embodiment of the present invention, in the case of the chemical polishing solution of the present invention, even if the copper concentration in the chemical polishing solution is increased due to repetitive use, the performance of the present chemical polishing solution to remove natural oxide films or organic substances is stable.

Brief Description of Drawings

[0007]

[Figure 1] Figure 1 is a photograph showing an example in which the color unevenness of a surface treated product due to a chemical polishing solution was observed.

[Figure 2] Figure 2 is a photograph showing an example in which the color unevenness of a surface treated product due to a chemical polishing solution was not observed.

Description of Embodiments

[0008]

1. Chemical polishing solution

The chemical polishing solution of the present invention is a chemical polishing solution used for the surface treatment of copper or copper alloy, which is characterized in that it comprises:

- (A) 0.1% to 3.5% by mass of hydrogen peroxide, based on the total amount of the chemical polishing solution,
- (B) 1% to 20% by mass of one or more types selected from the group consisting of sulfuric acid and nitric acid, based on the total amount of the chemical polishing solution,
- (C) 0.05% to 0.8% by mass of a fluoride, as a content relative to fluorine atoms, based on the total amount of the chemical polishing solution,
- (D) 0.01% to 4% by mass of one or more types selected from the group consisting of anthranilic acid, cyclohexylamine, cyclohexanol, and 1,5-pentanediol, based on the total amount of the chemical polishing solution,
- (E) 0.0005% to 0.005% by mass of a fluorine-based surfactant, based on the total amount of the chemical polishing solution, and
- (F) water.

The chemical polishing solution of the present invention is used to remove

natural oxide films or organic substances that are present on the surface of copper or copper alloy. Herein, the "copper alloy" is not particularly limited, as long as it is alloy comprising copper as a main component. The content of copper in such copper alloy is preferably 50% by mass or more, more preferably 60% by mass or more, further preferably 70% by mass or more, still further preferably 80% by mass or more, and particularly preferably 90% by mass or more. The content of the copper in the copper alloy may also be 95% by mass or more.

[0009]

(A) Hydrogen peroxide

In the chemical polishing solution of the present invention, hydrogen peroxide (hereinafter also referred to as a "component (A)") serves as an oxidizer having an action to oxidize copper, or copper contained in copper alloy. In general, hydrogen peroxide is preferably used as a hydrogen peroxide aqueous solution, in terms of availability and operability. The grade of the hydrogen peroxide aqueous solution is not particularly limited, and hydrogen peroxides having various grades, such as those for use in industry and electronics industry, can be used.

[0010]

In the chemical polishing solution of the present invention, the content of the hydrogen peroxide is 0.1% to 3.5% by mass, preferably 0.5% to 2.0% by mass, and more preferably 0.7% to 1.6% by mass, based on the total mass of the chemical polishing solution, and further, from the view point of the solubility of copper, the content of hydrogen peroxide is further preferably 0.7% to 1.2% by mass. If the content of hydrogen peroxide is within the above-described range, natural oxide films or organic substances can be appropriately removed from the surface of copper or copper alloy. Moreover, the amount of copper dissolved can be kept low, and the localized corrosion of the copper or the copper alloy can be suppressed. It is to be noted that a numerical value range is shown in the present description, the upper limit value and the lower limit value can be arbitrarily combined with each other.

[0011]

(B) One or more types selected from group consisting of sulfuric acid and nitric acid

In the chemical polishing solution of the present invention, sulfuric acid and nitric acid promote dissolution of copper or a copper compound contained in the copper oxidized by the component (A) or the copper alloy oxidized by the component (A), and the content of the one or more types selected from the group consisting of sulfuric acid and nitric acid (hereinafter also referred to as a "component (B)") is 1% to 20% by mass, preferably 3% to 18% by mass, more preferably 4% to 16% by mass, and further

preferably 5% to 15% by mass, based on the total mass of the chemical polishing solution. When both sulfuric acid and nitric acid are used as components (B), it is adequate if the total amount of these components satisfies the above-described range. If the content of the component (B) is within the above-described range, natural oxide films or organic substances can be appropriately removed from the surface of copper or copper alloy. Moreover, the amount of copper dissolved can be kept low, and the localized corrosion of the copper or the copper alloy can be suppressed. Sulfuric acid is particularly preferably used as such a component (B) because it widens the range of choices for containers used upon storage of the chemical polishing solution of the present invention.

[0012]

(C) Fluoride

In the chemical polishing solution of the present invention, a fluoride (hereinafter also referred to as a "component (C)") is not particularly limited, as long as it generates fluorine ions in the chemical polishing solution. The fluoride is preferably one or more types selected from the group consisting of potassium acid fluoride, ammonium acid fluoride, and hydrogen fluoride. Among these, from the viewpoint of low toxicity, potassium acid fluoride and ammonium acid fluoride are more preferable, and potassium acid fluoride is particularly preferable.

[0013]

In the chemical polishing solution of the present invention, the content of the fluoride is, as a content relative to fluorine atoms, 0.05% to 0.8% by mass, preferably 0.1% to 0.6% by mass, more preferably 0.15% to 0.5% by mass, and further preferably 0.2% to 0.4% by mass, based on the total mass of the chemical polishing solution. When two or more types of fluorides are used as components (C), it is adequate if the total amount of the fluorides satisfies the above-described range. If the content of the fluoride is within the above-described range, natural oxide films or organic substances can be appropriately removed from the surface of copper or copper alloy. Moreover, the amount of copper dissolved can be kept low, and the localized corrosion of the copper or the copper alloy can be suppressed.

[0014]

(D) One or more types selected from group consisting of anthranilic acid, cyclohexylamine, cyclohexanol, and 1,5-pentanediol

In the chemical polishing solution of the present invention, anthranilic acid, cyclohexylamine, cyclohexanol, and 1,5-pentanediol adsorb on the surface of copper or copper alloy, and act on the removability of natural oxide films or organic substances and the solubility of copper. The content of the one or more types selected from the group

consisting of anthranilic acid, cyclohexylamine, cyclohexanol, and 1,5-pentanediol (hereinafter also referred to as a "component (D)") is 0.01% to 4% by mass, preferably 0.05% to 3.5% by mass, more preferably 0.1% to 3.3% by mass, and further preferably 0.2% to 3% by mass, based on the total mass of the chemical polishing solution. When two or more types of substances are used as components (D), it is adequate if the total amount of the substances satisfies the above-described range. If the content of the component (D) is within the above-described range, natural oxide films or organic substances can be appropriately removed from the surface of copper or copper alloy. Moreover, the amount of copper dissolved can be kept low, and the localized corrosion of the copper or the copper alloy can be suppressed. Taking into consideration the storage stability of the chemical polishing solution, as such a component (D), cyclohexylamine, cyclohexanol, or a combination thereof is preferable.

[0015]

(E) Fluorine-based surfactant

In the chemical polishing solution of the present invention, a fluorine-based surfactant (hereinafter referred to as a "component (E)") adsorbs on the surface of copper or copper alloy, and acts on the removability of natural oxide films or organic substances and the solubility of copper. By allowing the chemical polishing solution of the present invention to comprise the component (E), even if the copper concentration increases in the chemical polishing solution due to repetitive use, the performance of the present chemical polishing solution to remove natural oxide films or organic substances tends to be stabilized.

The fluorine-based surfactant preferably comprises one or more types of groups selected from the group consisting of a perfluoroalkyl group, a perfluoroalkenyl group, and a perfluorophenyl group. Among others, the fluorine-based surfactant more preferably comprises a perfluoroalkyl group.

Examples of the fluorine-based surfactant may include:

perfluoroalkyl carboxylate, perfluoroalkyl sulfonate, perfluoroalkyl quaternary ammonium salt, perfluoroalkyl phosphate, perfluoroalkyl phosphonate, perfluoroalkyl ethylene oxide adduct, perfluoroalkylamine oxide, perfluoroalkyl carboxylic acid ester, perfluoroalkyl phosphoric acid ester, perfluoroalkyl phosphonic acid ester, and perfluoroalkyl-containing oligomer;

perfluoroalkenyl carboxylate, perfluoroalkenyl sulfonate, perfluoroalkenyl quaternary ammonium salt, perfluoroalkenyl phosphate, perfluoroalkenyl phosphonate, perfluoroalkenyl ethylene oxide adduct, perfluoroalkenylamine oxide, perfluoroalkenyl carboxylic acid ester, perfluoroalkenyl phosphoric acid ester, perfluoroalkenyl

phosphonic acid ester, and perfluoroalkenyl-containing oligomer; and

perfluorophenyl carboxylate, perfluorophenyl sulfonate, perfluorophenyl quaternary ammonium salt, perfluorophenyl phosphate, perfluorophenyl phosphonate, perfluorophenyl ethylene oxide adduct, perfluorophenylamine oxide, perfluorophenyl carboxylic acid ester, perfluorophenyl phosphoric acid ester, perfluorophenyl phosphonic acid ester, and perfluorophenyl-containing oligomer.

[0016]

In the chemical polishing solution of the present invention, the content of the fluorine-based surfactant is 0.0005% to 0.005% by mass, preferably 0.0006% to 0.004% by mass, more preferably 0.0007% to 0.003% by mass, and further preferably 0.0007% to 0.002% by mass, based on the total mass of the chemical polishing solution. When two or more types of fluorine-based surfactants are used as components (E), it is adequate if the total amount of the surfactants satisfies the above-described range. If the content of the fluorine-based surfactant is within the above-described range, the wettability of the surface of copper or copper alloy can be improved, and thus, a surface treatment can be more uniformly carried out. Moreover, even if the copper concentration increases in the chemical polishing solution due to repetitive use, the performance of the present chemical polishing solution to remove natural oxide films or organic substances tends to be stabilized.

[0017]

(F) Water

The chemical polishing solution of the present invention comprises water (hereinafter referred to as a "component (F)") as a diluent. Water, from which metal ions, organic impurities, particles and the like are removed by distillation, an ion exchange treatment, a filter treatment, various types of adsorption treatments, etc., is preferable, and pure water or ultrapure water is particularly preferable. The content of the water means the rest of the above-described components (A) to (E) and optional components, and it is preferably 40% by mass or more, more preferably in the range of 40% to 99% by mass, further preferably 50% to 97% by mass, still further preferably 60% to 95% by mass, and particularly preferably 70% to 95% by mass, based on the total mass of the chemical polishing solution.

[0018]

(G) Other components

Other than the above-described components (A) to (F), the chemical polishing solution of the present invention may comprise various types of additives including known hydrogen peroxide stabilizers, etc., such as alcohols, urea, and organic carboxylic

acids, which are commonly used in the chemical polishing solution, in a range in which the additives do not inhibit the effects of the chemical polishing solution.

[0019]

Besides, the chemical polishing solution of the present invention is preferably a solution, and the present chemical polishing solution does not contain solid particles such as polishing particles.

[0020]

< pH Range >

The pH range of the chemical polishing solution of the present invention is not particularly limited, and it is preferably pH 3 or less, more preferably pH 2 or less, and further preferably pH 1 or less. The pH value can be measured, for example, by the method described in Examples. For example, when the pH value is measured by the method described in Examples, the lower limit value of the pH of the chemical polishing solution of the present invention is preferably pH -2.

In order to adjust the pH range of the chemical polishing solution of the present invention, a pH adjuster may be added to the present chemical polishing solution, as necessary. Examples of the pH adjuster that can be used herein may include potassium hydroxide, sodium hydroxide, lithium hydroxide, cesium hydroxide, triethylamine, ammonia, tetramethyl ammonium hydroxide, ethanolamine, and 1-amino-2-propanol. The pH adjuster may be used alone as a single type, or may also be used in combination of two or more types.

[0021]

< Preparation method >

The chemical polishing solution of the present invention can be prepared by uniformly stirring the component (A) to the component (F) and further, as necessary, other components. The method of stirring these components is not particularly limited, and a stirring method generally used in the preparation of a chemical polishing solution can be adopted. Besides, a part of or the entire water used as a component (F) may be added later. Moreover, a solution comprising the component (A) to the component (E), a part of the component (F), and further, as necessary, other components, has been previously prepared and stored, and then, at the time of use, the storage solution may be diluted with the rest of the component (F) and may be used.

[0022]

< Amount of copper or copper alloy dissolved >

By performing a surface treatment using the chemical polishing solution of the present invention, natural oxide films or organic substances that are present on the surface

of copper or copper alloy can be removed from the surface thereof. During this surface treatment, the amount of the copper or the copper alloy dissolved is preferably as small as possible. If the amount of the copper or the copper alloy dissolved is large, a difference is easily made in the thickness of the copper or the copper alloy. Thus, when plating is then performed, it becomes difficult to uniform the plating thickness. In addition, if the amount of the copper or the copper alloy dissolved is large, color unevenness may unfavorably occur on the surface of the copper or the copper alloy. For example, from the economic viewpoint, the amount of the copper or the copper alloy dissolved by the surface treatment is preferably 4 μm or less, more preferably 2 μm or less, and further preferably 1 μm or less. The amount of the copper or the copper alloy dissolved can be measured by the method described in Examples.

The dissolving rate of the copper or the copper alloy associated with the surface treatment using the chemical polishing solution of the present invention is not particularly limited. In order to adjust the treatment time to an appropriate range, the dissolving rate is preferably 0.1 to 24 $\mu\text{m}/\text{min}$, more preferably 0.2 to 10 $\mu\text{m}/\text{min}$, and further preferably 0.4 to 5 $\mu\text{m}/\text{min}$.

[0023]

According to a preferred embodiment of the present invention, by treating the surface of copper or copper alloy using the chemical polishing solution of the present invention, natural oxides or organic substances present on the surface of the copper or the copper alloy can be appropriately removed from the surface thereof, while keeping the amount of the copper or the copper alloy dissolved low, and thus, the surface of the copper or the copper alloy, on which no color unevenness occurs or the occurrence of color unevenness is suppressed, can be obtained.

[0024]

2. Surface treatment method

The surface treatment method of the present invention comprises contacting the aforementioned chemical polishing solution of the present invention with the surface of copper or copper alloy to perform a surface treatment on the copper or the copper alloy. According to a preferred embodiment of the present invention, by performing a surface treatment on copper or copper alloy using the chemical polishing solution of the present invention, natural oxides or organic substances present on the surface of the copper or the copper alloy can be appropriately removed from the surface thereof, while keeping the amount of the copper or the copper alloy dissolved low. Accordingly, the surface of the copper or the copper alloy, on which no color unevenness occurs or the occurrence of color unevenness is suppressed, can be obtained.

[0025]

In the present invention, the method of contacting the surface of copper or copper alloy with a chemical polishing solution is not particularly limited. For example, a method of contacting the surface of copper or copper alloy with the chemical polishing solution by a system such as dropping (a single-wafer spinning treatment) or spraying of the chemical polishing solution, and a method of immersing the surface of copper or copper alloy in the chemical polishing solution, are preferably adopted herein as methods of contacting the surface of copper or copper alloy with the chemical polishing solution.

[0026]

The temperature of the chemical polishing solution upon performing a surface treatment on the copper or the copper alloy is not particularly limited. In general, the temperature of the chemical polishing solution is, for example, 0°C to 70°C, preferably 25°C to 50°C, more preferably 25°C to 45°C, and further preferably 30°C to 40°C. If the temperature of the chemical polishing solution is 25°C or higher, the chemical polishing rate does not become too slow, and thus, a reduction in production efficiency can be suppressed. On the other hand, if the temperature of the chemical polishing solution is 50°C or lower, a change in the solution composition can be suppressed, and surface treatment conditions can be kept constant. The chemical polishing rate is increased by increasing the temperature of the chemical polishing solution. Taking into consideration keeping a change in the composition of the chemical polishing solution low, etc., the optimal treatment temperature may be determined, as appropriate.

[0027]

The time required for contacting the chemical polishing solution with the surface of copper or copper alloy to perform a surface treatment on the copper or the copper alloy (i.e. the treatment time) is not particularly limited. In general, the treatment time is preferably 1 second or more and 10 minutes or less, more preferably 10 seconds or more and 5 minutes or less, and further preferably 20 seconds or more and 3 minutes or less. The optimal treatment time may be selected, as appropriate, depending on the method of contacting the surface of copper or copper alloy with the chemical polishing solution, the temperature of the chemical polishing solution, and the like.

[0028]

Before performing a surface treatment on copper or copper alloy using the chemical polishing solution of the present invention, a degreasing treatment may be performed on the surface of the copper or the copper alloy, as necessary, using an organic solvent such as alcohol or acetone.

After contacting the chemical polishing solution of the present invention with

the surface of the copper or the copper alloy to perform a surface treatment on the surface of the copper or the copper alloy, the surface may be appropriately washed with water or sulfuric acid, as necessary. In addition, a neutralization treatment with sodium carbonate, or an anti-corrosion treatment with an aqueous solution containing a corrosion inhibitor may also be carried out.

[0029]

3. Method for producing copper or copper alloy whose surface is treated

The present invention also includes a method for producing copper or copper alloy whose surface is treated, wherein the method comprises contacting the above-described chemical polishing solution with the surface of copper or copper alloy to perform a surface treatment on the copper or the copper alloy.

By contacting the chemical polishing solution of the present invention with the surface of copper or copper alloy to perform a surface treatment on the copper or the copper alloy, natural oxide films or organic substances that are present on the surface of the copper or the copper alloy can be removed from the surface thereof, so that the copper or the copper alloy, on the surface of which no color unevenness occurs or the occurrence of color unevenness is suppressed, can be obtained.

Examples

[0030]

Hereinafter, the present invention will be described in more detail, using examples and comparative examples. However, these examples are not intended to limit the scope of the present invention.

[0031]

The method of measuring the physical properties of a chemical polishing solution, the physical properties of copper or copper alloy, the method of evaluating the amount of copper or copper alloy dissolved of a surface treated product, the method of evaluating the treatment unevenness of a surface treated product, which are applied in the following examples and comparative examples, are as follows.

[0032]

(1) Measurement of pH of chemical polishing solution

Using a pH meter (HORIBA, Ltd., product name: "D-53"), the pH of a chemical polishing solution at 25°C was measured in accordance with JIS Z 8802.

[0033]

(2) Types of coppers and copper alloy

The following 4 types of coppers and copper alloy were used.

- (a) Corson alloy (NKC-4419-H): thickness: 0.2 mm, 50 x 30 mm (depth x width) (manufactured by Test-Piece K.K.), Co: 1.9% by mass, Si: 0.44% by mass, Cu: the rest
- (b) Pure copper: thickness: 0.2 mm, 50 x 30 mm (depth x width) (manufactured by Test-Piece K.K.), Cu: 100% by mass
- (c) Phosphor bronze: thickness: 0.2 mm, 50 x 30 mm (depth x width) (manufactured by Test-Piece K.K.), Sn: 5.5% to 7.0% by mass, P: 0.03% to 0.35% by mass, Pb: 0.02% by mass or less, Fe: 0.1% by mass or less, Zn: 0.2% by mass or less, Cu: the rest, Cu + Sn + P: 99.5% by mass or more
- (d) Be bronze: thickness: 0.2 mm, 50 x 30 mm (depth x width) (manufactured by Test-Piece K.K.), Be: 1.8% to 2.0% by mass, Co + Ni: 0.2% by mass or more, Co + Ni + Fe: 0.6% by mass or less, Cu + Be + Co + Ni + Fe: 99.5% by mass or more

[0034]

(3) Evaluation of amount of copper or copper alloy dissolved by surface treatment

A copper piece or copper alloy piece was immersed in a chemical polishing solution at a liquid temperature of 30°C for 30 seconds. Subsequently, after completion of the immersion, the copper piece or the copper alloy piece was removed from the chemical polishing solution. Thereafter, the copper piece or the copper alloy piece was fully washed with ion exchange water, and was then fully dried to obtain a surface treated product. The amount of the copper or the copper alloy dissolved was calculated as a weight reduced before and after the surface treatment according to the following equation:

$$\text{Amount dissolved } [\mu\text{m}] = (\text{Mass before treatment [g]} - \text{mass after treatment [g]}) / (\text{Treated area [m}^2\text{] of copper piece or copper alloy piece} \times 8.92 \text{ [g/cm}^3\text{] (copper specific gravity)}).$$

[0035]

(4) Evaluation of treatment unevenness of surface treated product

The surface condition of a surface treated product was observed by visual inspection, and the presence or absence of treatment unevenness was evaluated. Figure 1 is a photograph showing an example in which the color unevenness of a surface treated product due to a chemical polishing solution was observed. Figure 2 is a photograph showing an example in which the color unevenness of a surface treated product due to a chemical polishing solution was not observed.

[0036]

Example 1

(1) Preparation of chemical polishing solution

1.6 Parts by mass of hydrogen peroxide (manufactured by MITSUBISHI GAS CHEMICAL COMPANY, INC., 60% by mass aqueous solution) (wherein 1.6 parts by

mass indicate the active ingredient ratio as hydrogen peroxide; hydrogen peroxide is also referred to as "HP" in the Tables of Examples and Comparative Examples), 14.1 parts by mass of sulfuric acid (manufactured by MITSUBISHI GAS CHEMICAL COMPANY, INC., 46% by mass aqueous solution) (wherein 14.1 parts by mass indicate the active ingredient ratio as sulfuric acid), 0.9 parts by mass of potassium acid fluoride (manufactured by Daiwa Fine Chemicals Co., Ltd.) (0.4 parts by mass relative to fluorine atoms), 0.09 parts by mass of anthranilic acid (manufactured by Mitsuboshi Chemical Co., Ltd.), and 0.0018 parts by mass of a fluorine-based surfactant "Surflon S-243" (manufactured by AGC SEIMI CHEMICAL CO., LTD., a fluorine-based nonionic surfactant having a perfluoroalkyl group) were mixed with one another, and water was further added to the mixture, so that the amount of the water became 83.3 parts by mass (the rest) in the total mass of a chemical polishing solution, thereby preparing a chemical polishing solution.

[0037]

(2) Surface treatment of copper and copper alloy

A copper piece or copper alloy piece was immersed in a chemical polishing solution at a liquid temperature of 30°C for 30 seconds. Subsequently, after completion of the immersion, the copper piece or the copper alloy piece was removed from the chemical polishing solution. Thereafter, the copper piece or the copper alloy piece was fully washed with ion exchange water, and was then fully dried to obtain a surface treated product.

The evaluation results of the amount of the copper or the copper alloy dissolved by the surface treatment and the treatment unevenness of the surface treated product are shown in Table 1-2.

[0038]

Examples 2 to 12

Chemical polishing solutions were prepared in the same manner as that of Example 1, with the exception that the compositions of the chemical polishing solutions were changed to those shown in Table 1-1, and a surface treatment was then carried out on copper and copper alloy, using each chemical polishing solution. It is to be noted that (A), (B), (C), (D), (E) and (F) in Table 1-1 indicate the component (A), the component (B), the component (C), the component (D), the component (E) and the component (F), respectively. The same applies to Table 2 to Table 5.

The evaluation results of the amount of the copper or the copper alloy dissolved by the surface treatment and the treatment unevenness of the surface treated product are shown in Table 1-2.

[0039]

[Table 1-1]

Table 1-1

	Composition of chemical polishing solution [wt%]						
	(A)	(B)	(C)	(C)	(D)	(E)	(F)
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Anthranilic acid	Surflon S-243	Water
Example 1	1.6	14.1	0.9	0.4	0.09	0.0018	Rest wt%
Example 2	1.1	9.6	0.6	0.3	0.06	0.0012	Rest wt%
Example 3	0.8	7.3	0.5	0.2	0.05	0.0009	Rest wt%
Example 4	0.7	5.7	0.4	0.2	0.04	0.0007	Rest wt%
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Cyclohexylamine	Surflon S-243	Water
Example 5	1.6	14.1	0.9	0.4	0.06	0.0018	Rest wt%
Example 6	1.1	9.6	0.6	0.3	0.04	0.0012	Rest wt%
Example 7	0.8	7.3	0.5	0.2	0.03	0.0009	Rest wt%
Example 8	0.7	5.7	0.4	0.2	0.02	0.0007	Rest wt%
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Cyclohexanol	Surflon S-243	Water
Example 9	1.6	14.1	0.9	0.4	0.6	0.0018	Rest wt%
Example 10	1.1	9.6	0.6	0.3	0.4	0.0012	Rest wt%
Example 11	0.8	7.3	0.5	0.2	0.3	0.0009	Rest wt%
Example 12	0.7	5.7	0.4	0.2	0.2	0.0007	Rest wt%

[0040]

[Table 1-2]

Table 1-2

	Evaluation results							
	NKC-4419-H		Pure copper		Phosphor bronze		Be bronze	
	Amount dissolved [μm]	Treatment unevenness	Amount dissolved [μm]	Treatment unevenness	Amount dissolved [μm]	Treatment unevenness	Amount dissolved [μm]	Amount dissolved [μm]
Example 1	0.4	No	0.4	No	0.5	No	0.6	No
Example 2	0.3	No	0.3	No	0.4	No	0.5	No
Example 3	0.3	No	0.2	No	0.3	No	0.4	No
Example 4	0.2	No	0.2	No	0.2	No	0.3	No
	Amount dissolved [μm]	Treatment unevenness	Amount dissolved [μm]	Treatment unevenness	Amount dissolved [μm]	Treatment unevenness	Amount dissolved [μm]	Amount dissolved [μm]
Example 5	1.7	No	1.8	No	1.1	No	1.5	No
Example 6	1	No	1.2	No	0.7	No	1	No
Example 7	0.9	No	1	No	0.6	No	0.7	No
Example 8	0.6	No	0.8	No	0.4	No	0.6	No
	Amount dissolved [μm]	Treatment unevenness	Amount dissolved [μm]	Treatment unevenness	Amount dissolved [μm]	Treatment unevenness	Amount dissolved [μm]	Amount dissolved [μm]
Example 9	1.7	No	1.8	No	1.2	No	1.6	No
Example 10	1.2	No	1.3	No	0.8	No	1.1	No
Example 11	0.9	No	0.9	No	0.6	No	0.8	No
Example 12	0.7	No	0.8	No	0.5	No	0.7	No

[0041]

Examples 13 to 15

Chemical polishing solutions were prepared in the same manner as that of Example 1, with the exception that the compositions of the chemical polishing solutions were changed to those shown in Table 2, and a surface treatment was then carried out on copper and copper alloy, using each chemical polishing solution.

The evaluation results of the amount of the copper or the copper alloy dissolved by the surface treatment and the treatment unevenness of the surface treated product are shown in Table 2.

[0042]

[Table 2]

Table 2

	Composition of chemical polishing solution [wt%]							Evaluation results	
	(A)	(B)	(C)	(C)	(D)	(E)	(F)	NKC-4419-H	
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Cyclohexylamine	Surflon S-243	Water	Amount dissolved [μ m]	Treatment unevenness
Example 13	1.6	14.1	0.9	0.4	2.9	0.0018	Rest wt%	1.4	No
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Cyclohexanol	Surflon S-243	Water	Amount dissolved [μ m]	Treatment unevenness
Example 14	1.6	14.1	0.9	Relative to F atoms	2.9	0.0018	Rest wt%	1.6	No
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	1,5-pentanediol	Surflon S-243	Water	Amount dissolved [μ m]	Treatment unevenness
Example 15	1.6	14.1	0.9	0.4	2.9	0.0018	Rest wt%	1.4	No

[0043]

Comparative Examples 1 to 15

Chemical polishing solutions were prepared in the same manner as that of Example 1, with the exception that the compositions of the chemical polishing solutions were changed to those shown in Table 3, and a surface treatment was then carried out on copper and copper alloy, using each chemical polishing solution.

The evaluation results of the amount of the copper or the copper alloy dissolved by the surface treatment and the treatment unevenness of the surface treated product are shown in Table 3.

[0044]

[Table 3]

Table 3

	Composition of chemical polishing solution [wt%]						Evaluation results	
	(A)	(B)	(C)	(C)	(D)	(E)	(F)	NKC-4419-H
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms		Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 1	1.6	14.1	0.9	0.4		0.0018	Rest wt%	1.2
								Yes
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	3-Aminobenzoic acid	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 2	1.6	14.1	0.9	0.4	0.09	0.0018	Rest wt%	0.3
								Slightly
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Benzoic acid	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 3	1.6	14.1	0.9	0.4	0.09	0.0018	Rest wt%	1.2
								Treatment unevenness
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Aniline	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 4	1.6	14.1	0.9	0.4	0.09	0.0018	Rest wt%	1.2
								Yes
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Citric acid	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 5	1.6	14.1	0.9	0.4	0.6	0.0018	Rest wt%	1.2
								Slightly
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	DL-Tartaric acid	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 6	1.6	14.1	0.9	0.4	0.6	0.0018	Rest wt%	1
								Treatment unevenness
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Dimethylamine	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 7	1.6	14.1	0.9	0.4	0.06	0.0018	Rest wt%	1.1
								Yes
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Diethanolamine	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 8	1.6	14.1	0.9	0.4	0.06	0.0018	Rest wt%	1.2
								Yes
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Sulfamic acid	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 9	1.6	14.1	0.9	0.4	0.6	0.0018	Rest wt%	1.2
								Treatment unevenness
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Tetraethylene pentamine	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 10	1.6	14.1	0.9	0.4	0.6	0.0018	Rest wt%	0.5
								Slightly
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Diisopropylamine	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 11	1.6	14.1	0.9	0.4	0.6	0.0018	Rest wt%	1.2
								Yes
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Propylene glycol	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 12	1.6	14.1	0.9	0.4	0.06	0.0018	Rest wt%	1.2
								Yes
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Ethylene glycol	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 13	1.6	14.1	0.9	0.4	0.06	0.0018	Rest wt%	1.1
								Yes
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Cyclohexylamine	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 14	4.0	14.1	0.9	0.4	0.06	0.0018	Rest wt%	4.2
								No
	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Cyclohexylamine	Surflon S-243	Water	Amount dissolved [μm]
Comp.Ex. 15	6.0	14.1	0.9	0.4	0.06	0.0018	Rest wt%	5.4
								No

[0045]

Examples 16 to 21

Surface treated products were obtained by changing the compositions of chemical polishing solutions to those shown in Table 4. Specifically, a storage solution prepared by mixing the components (A) to (F) with one another was stored at room temperature ($20^{\circ}\text{C}\pm 5^{\circ}\text{C}$) for 3 months, and thereafter, the storage solution was diluted with water to prepare a chemical polishing solution. Subsequently, a surface treatment was carried out on copper and copper alloy in the same manner as that of Example 1, using the prepared chemical polishing solution, so as to obtain a surface treated product.

The evaluation results of the amount of the copper or the copper alloy dissolved by the surface treatment and the treatment unevenness of the surface treated product are shown in Table 4. In Table 4, for comparison, the evaluation results of the amount of the copper or the copper alloy dissolved by the surface treatment and the treatment unevenness of the surface treated product, which were obtained using a chemical polishing solution having the same composition with the exception that a storage solution was not stored at room temperature for 3 month, are also shown.

As shown in Table 4, it was found that, when cyclohexylamine or cyclohexanol was used as a component (D), the obtained chemical polishing solution was excellent also in terms of storage stability.

[0046]

[Table 4]

Table 4

	Composition of chemical polishing solution [wt%]							Evaluation results		
	(A)	(B)	(C)	(G)	(D)	(E)	(F)	Amount dissolved [μm]	Treatment unevenness	Remarks
HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Anthranilic acid	Surflon S-243	Water				
2.8	24.0	1.5	0.7	0.15	0.0030	Rest wt%		–	–	Composition of storage solution
Identical to Ex. 1	1.6	14.1	0.9	0.4	0.0018	Rest wt%		0.4	No	Not stored for 3 months
Ex. 16	1.6	14.1	0.9	0.4	0.0018	Rest wt%		0.8	Yes	Use after storage at room temperature for 3 months
Identical to Ex. 2	1.1	9.6	0.6	0.3	0.0012	Rest wt%		0.3	No	Not stored for 3 months
Ex. 17	1.1	9.6	0.6	0.3	0.0012	Rest wt%		0.6	Yes	Use after storage at room temperature for 3 months
HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Cyclohexylamine	Surflon S-243	Water				
2.8	24.0	1.5	0.7	0.10	0.0030	Rest wt%		–	–	Composition of storage solution
Identical to Ex. 5	1.6	14.1	0.9	0.4	0.0018	Rest wt%		1.7	No	Not stored for 3 months
Ex. 18	1.6	14.1	0.9	0.4	0.0018	Rest wt%		1.6	No	Use after storage at room temperature for 3 months
Identical to Ex. 6	1.1	9.6	0.6	0.3	0.0012	Rest wt%		1	No	Not stored for 3 months
Ex. 19	1.1	9.6	0.6	0.3	0.0012	Rest wt%		1.1	No	Use after storage at room temperature for 3 months
HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Cyclohexanol	Surflon S-243	Water				
2.8	24.0	1.5	0.7	1.0	0.0030	Rest wt%		–	–	Composition of storage solution
Identical to Ex. 9	1.6	14.1	0.9	0.4	0.0018	Rest wt%		1.7	No	Not stored for 3 months
Ex. 20	1.6	14.1	0.9	0.4	0.0018	Rest wt%		1.7	No	Use after storage at room temperature for 3 months
Identical to Ex. 10	1.1	9.6	0.6	0.3	0.0012	Rest wt%		1.2	No	Not stored for 3 months
Ex. 21	1.1	9.6	0.6	0.3	0.0012	Rest wt%		1.2	No	Use after storage at room temperature for 3 months

[0047]

Example 22

A chemical polishing solution was prepared in the same manner as that of Example 1, with the exceptions that the composition of the chemical polishing solution was changed to that shown in Table 5, and further that the copper alloy (NKC-4419-H) was dissolved in an amount of 5 g/L, and thereafter, a surface treatment was then carried out on the copper alloy (NKC-4419-H), thereby obtaining a surface treated product.

The evaluation results of the amount of the copper dissolved by the surface treatment and the treatment unevenness of the surface treated product are shown in Table 5. In Table 5, for comparison, the evaluation results of the amount of the copper dissolved by the surface treatment and the treatment unevenness of the surface treated product, which were obtained using the chemical polishing solution of Example 5 having the same composition as that of Example 22, with the exception that the copper alloy (NKC-4419-H) was not dissolved, are also shown.

[0048]

Comparative Examples 16 and 17

Chemical polishing solutions were prepared in the same manner as that of Example 1, with the exceptions that the compositions of chemical polishing solutions were changed to those shown in Table 5, and further that, regarding Comparative Example 17, the copper alloy (NKC-4419-H) was dissolved in an amount of 5 g/L. Thereafter, a surface treatment was carried out on the copper alloy (NKC-4419-H) using each chemical polishing solution, thereby obtaining each surface treated product.

The evaluation results of the amount of the copper dissolved by the surface treatment and the treatment unevenness of the surface treated product are shown in Table 5.

[0049]

[Table 5]

Table 5

	Composition of chemical polishing solution [wt%]						Evaluation results		
	(A)	(B)	(C)	(D)	(E)	(F)	NKC-4419-H	Amount dissolved [μm]	Remarks
Identical to Ex. 5 Ex. 22	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Surflon S-243	Water			
	1.6	14.1	0.9	0.4	0.0018	Rest wt%		1.7	No
	1.6	14.1	0.9	0.4	0.0018	Rest wt%		1.4	No
Comp.Ex. 16 Comp.Ex. 17	HP	Sulfuric acid	Potassium acid fluoride	Relative to F atoms	Surflon S-243	Water			
	1.6	14.1	0.9	0.4	—	Rest wt%		1.9	No
	1.6	14.1	0.9	0.4	—	Rest wt%		1.4	Yes

[0050]

As shown in Table 5, by comparing the results of Comparative Example 16 with the results of Comparative Example 17, it was found that treatment unevenness occurs upon dissolution of copper, in a case where the component (E) is not mixed. Since the chemical polishing solution of the present invention comprises the component (E), the occurring of such treatment unevenness can be suppressed even if the amount of copper dissolved in the solution becomes large, and a chemical polishing solution having stable removing performance can be provided.

CLAIMS

[Claim 1]

A chemical polishing solution used for the surface treatment of copper or copper alloy, comprising:

(A) 0.1% to 3.5% by mass of hydrogen peroxide, based on the total amount of the chemical polishing solution,

(B) 1% to 20% by mass of one or more types selected from the group consisting of sulfuric acid and nitric acid, based on the total amount of the chemical polishing solution,

(C) 0.05% to 0.8% by mass of a fluoride, as a content relative to fluorine atoms, based on the total amount of the chemical polishing solution,

(D) 0.01% to 4% by mass of one or more types selected from the group consisting of anthranilic acid, cyclohexylamine, cyclohexanol, and 1,5-pentanediol, based on the total amount of the chemical polishing solution,

(E) 0.0005% to 0.005% by mass of a fluorine-based surfactant, based on the total amount of the chemical polishing solution, and

(F) water.

[Claim 2]

The chemical polishing solution according to claim 1, wherein the pH of the chemical polishing solution is 3 or less.

[Claim 3]

The chemical polishing solution according to claim 1 or 2, wherein the component (C) is one or more types selected from the group consisting of potassium acid fluoride, ammonium acid fluoride, and hydrogen fluoride.

[Claim 4]

The chemical polishing solution according to any one of claims 1 to 3, wherein the component (B) is sulfuric acid.

[Claim 5]

The chemical polishing solution according to any one of claims 1 to 4, wherein the component (D) comprises one or more types selected from the group consisting of cyclohexanol and cyclohexylamine.

[Claim 6]

The chemical polishing solution according to any one of claims 1 to 5, wherein the component (E) comprises one or more types selected from the group consisting of a perfluoroalkyl group, a perfluoroalkenyl group, and a perfluorophenyl group.

[Claim 7]

A surface treatment method for copper or copper alloy, the method comprising contacting the chemical polishing solution according to any one of claims 1 to 6 with the surface of copper or copper alloy to perform a surface treatment on the copper or the copper alloy.

[Claim 8]

The surface treatment method according to claim 7, wherein the temperature of the chemical polishing solution is 25°C to 50°C upon performing the surface treatment on the copper or the copper alloy.

[Claim 9]

The surface treatment method according to claim 7 or 8, wherein the time required for contacting the chemical polishing solution with the surface of the copper or the copper alloy to perform the surface treatment on the copper or the copper alloy is 1 second or more and 10 minutes or less.

[Claim 10]

A method for producing copper or copper alloy whose surface is treated, the method comprising contacting the chemical polishing solution according to any one of claims 1 to 6 with the surface of copper or copper alloy to perform a surface treatment on the copper or the copper alloy.

[Claim 11]

A method for producing the chemical polishing solution according to any one of claims 1 to 6, the method comprising uniformly stirring, at least, the component (A), the component (B), the component (C), the component (D), the component (E), and the component (F).