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(54) **POLISHING COMPOSITION, POLISHING METHOD, AND METHOD FOR FORMING COPPER WIRING FOR SEMICONDUCTOR INTEGRATED CIRCUIT**

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(57) **ABSTRACT**

The present invention provides a technique for realizing highly flat surface of a semiconductor integrated circuit employing copper as a wiring metal.

The present invention provides a polishing composition containing a neutralized carboxylic acid, an oxidizer and water, wherein a part of the carboxylic acid is an alicyclic resin acid (A) and the pH value is within a range of from 7.5 to 12. The alicyclic resin acid is preferably at least one type selected from the group consisting of abietic acid, an isomer of abietic acid, pimaric acid, an isomer of pimaric acid and derivatives of these, or a rosin. Further, the present invention provides a polishing method of semiconductor integrated circuit surface in which a copper film formed on a surface having a groove for wiring, by using the polishing composition, and the present invention provides a copper wiring for semiconductor integrated circuit formed by this polishing method.

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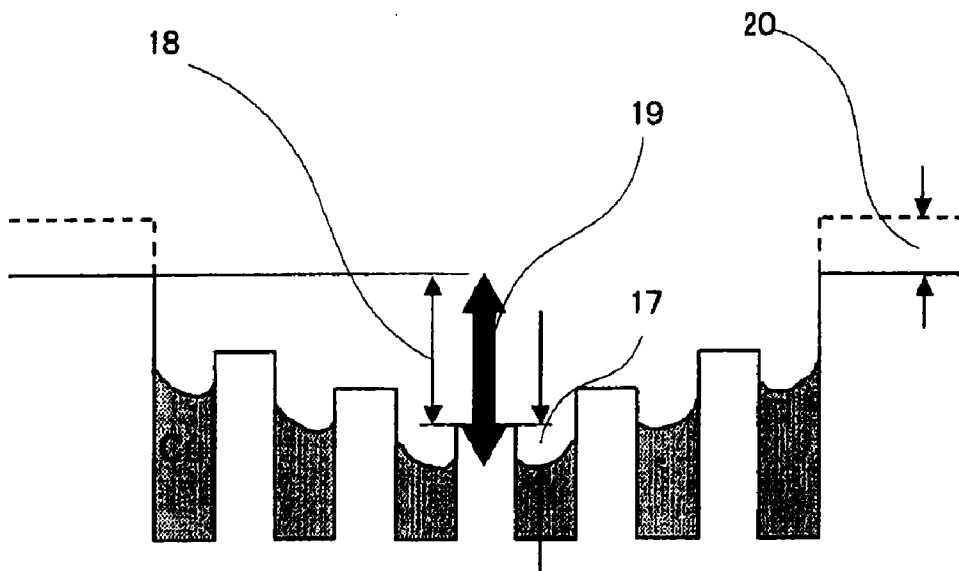


Fig. 1(a)

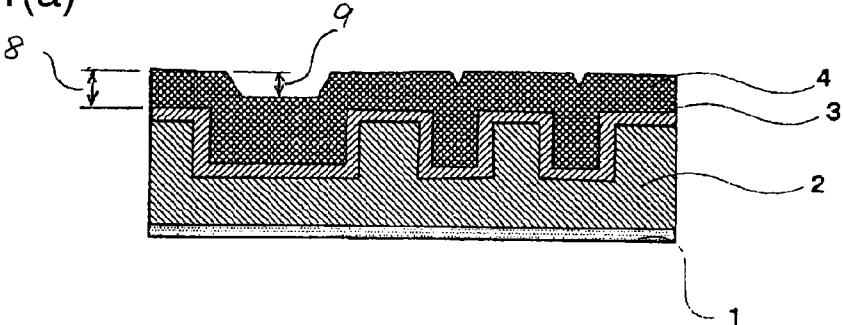


Fig. 1(b)

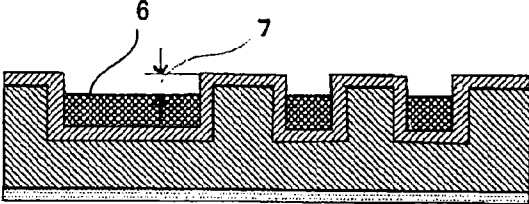


Fig. 1(c)

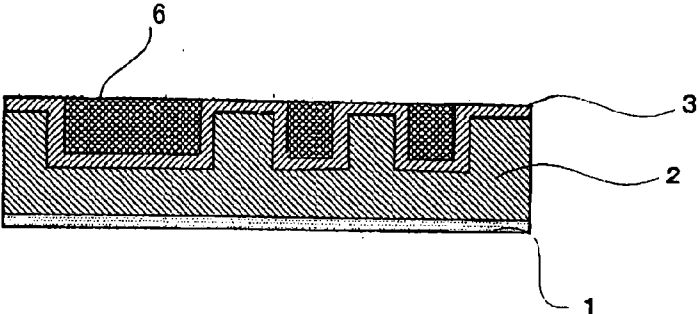
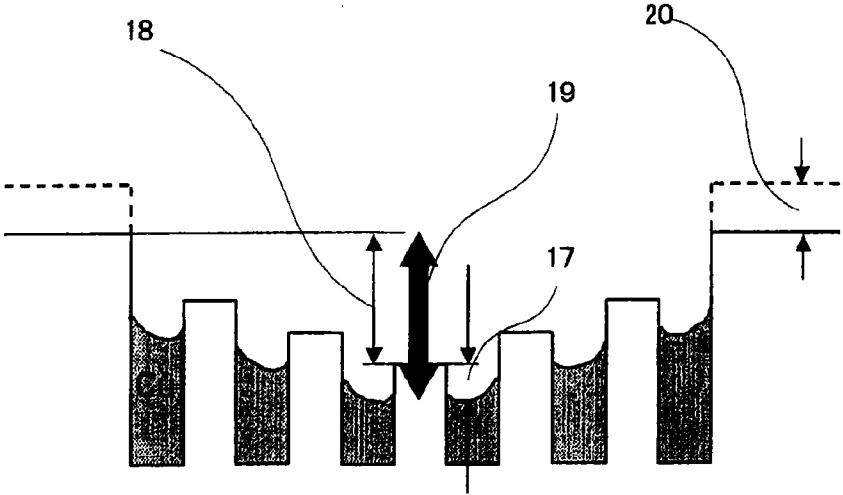


Fig. 2



POLISHING COMPOSITION, POLISHING METHOD, AND METHOD FOR FORMING COPPER WIRING FOR SEMICONDUCTOR INTEGRATED CIRCUIT

TECHNICAL FIELD

[0001] The present invention relates to a polishing composition and a technique for polishing a surface of semiconductor integrated circuit by using the polishing composition.

BACKGROUND ART

[0002] In recent years, to meet needs for high integration of semiconductor integrated circuit, various microfabrication techniques such as reduction of pattern size or increase of the number of wiring layers in a semiconductor element, have been developed.

[0003] The increase of the number of wiring layers is to form a new circuit pattern on an existing circuit pattern by using e.g. a lithography, but if there are protrusions or recessed portions are present on a surface of the under layer circuit pattern, protrusions and recessed portions are also formed on a surface of the newly formed circuit pattern, these portions depart from the depth of lithography, and thus, wiring patterns can not be formed as they are designed. To cope with this problem, in the design of semiconductor integrated circuit in recent years, it is required to improve the flatness of a surface of each circuit pattern layer with extremely high precision, so that the surface does not affect a surface of a layer formed thereon.

[0004] For example, in a damascene method for forming a wiring circuit and flattening the surface of the wiring circuit at the same time, a groove pattern for wiring is formed on the objecting surface of a semiconductor integrated circuit device, and a metal having relatively low resistivity such as aluminum or a copper metal for forming wiring is formed so that it is embedded in the groove. The metal is initially formed as a film on the surface by using a plating method or a sputtering method, and in most cases, the film is polished by a technique called Chemical Mechanical Polishing (hereinafter referred to as CMP), to remove the metal film other than the wiring portion to form a wiring corresponding to the groove. At this time, flattening of the polished surface is achieved at the same time.

[0005] In order not to affect flatness of a surface of overlying layer, the flatness of the polished surface is important and the CMP technique is an essential important technique for producing a highly-integrated semiconductor integrated circuit.

[0006] However, in CMP that is a method for flattening a surface by polishing, there are problems to be solved, such as a phenomenon called dishing that is a phenomenon that a wiring portion is more deeply removed than the rest of flat surface, or a phenomenon called erosion that is a phenomenon that a plurality of proximate wirings are removed together with surrounding material such as an insulation material, that occurs according to reduction of metal wiring width. With respect to dishing or erosion, many solutions have been proposed, but they are not sufficiently satisfactory yet.

[0007] For example, Patent Document 1 describes an invention of polishing solution containing a water-soluble polymer for suppressing erosion, and Patent Document 2 describes an invention of polishing solution containing a het-

erocyclic compound for suppressing erosion. Further, Patent Document 3 describes a method of suppressing dishing or erosion by using a polishing solution containing phosphoric acid ester, and Patent Document 4 describes a method of adjusting polishing reaction with copper by using a polishing solution containing fatty acid.

[0008] Patent Document 1: JP-A-2002-176015

[0009] Patent Document 2: JP-A-2002-12854

[0010] Patent Document 3: JP-A-2005-167231

[0011] Patent Document 4: JP-A-2002-231666

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0012] It is an object of the present invention to solve the above problems and to provide a technique which realizes surface flattening with high precision in a device using copper as a metal for wiring. Other objects and merits of the present invention will become clear in the following description.

Means for Solving the Problems

[0013] The present invention has the following gists.

1. A polishing composition comprising a neutralized carboxylic acid, an oxidizing agent and water, wherein a part of the carboxylic acid is an alicyclic resin acid (A), and the polishing composition has a pH value of from 7.5 to 12.

2. The polishing composition according to the above 1, wherein the alicyclic resin acid (A) is at least one type of carboxylic acid selected from the group consisting of abietic acid, an isomer of abietic acid, pimaric acid, an isomer of pimaric acid, a rosin and these derivatives.

3. The polishing composition according to the above 1 or 2, wherein the alicyclic resin acid (A) is neutralized by a basic potassic compound, an ammonium or an organic amine.

4. The polishing composition according to the above 1, 2 or 3, wherein the other part of the carboxylic acid contains at least one type of carboxylic acid (B-1a) selected from the group consisting of: a polycarboxylic acid having at least two carboxylic groups; and a carboxylic acid having at least one carboxylic group and at least one type of group selected from the group consisting of nitrogen-containing heterocyclic group, amino group a hydroxyl group and thiol group.

5. The polishing composition according to the above 4, wherein said the other part of the carboxylic group contains besides at least one type of the carboxylic acid (B-1a), an aliphatic carboxylic acid (B-2) containing total at least 11 carbon atoms and having at least one long-chain hydrocarbon group containing at least 10 carbon atoms and at least one carboxylic group.

6. The polishing composition according to the above 5, wherein the aliphatic carboxylic acid (B-2) is an unsaturated aliphatic carboxylic acid containing total from 12 to 23 carbon atoms and having at least one unsaturated group in its long-chain hydrocarbon portion.

7. The polishing composition according to the above 5, wherein the aliphatic carboxylic acid (B-2) is a saturated aliphatic carboxylic acid wherein the long-chain hydrocarbon group portion has from 11 to 17 carbon atoms in total.

8. The polishing composition according to any one of the above 1 to 7, wherein the ratio of the alicyclic resin acid (A) based on the total amount of carboxylic acid is from 0.1 to 70 mass %.

9. The polishing composition according to the above 5, 6 or 7, wherein the content of the aliphatic carboxylic acid (B-2) is from 0.001 to 0.5 mass % based on the total amount of the polishing composition.

10. The polishing composition according to any one of the above 1 to 9, wherein the oxidizer is at least one type of oxidizer selected from the group consisting of hydrogen peroxide, ammonium persulfate and potassium persulfate.

11. The polishing composition according to any one of the above 1 to 10, which further contains abrasive particles.

12. The polishing composition according to any one of the above 1 to 11, which contains from 0.11 to 8 mass % of carboxylic acid, 0.1 to 5 mass % of oxidizer and at least 90 mass % of water based on the polishing composition.

13. A polishing composition containing based on the polishing composition:

[0014] from 0.01 to 2 mass % of alicyclic resin acid (A);

[0015] from 0.1 to 5 mass % of at least one type of carboxylic acid (B-1a) selected from the group consisting of a polycarboxylic acid having at least two carboxylic groups, and a carboxylic acid having at least one carboxylic group and at least one type of group selected from the group consisting of a nitrogen-containing heterocyclic group, an amino group, a hydroxyl group and thiol group;

[0016] from 0 to 0.5 mass % of aliphatic carboxylic acid (B-2) having a long-chain hydrocarbon group having at least 10 carbon atoms and at least one carboxylic group, and having at least 11 carbon atoms in total;

[0017] from 0.1 to 5 mass % of an oxidizer; and

[0018] at least 90 mass % of water;

[0019] wherein the alicyclic resin acid (A), the carboxylic acid (B-1a) and the aliphatic carboxylic acid (B-2) are neutralized, and the polishing composition has a pH value of from 8.0 to 11.

14. A polishing composition characterized in that increase of dishing amount is at most 10 nm and that the final dishing amount is at most 20 nm, when the polishing composition is used for polishing a copper layer formed on an insulation layer via a barrier layer to form a pattern in which copper buried wirings of each 100 μm wide and insulation layers of each 100 μm are alternately arranged, and when the polishing composition is used to further polish the copper after the barrier layers adjacent to the copper buried wirings are exposed at the same removal rate as that before the barrier layers are exposed, for a time required to remove 200 nm of copper before the barrier layers are exposed.

15. The polishing composition according to the above 14, wherein the removal rate of copper before the barrier layers are exposed is at least 100 times of the removal rate of the barrier layer.

16. The polishing composition according to the above 14 or 15, which contains an oxidizer, a dissolving agent for metal oxide, an agent for forming protection film and water.

17. The polishing composition according to the above 16, wherein the agent for forming protection film is an alicyclic resin acid (A) and the pH value of the polishing composition is from 7.5 to 12.

18. The polishing composition according to the above 16 or 17, wherein the solvent for metal oxide is at least one type of carboxylic acid (B-1a) selected from the group consisting of a polycarboxylic acid having at least two carboxylic groups; and a carboxylic acid having at least one carboxylic group and at least one type of group selected from the group

consisting of a nitrogen-containing heterocyclic group, an amino group, a hydroxyl group and thiol group.

[0020] 19. The polishing composition according to the above 17 or 18, which further contains an aliphatic carboxylic acid (B-2) having a long-chain hydroxyl group having at least 8 carbon atoms and at least one carboxyl group, the aliphatic carboxylic acid (B-2) having at least 11 carbon atoms.

20. The polishing composition according to any one of the above 16 to 19, wherein the oxidizer is at least one type of oxidizer selected from the group consisting of hydrogen peroxide, ammonium persulfate and potassium persulfate.

21. The polishing composition according to any one of the above 16 to 20, which further contains abrasive particles.

22. A method for polishing a surface of a semiconductor integrated circuit, which comprises polishing a copper film for wiring formed on a surface having grooves by using the polishing composition as defined in any one of the above 1 to 20.

23. A method for producing a copper wiring for a semiconductor integrated circuit, which comprises polishing a copper film for wiring formed on a surface having grooves by using the polishing composition as defined in any one of the above 1 to 20.

EFFECTS OF THE INVENTION

[0021] According to the present invention, it is possible to realize surface flattening with high precision in a case of using copper as a metal for wiring. Accordingly, the present invention enables to obtain a semiconductor integrated circuit having little dishing or erosion and having excellent and flat surface state, and thus, the present invention is extremely useful for multi-layer structure and fine patterning of semiconductor integrated circuits.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] FIGS. 1(a) to 1(c): Schematic cross sectional views of a wafer with a pattern before and after a CMP step in a process of producing copper buried wirings; wherein FIG. 1(a) is a cross sectional view of a semiconductor integrated circuit before polishing, FIG. 1(b) is a cross sectional view of a semiconductor integrated circuit in which dishing is formed by polishing, and FIG. 1(c) is a cross sectional view of a semiconductor integrated circuit after polishing that is ideally polished.

[0023] FIG. 2: A schematic cross sectional view of a patterned wafer for explaining erosion.

EXPLANATION OF NUMERALS

- [0024]** 1: Si Substrate
- [0025]** 2: Insulation layer
- [0026]** 3: Barrier layer
- [0027]** 4: Metal wiring layer
- [0028]** 6: Copper buried wiring
- [0029]** 7: Dishing amount
- [0030]** 8: Initial thickness of copper film
- [0031]** 9: Initial stepheight of copper film
- [0032]** 17: Dishing portion
- [0033]** 18: Erosion portion
- [0034]** 19: Maximum stepheight
- [0035]** 20: Polished portion of global portion

BEST MODE FOR CARRYING OUT THE INVENTION

[0036] The behavior of the polishing composition according to the present invention is described with respect to a case of polishing a copper film on a surface of a semiconductor integrated circuit having a groove for wiring. In the following, explanation will be made mainly with respect to a case of applying the present invention to a semiconductor integrated circuit device having a copper wiring that is a particularly preferred application, but it is matter of course that the polishing composition according to the present invention is usable also in other cases so long as the polishing composition is used for polishing copper wirings.

[0037] Further, the following description shows examples of the present invention, and they do not limit the scope of the present invention, and it is a matter of course that other embodiments can belong to the scope of the present invention so long as they agree with the gist of the present invention.

[0038] The polishing composition of the present invention contains neutralized carboxylic acid, an oxidizing agent and water, wherein a part of the carboxylic acid is an alicyclic resin acid and the pH value of the polishing composition is from 7.5 to 12. The polishing composition of the present invention may contain other components besides the above components, and preferably contains abrasive particles or a surfactant. The polishing composition of the present invention is characterized by containing an alicyclic resin acid and a carboxylic acid other than alicyclic resin acid.

Alicyclic Resin Acid

[0039] A resin acid is an organic acid (carboxylic acid) present in a state of free or ester in a natural resin, and an alicyclic resin acid is a compound having an alicyclic structure (refer to "Kagaku Daijiten 4" (chemical encyclopedia 4) published by KYORITSU SHUPPAN CO., LTD., the section of "resin acid"). The alicyclic resin acid (A) of the present invention includes a natural resin containing an alicyclic resin acid; a purified resin acid containing as the main component an alicyclic resin acid produced by purifying (e.g. isomerization may occur at the same time) a natural resin; an alicyclic resin acid being a single compound extracted from a natural resin; and a mixture of at least two types of them.

[0040] As the purified resin acid, a rosin obtainable from e.g. a pine rosin, a tall oil, or a tall oil rosin may, for example, be mentioned. Particularly, a purified resin acid containing as the main component an alicyclic resin acid such as abietic acid or its isomer, pimaric acid or its isomer or a hydrogenated abietic acid, is preferred and a commercially available rosin can be used as an alicyclic resin acid of the present invention. Further, in such a rosin, the type or the content of a compound contained in the rosin changes depending on the type of natural resin from which the rosin derives. However, any type of rosin can be used so long as it contains an alicyclic resin acid as the main component.

[0041] Some commercially available rosin includes a small amount of aliphatic resin acid. Such an aliphatic resin acid is mainly an unsaturated higher fatty acid such as oleic acid or linoleic acid, and its content is usually about 10 mass % based on total resin. These aliphatic resin acids are preferred compounds as an aliphatic carboxylic acid (B-2) to be described later. Accordingly, in a case of producing a polishing composition containing an alicyclic resin acid (A) and an aliphatic carboxylic acid (B-2) to be described later, it is possible to

produce a polishing composition of the present invention by using a commercially available rosin containing aliphatic resin acid without using an aliphatic carboxylic acid (B-2) to be described later separately from the rosin. As an alternative, the polishing composition of the present invention may be produced by using a commercially available rosin containing an aliphatic resin acid and further using an aliphatic carboxylic acid (B-2) separately from the rosin.

[0042] As the alicyclic resin acid (A) being a single compound, abietic acid; an isomer of abietic acid such as neoabietic acid, parastrinic acid or levopimaric acid; a hydride of abietic acid such as dihydroabietic acid or tetrahydroabietic acid; or a dehydrogenated product of abietic acid such as dehydroabietic acid or secodehydroabietic acid. Besides these, pimaric acid, isopimaric acid, sandaracopimaric acid, communic acid or dihydroagathic acid are mentioned.

[0043] In the polishing composition of the present invention, at least two types of the above alicyclic resin acid (A) may be contained. A purified resin acid such as a rosin is originally a mixture of at least two types of alicyclic resin acids (each single compound), and it is regarded as a type of alicyclic resin acid (A) in the present invention. Accordingly, in the polishing composition of the present invention, at least two types of rosins may be contained or as an alternative, a rosin and at least one type of alicyclic resin acid that is a single compound, may be contained.

[0044] Further, the alicyclic resin acid (A) of the present invention may be a compound having at least one carboxylic group or a mixture containing such a compound, that is a derivative of the above purified resin acid or alicyclic resin acid that is a single compound. As the derivative, besides an alicyclic resin acid extracted from a natural resin, an isomerized product, a hydride, a dehydrogenated product, a polysulfide, or a modified product obtainable by adding an unsaturated compound (such as an unsaturated carboxylic acid such as maleic anhydride, fumaric acid, acrylic acid or its anhydride) to an unsaturated group of an alicyclic resin acid by Diels-Alder reaction, may, for example, be mentioned. It is preferably at least one type selected from the group consisting of maleic anhydride addition product (maleic acid modified product), a fumaric acid addition product (fumaric acid modified product) an acrylic acid addition product (acrylic acid modified product) and a dehydrogenated product. The dehydrogenated product includes a compound a part of whose alicycle becomes an aromatic cycle by the dehydrogenation.

Carboxylic Acid Other than Alicyclic Resin Acid

[0045] The polishing composition of the present invention contains a carboxylic acid other than the alicyclic resin acid (A). Among carboxylic acids contained in the polishing composition of the present invention, a carboxylic acid ("the other part of the carboxylic acid") other than alicyclic resin acid is referred to as "another organic carboxylic acid (B)". Said another organic carboxylic acid (B) may be any compound so long as it has at least one carboxylic group. Said another organic carboxylic acid (B) is preferably a compound having at least two functional groups including a carboxylic group. Hereinafter a compound having at least two functional groups including carboxylic group is referred to as a carboxylic acid (B-1). The carboxylic acid (B-1) is preferably a compound (hereinafter referred to as polycarboxylic acid) having at least two carboxylic groups or a compound (hereinafter referred to as monocarboxylic acid) having one carboxylic group and at least one functional group other than carboxylic group. The polycarboxylic acid may have at least one functional group

other than carboxylic groups. Further, as said another organic carboxylic acid (B), an aliphatic carboxylic acid having total at least 11 carbon atoms and having a long-chain hydrocarbon group having at least 8 carbon atoms, is preferably used in combination with the preferred carboxylic acid (B-1). An aliphatic carboxylic acid having total at least 11 carbon atoms and having a long-chain hydrocarbon group having at least 8 carbon atoms and at least one carboxylic group, is hereinafter referred to as aliphatic carboxylic acid (B-2). The aliphatic carboxylic acid (B-2) is preferably an aliphatic carboxylic acid having total at least 11 carbon atoms and having a long-chain hydrocarbon group having at least 10 carbon atoms and at least one carboxylic group. In order to distinguish the aliphatic carboxylic acid (B-2) from the preferred carboxylic acid (B-1), a portion where the aliphatic carboxylic acid (B-2) and the carboxylic acid (B-1) overlap, is regarded as an aliphatic carboxylic acid (B-2) in this specification. For example, a carboxylic acid having at least two functional groups including a carboxylic group, that is included in a category of aliphatic carboxylic acid (B-2) (hereinafter it is also referred to as aliphatic polycarboxylic acid) is designated as an aliphatic carboxylic acid (B-2).

[0046] Accordingly, a carboxylic acid in the explanation of the present invention is categorized into an alicyclic resin acid (A) and another organic carboxylic acid (B), and said another organic carboxylic acid (B) in the present invention is categorized into an aliphatic carboxylic acid (B-2), a carboxylic acid (B-1) and an organic carboxylic acid (hereinafter referred to as carboxylic acid (B-3)) other than these carboxylic acids. The total number of carbon atoms (including carbon atoms of carboxylic groups) of said another organic carboxylic acid (B) other than the aliphatic carboxylic acid (B-2), namely total number of carbon atoms in each of carboxylic acid (B-1) and carboxylic acid (B-3), is not particularly limited but it is preferably at most 12, more preferably at most 10. In a case of aliphatic polycarboxylic acid, the total number of its carbon atoms is preferably at most 6. The number of carboxylic groups in such a polycarboxylic acid is preferably from 2 to 3.

[0047] A functional group other than carboxylic group in the carboxylic acid (B-1) is preferably amino group, hydroxyl group or thiol group etc. The amino group may be a secondary amino group (imino group) or a tertiary amino group. Further, the functional group may be a heterocyclic group, and is particularly preferably a heterocyclic group (hereinafter it is also referred to as nitrogen-containing heterocyclic group) having a nitrogen atom as a ring-constituting atom. A hydrogen atom may be bonded or not bonded to the nitrogen atom constituting the ring. The nitrogen-containing heterocyclic group is particularly preferably a pyridine ring (namely, quinoline ring) that is a condensed product of a pyridine ring and a benzene ring. A carboxylic group in a carboxylic acid having a heterocyclic group may be bonded to a carbon atom constituting the ring, or may be bonded to a carbon atom other than the ring. A carboxylic group in a carboxylic acid having a pyridine ring or a quinoline ring is preferably bonded to a carbon atom constituting the ring. The number of carbon atoms other than carbon atoms constituting a ring in a carboxylic acid having a pyridine ring or a quinoline ring, is preferably at most 4 including the carbon atoms of carboxylic group.

[0048] The carboxylic acid (B-1) is preferably at least one type of carboxylic acid selected from the group consisting of polycarboxylic acid; and a carboxylic acid having at least one type of group selected from the group consisting of a nitro-

gen-containing heterocyclic group, amino group, hydroxyl group and thiol group, and at least one carboxylic group; and hereinafter this carboxylic acid is referred to as carboxylic acid (B-1a). The polycarboxylic group may have a functional group such as a nitrogen-containing heterocyclic group. More preferably, the carboxylic acid (B-1) is preferably a polycarboxylic group or a monocarboxylic group having a pyridine ring or a quinoline ring, or an aliphatic polycarboxylic acid having at least 6 carbon atoms such as oxalic acid.

[0049] A specific carboxylic acid (B-1a) is exemplified in the following (a) to (e), but it is not limited thereto.

(a) Carboxylic acid (monocarboxylic acid, polycarboxylic acid) having a nitrogen-containing heterocyclic group: 2-pyridinecarboxylic acid, 3-pyridinecarboxylic acid, 4-pyridinecarboxylic acid, 2,3-pyridinedicarboxylic acid, 2,4-pyridinedicarboxylic acid, 2,5-pyridinedicarboxylic acid, 2,6-pyridinedicarboxylic acid, 3,4-pyridinedicarboxylic acid, 3,5-pyridinedicarboxylic acid, pyrazinecarboxylic acid, 2,3-pyrazinedicarboxylic acid, 2-quinolinecarboxylic acid (quinaldic acid), 3-quinolinecarboxylic acid, 4-quinolinecarboxylic acid or 8-quinolinecarboxylic acid.

(b) Carboxylic acid (such as amino acid) having an amino group: alanine, glycine, proline, phenylalanine.

(c) Carboxylic acid (such as hydroxycarboxylic acid) having a hydroxyl group: lactic acid, malic acid, citric acid, isocitric acid, tartaric acid, glycolic acid, gluconic acid or salicylic acid.

(d) Other polycarboxylic acids: oxalic acid, malonic acid, succinic acid, fumaric acid, maleic acid, oxalacetic acid, glutaric acid, adipic acid, citraconic acid, itaconic acid, diglycolic acid, thiodiglycolic acid or phthalic acid.

(e) Carboxylic acid having a thiol group: thioglycolic acid or thiosalicylic acid.

[0050] As the carboxylic acid (B-3), an aliphatic monocarboxylic acid having no long chain-chain hydrocarbon group having at least 8 carbon atoms, an aliphatic monocarboxylic acid having less than 10 carbon atoms and having no functional group, or an aromatic monocarboxylic acid having no functional group, is mentioned. In the present invention, the carboxylic acid (B-3) can be appropriately used according to the purpose, but it is usually not an essential component. Here, the polishing composition of the present invention may contain at least two types of each of the carboxylic acid (B-1) and the carboxylic acid (B-3).

[0051] The aliphatic carboxylic acid (B-2) is an aliphatic carboxylic acid having total at least 11 carbon atoms and having a long-chain hydrocarbon group having at least 8 carbon atoms and at least one carboxylic group. The aliphatic carboxylic acid (B-2) is preferably an aliphatic carboxylic acid containing no functional group other than carboxylic group and containing from 1 to 3 carboxylic groups. The number of carboxylic groups is particularly preferably 1 or 2. Further, the long chain hydrocarbon group is preferably a hydrocarbon group having a chain of at least 6 continuous carbon atoms having no side chain alkyl group or having one or more alkyl groups each containing at most 2 carbon atoms. The number of continuous carbon atoms in the long-chain hydrocarbon group, namely the number of carbon atoms in the main chain, is preferably from 6 to 30, more preferably from 10 to 22. Further, the number of carbon atoms in the long-chain hydrocarbon group including side chain carbon atoms is preferably at least 8, more preferably from 8 to 26, particularly preferably from 10 to 22. Here, the long-chain hydrocarbon group means a portion other than a carbon atom

to which a carboxyl group is connected. The total number of carbon atoms in the aliphatic carboxylic acid (B-2) (including carbon atoms in the carboxylic group) is preferably from 11 to 23, more preferably from 12 to 22.

[0052] The long-chain hydrocarbon group may have one or more unsaturated bonds, and is particularly preferably a hydrocarbon group (namely, alkenyl group) containing from 1 to 3 unsaturated double bonds. The carboxylic group is preferably present at the end of a linear hydrocarbon or in the vicinity of the end. Also in an aliphatic polycarboxylic acid having a long-chain hydrocarbon group having one or more unsaturated bonds, at least two carboxylic groups are preferably bonded to the same or different carbon atoms at the end of a linear hydrocarbon or in the vicinity of the end. For example, in alkenylsuccinic acid, carboxylic groups are bonded to two adjacent carbon atoms at the end.

[0053] The aliphatic carboxylic acid (B-2) may, for example, be an aliphatic acid such as an unsaturated aliphatic acid such as maleic acid, myristoleic acid, palmistoleic acid, oleic acid, erucic acid, brassidic acid, linolic acid, linolenic acid, arakidonic acid, eicosapentaenoic acid or docosahexaenoic acid, or a saturated aliphatic acid such as lauric acid, myristic acid, palmitic acid or stearic acid; or an aliphatic polycarboxylic acid. The aliphatic acid is more preferably an unsaturated aliphatic acid having total from 12 to 23 carbon atoms or a saturated aliphatic acid having total from 11 to 17 carbon atoms, particularly preferably an unsaturated aliphatic acid having total from 14 to 22 carbon atoms or a saturated aliphatic acid having total from 12 to 16 carbon atoms. The aliphatic polycarboxylic acid is preferably alkenylsuccinic acid. Alkenylsuccinic acid is a compound similar to succinic acid except that the above-mentioned alkenyl group is bonded to the second carbon atom of succinic acid, and it may, for example, be decenylsuccinic acid, dodecenylnsuccinic acid, tetradecenylnsuccinic acid, hexadecenylnsuccinic acid or octadecenylnsuccinic acid. The number of total carbon atoms of the alkenylsuccinic acid is preferably from 14 to 22.

[0054] The aliphatic carboxylic acid (B-2) may be the above-mentioned aliphatic resin acid. Some of commercially available rosins containing alicyclic resin acid as the main component contain about from 5 to 20 mass % of aliphatic resin acid containing as the main component an unsaturated aliphatic acid having 18 carbon atoms such as oleic acid, linolic acid or linolenic acid. When such an aliphatic-resin-acid-containing rosin is used, it is possible to produce the polishing composition of the present invention without using the aliphatic carboxylic acid (B-2) separately. Even in this case, when the amount of aliphatic carboxylic acid (B-2) is small in such a commercially available rosin containing aliphatic carboxylic acid (B-2), besides such a rosin, the aliphatic carboxylic acid (B-2) may further be used. Further, the polishing composition of the present invention may be produced by using a desired amount of aliphatic carboxylic acid (B-2) in addition to a rosin containing substantially no aliphatic resin acid.

[0055] The aliphatic carboxylic acid (B-2) is preferably an aliphatic monocarboxylic acid having at least one unsaturated group in its long-chain hydrocarbon group portion and alkenylsuccinic acid, particularly preferably oleic acid, linolic acid, linolenic acid or an alkenylsuccinic acid having total from 14 to 22 carbon atoms. Further, it is preferably an aliphatic resin acid (which mainly contains oleic acid, linolic acid or linolenic acid) that is contained with small amount in

a commercially available rosin. Here, at least two type of these aliphatic carboxylic acids may be used in combination.

[0056] The aliphatic carboxylic acid (B-2) having the above structure is not an essential component in the polishing composition of the present invention, but small amount of it is preferably used in combination with the carboxylic acid (B-1), particularly with the above carboxylic acid (B-1a). The aliphatic carboxylic acid (B-2) is considered to exhibit a surfactant-like function in the polishing composition of the present invention. The reason is considered as follows. When the aliphatic carboxylic acid (B-2) is contained, an effect of increasing solubility or dispersibility of the above alicyclic resin acid (A) to water in the polishing composition of the present invention, or an effect of promoting a function of the alicyclic resin acid (A) for forming a protection film on a surface of copper film, are obtained, whereby dishing amount is more effectively suppressed.

Neutralized Carboxylic Acid

[0057] The polishing composition of the present invention contains a neutralized carboxylic acid, an oxidizer and water, wherein a part of the carboxylic acid is an alicyclic resin acid (A) and the pH value is within a range of from 7.5 to 12. The neutralized carboxylic acid preferably contains besides the alicyclic resin acid (A) a carboxylic acid (B-1), particularly preferably contains at least three types of carboxylic acids that are the alicyclic resin acid (A), the carboxylic acid (B-1) and an aliphatic carboxylic acid (B-2).

[0058] This polishing composition is a basic composition, and thus, these carboxylic acids are considered to be neutralized and ionized in the composition. The carboxylic acids neutralized in the composition is obtained by blending a salt of carboxylic acid with a water-based medium (a liquid medium such as water or a mixture of water and a water-base medium). Further, such a neutralized carboxylic acid is obtainable by blending a carboxylic acid with a water-base medium containing a basic compound and making it react with the basic compound. In a case of carboxylic acid having low solubility to water, it is preferred to blend such a carboxylic acid by using these methods. In a case of carboxylic acid having high solubility to water, it is also possible to blend the carboxylic acid by such another method of dissolving the carboxylic acid in a water-base medium followed by blending a basic compound to neutralize it. The above alicyclic resin acid is a carboxylic acid having relatively low solubility to water, and thus, it is preferably neutralized by using a method of forming a salt followed by blending it with a water-base medium. Further, it is also preferred that the carboxylic acid is made into fine particles by means of e.g. emulsification and dispersed in a water-base medium and is made to react with a basic compound. Another organic carboxylic acid (B) is also preferably formed into a salt, and thereafter, blended in a water-base medium, since a compound can be produced more easily by such a method.

[0059] The salt of carboxylic acid is a salt produced by combining the above carboxylic acid and a base, and such a salt is preferably an alkaline metal salt, an ammonium salt or an organic amine salt. Particularly, a potassium salt or an ammonium salt is preferred. The organic amine is preferably an organic amine of low molecular weight having at most 6 carbon atoms, such as an alkylamine, a dialkylamine, a trialkylamine, an alkanolamine, a dialkanolamine or a trialkanolamine.

[0060] The salt of the alicyclic resin acid (A) is preferably an alkaline metal salt (particularly potassium salt) of rosin, that is also called as rosin, an ammonium salt of rosin or an organic amine salt of rosin. Further, as the salt of alicyclic resin acid being a single compound, for example, the following salts are mentioned, and a mixture of at least two types of them may also be used: potassium abietate salt, potassium dehydroabietate salt, potassium tetrahydroabietate salt, potassium dihydroabietate salt, potassium pimarate salt, ammonium abietate salt, ammonium dehydroabietate salt, ammonium tetrahydroabietate salt, ammonium dihydroabietate salt, ammonium pimarate salt, an organic amine abietate salt, an organic amine dehydroabietate salt, an organic amine tetrahydroabietate salt, an organic amine dehydroabietate salt or an organic amine pimarate salt.

[0061] Here, in the present invention, even in a case of using a salt of the above alicyclic resin acid (A) or a salt of another organic carboxylic acid (B), the mass or the mass percentage of carboxylic acid is represented by the mass or the mass percentage converted to those of carboxylic acid (COOH). Namely, between a case of preparing the polishing composition of the present invention by using a carboxylic acid and a case of preparing it by using a carboxylate, their mass or mass percentage is the same so long as their molar amount that is converted to that of carboxylic acid is the same.

[0062] In a polishing composition, an effect of suppressing dishing amount is obtained by containing an alicyclic fatty acid (A). The mechanism of obtaining such an effect is not clear, but it is considered that the composition performs some chemical reaction or physical reaction with a surface of copper film of semiconductor integrated circuit at a time of polishing, and functions as a surface protecting agent for forming a protection layer on a surface of the cover film. This surface protection layer is not strong enough to completely prevent polishing of copper film, and in a copper film on a semiconductor integrate circuit substrate, polishing progresses at a convex portion to which a pressure of polishing pad is large, and polishing does not progress at a concave portion at which the pressure is small. By this mechanism, highly smooth polished surface profile is considered to be realized.

[0063] The content of the alicyclic resin acid (A) in the polishing composition is preferably from 0.01 to 2 mass %, particularly preferably from 0.03 to 1 mass %. When the content is less than 0.01 mass %, the protection function of the copper film surface is considered to be insufficient, and corrosion and dishing tend to occur during polishing. Further, if the content exceeds 2 mass %, removal rate of copper may decrease. Here, the content in this specification means a mass % based on total amount of polishing composition, and it means a content based on a diluted polishing composition when it is diluted to be used for polishing.

[0064] In a polishing composition, the removal rate of copper increases when the polishing composition contains a carboxylic acid (B-1) although its mechanism is unclear.

[0065] The carboxylic acid (B-1) is preferably a carboxylic acid (B-1a). Further, the carboxylic acid (B-1a) is preferably a polycarboxylic acid or a monocarboxylic acid that have nitrogen-containing heterocyclic group, or an aliphatic polycarboxylic acid such as oxalic acid, particularly preferably 2-pyridinecarboxylic acid. By using a carboxylic acid having a nitrogen-containing heterocyclic group such as 2-pyridinecarboxylic acid, an effect of increasing removal rate of copper and an effect of preventing addition or residual of e.g. copper complex on a polishing pad, are exhibited.

[0066] The total amount of carboxylic acid contained in the polishing composition of the present invention, is preferably from 0.11 to 8 mass % based on the polishing composition. Among these, the amount of another organic carboxylic acid (B) is preferably from 0.1 to 5 mass % based on the polishing composition. If it is less than 0.1 mass %, the removal rate of copper may decrease, and if it exceeds 5 mass %, corrosion or dishing on a copper surface may occur. The total amount of said another organic carboxylic acid (B) except for the aliphatic carboxylic acid (B-2), is preferably the carboxylic acid (B-1). The carboxylic acid (B-1) is at least 0.1 mass % in the polishing composition.

[0067] Further, the ratio of alicyclic resin acid (A) based on the total amount of carboxylic acid is preferably from 1 to 50 mass %. Namely, based on the total carboxylic acid, said other organic carboxylic acid (B) is preferably from 50 to 99 mass %. The ratio of alicyclic resin acid (A) based on the total amount of carboxylic acid, is preferably from 3 to 40 mass % that is converted to the ratio of carboxylic acid.

[0068] Further, it is not essential that the polishing composition of the present invention contains the above aliphatic carboxylic acid (B-2), but if it contains, it is considered that an effect of increasing solubility or dispersibility of the alicyclic resin acid (A) to water in the polishing composition of the present invention, or an effect of promoting a function of the alicyclic resin acid (A) for forming a protection film on a copper film surface, are obtained, whereby the dishing amount is more efficiently suppressed. The content of the aliphatic carboxylic acid (B-2) is preferably at least 0.001 mass % based on the total amount of polishing composition in order to obtain the above effects. The content of the aliphatic carboxylic acid (B-2) is preferably at most 0.5 mass %, more preferably at most 0.2 mass % based on the total amount of polishing composition since the copper removal rate may decrease if its content is large.

[0069] Here, in a case of using an alicyclic resin acid containing an aliphatic carboxylic acid (B-2) such as a rosin containing an aliphatic carboxylic acid (B-2), the ratio of aliphatic carboxylic acid (B-2) based on the total amount of aliphatic carboxylic acid (B-2) and the alicyclic resin acid (A), is preferably from 0.1 to 70 mass %, particularly preferably from 1 to 60 mass %. However, so long as the relative amount between the alicyclic resin acid (A) and the aliphatic carboxylic acid (B-2) in the polishing composition of the present invention is not inconvenient, an alicyclic resin acid containing more amount of aliphatic carboxylic acid (B-2) may be used. In a case of using an alicyclic resin acid not containing aliphatic resin acid, there is no possibility of occurring such an inconvenience since an aliphatic carboxylic acid (B-2) is used separately.

Oxidizer

[0070] An oxidizer serves to oxidize a metal such as copper and produces a metallic ion or an oxide although its mechanism is unclear. It is considered that copper ions produced by the reaction of oxidizer, the carboxylic acid (B-1) and the carboxylic acid (B-1a) form a complex to promote polishing.

[0071] The oxidizer is preferably a peroxide since it shows strong oxidizing power. An example of peroxide type oxidizer includes an inorganic peroxide such as hydrogen peroxide, a persulfate, a peroxocarbonate, a peroxosulfate or a peroxophosphate, or an organic peroxide such as a benzoyl peroxide, t-butyl hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, performic acid or per-

acetic acid. A preferred oxidizer is hydrogen peroxide, ammonium persulfate or potassium persulfate. Among these oxidizers, an ammonium salt, particularly ammonium persulfate is preferred since it provides high removal rate of copper film. Next to these oxidizers, hydrogen peroxide or potassium persulfate is preferred. The content of oxidizer based on the polishing composition is preferably at least 0.1 mass %, and if the content is smaller, the removal rate of copper may decrease. If the content of oxidizer is excess, corrosion or dishing of a copper surface tends to occur, and accordingly, the content of oxidizer in the polishing composition is preferably at most 5 mass %. In order to polish a copper film at high removal rate while suppressing dishing, it is preferred to use at least one type of oxidizer of 0.1 to 5 mass % selected from the group consisting of ammonium persulfate, hydrogen peroxide and potassium persulfate. Particularly, from 0.1 to 5 mass % of ammonium persulfate is preferred.

Water

[0072] The main liquid medium in the polishing composition of the present invention is water, and the liquid medium is preferably water only or a mixture of water and a water-soluble solute. The water is preferably a purified water that is ion-exchanged to remove impurities therefrom. As the water-soluble solute, a water-soluble alcohol, a water-soluble polyol, a water-soluble ester, a water-soluble ether etc. may be used. The liquid medium in the polishing composition of the present invention is preferably water only or a mixed medium of at least 80 mass % of water and a water-soluble organic solute, the most preferably substantially water only. Further, the ratio of liquid medium in the polishing composition of the present invention is at least 90 mass %, particularly preferably at least 95 mass %. Substantially entire amount of the liquid medium is preferably water and in this case, the content of water in the polishing composition of the present invention is at least 90 mass %, particularly preferably at least 95 mass %.

[0073] As mentioned above, the percentage of each component in the polishing composition of the present invention means a composition percentage when the composition is used for polishing. In a case where a condensed polishing composition is diluted prior to polishing and the diluted product is used for polishing, the above mentioned and the following percentage of each component means the percentage in the diluted product. A condensed polishing composition is usually diluted by a liquid medium (particularly by water), and accordingly, the relative percentage among components other than the liquid medium usually does not change between before and after the dilution.

[0074] The pH value of the polishing composition of the present invention is from 7.5 to 12. When the pH value is lower than 7.5, an alicyclic resin acid (A) contained in the polishing composition of the present invention may be separated in the polishing composition and its distribution may become uneven. In order to polish copper at high speed, it is preferred to make the pH value at least 8.0. If the pH value is 12 or higher, corrosion of copper film becomes significant, such being not preferred. In order to sufficiently suppress unpolished residue or corrosion of copper film, it is preferred to make the pH value 11 or lower. Accordingly, the pH value of the polishing composition of the present invention is preferably from 8.0 to 11.

[0075] Further, in the polishing composition of the present invention comprising the alicyclic resin acid (A); another

organic carboxylic acid (B) that is a carboxylic acid having a pyridine ring or a quinoline ring; an oxidizer that is at least one type selected from the group consisting of ammonium persulfate, hydrogen peroxide and potassium persulfate; and abrasive particles; the pH value is preferably from 8.0 to 11, particularly preferably from 8.2 to 10.8. If the pH value is lower than 8.2, the alicyclic resin acid (A) contained in the polishing composition of the present invention may be separated in the polishing composition of the present invention and its distribution may become uneven to cause precipitation. If the pH value is higher than 11, corrosion of copper film may occur, and accordingly, in order to sufficiently suppress unpolished residue or corrosion of copper film, the pH value is preferably at most 10.8.

[0076] In order to adjust the polishing composition of the present invention to have the above pH value, it is possible to use a pH adjusting agent. In order to adjust the polishing composition to base side, potassium hydroxide, an organic amine or ammonium is preferably employed. Any of these may be employed, but when an organic amine or ammonium that are capable of forming a complex ion with copper is employed, large removal rate of copper film is obtained, such being preferred. Further, in the pH adjustment, the polishing composition may be once adjusted to more basic side than a desired pH value followed by adjusting it towards acidic side by adding nitric acid, sulfuric acid, phosphoric acid etc. to adjust it to the desired pH value.

[0077] In the process for preparing the polishing composition of the present invention, the timing of the step for mixing pH adjusting agent is not particularly limited, but when e.g. an alicyclic resin acid (A) not forming a salt is mixed into a liquid medium, it is preferred to mix a pH adjusting agent into the original liquid medium to form a basic liquid medium (which may already contain a part or all of other components) in advance, so that e.g. alicyclic resin acid (A) becomes easily dissolved and mixed in the liquid medium and becomes hardly separated.

Abrasive Particles

[0078] The polishing composition of the present invention can exhibit its effect even in a case of not blending abrasive particles, but abrasive particles may be blended into the polishing composition, and in this case, it is possible to polish copper at higher removal rate.

[0079] As a type of abrasive particles that may be blended into the polishing composition of the present invention may, for example, be α -alumina, δ -alumina, γ -alumina, a silica or a ceria. Among these, a silica is preferably employed. In a case of employing a silica, from the viewpoint of dispersibility, stability, polishing power etc., a colloidal silica is more preferably employed.

[0080] In the case of blending abrasive particles, the average primary particle size of abrasive particles is preferably from 0.005 to 0.5 μm . It is more preferably within a range of from 0.01 to 0.3 μm . The specific surface area of the abrasive particles is preferably from 30 to 300 m^2/g . If the specific surface area is less than 30 m^2/g , the average primary particle size is too large, and if the specific surface area exceeds 300 m^2/g , the primary particle size is too small. When the average primary particle size of the abrasive particles is not too small, sufficient removal rate can be obtained, and when the average primary particle size is not too large, smooth and flat polished surface is obtained. The content of abrasive particles in the polishing composition of the present invention is preferably

from 0 to 10 mass %. It is more preferably from 0.05 to 8 mass %, the most preferably from 0.09 to 5 mass %.

Other Components

[0081] In the polishing composition employed in the polishing method of the present invention, besides the above components, a surfactant, a reducing agent, a viscosity adjusting agent, a dispersing agent, an antiseptic agent etc. may be appropriately blended so long as such blending does not deviate from the purpose of the present invention.

[0082] For example, when a surfactant is contained in the polishing composition to be employed in the polishing method of the present invention, the surfactant causes chemical and physical reaction with a copper film surface and provides an effect of protecting the copper film surface although its principle is not unclear. Further, in this case an effect of improving dispersibility of abrasive particles is obtained. Preferred surfactant to be contained in the polishing composition may, for example, be dodecylbenzenesulfonic acid, dodecyl sulfonic acid or these salts, and its preferred content in the polishing composition of the present invention is from 0.01 to 0.2 mass %. As the above salt, a potassium salt or an ammonium salt is preferably employed.

[0083] In the polishing composition of the present invention having the above construction, quantitative percentages of its components are preferably such that based on the polishing composition, carboxylic acid is from 0.11 to 8 mass %, the oxidizer is from 0.1 to 5 mass % and water is at least 90 mass %. In the polishing composition having this composition, quantitative percentages of respective carboxylic acids are such that based on the polishing composition, the alicyclic resin acid (A) is 0.01 to 2 mass %, the aliphatic carboxylic acid (B-2) is 0.001 to 0.5 mass % based on the total amount of the polishing composition if the aliphatic carboxylic acid (B-2) is contained, and carboxylic acid(s) in total other than these is preferably from 0.1 to 5 mass %. Here, the carboxylic acid(s) other than these is preferably the carboxylic acid (B-1), particularly preferably the carboxylic acid (B-1a).

[0084] Further preferred polishing composition of the present invention contains based on the polishing composition, from 0.01 to 2 mass % of rosin, from 0.1 to 5 mass % of 2-pyridinecarboxylic acid, from 0.1 to 5 mass % of at least one type of oxidizer selected from the group consisting of ammonium persulfate, hydrogen peroxide and potassium persulfate, from 0.01 to 5 mass % of abrasive particles and at least 90 mass % of water, wherein the pH value of the polishing composition is adjusted to be within a range of from 8.0 to 11 by at least one type of base selected from the group consisting of potassium hydroxide, ammonium and an organic amine. Here, the rosin may contain the aliphatic carboxylic acid (B-2), or it may contain no such aliphatic carboxylic acid (B-2). The rosin containing aliphatic carboxylic acid (B-2) is preferably a rosin containing from 10 to 15 mass % of aliphatic resin acid that is an aliphatic carboxylic acid (B-2). Regardless of whether the aliphatic carboxylic acid (B-2) is present in the rosin or not, the polishing composition preferably contains based on the polishing composition, from 0.001 to 0.5 mass % of aliphatic carboxylic acid (B-2), particularly preferably from 0.005 to 0.2 mass %. The aliphatic carboxylic acid (B-2) is preferably at least one type selected from the group consisting of oleic acid, linolic acid, linolenic acid and an alkenylsuccinic acid having total from 14 to 22 carbon atoms. Particularly, oleic acid, linolic acid or a combination thereof is preferred.

[0085] The polishing composition having such a construction realizes a flat surface having high precision when it is used for polishing copper used as a metal for wiring. For this reason, it is possible to obtain a semiconductor integrated circuit surface having excellent flat surface state having little dishing or erosion, and thus, the polishing composition is extremely effective for multi-layer wiring and reduction in pattern size in the semiconductor integrated circuit. More specifically, since the polishing composition effectively suppresses progress of dishing or erosion in a production process of semiconductor integrated circuit device in which copper wiring is formed by a damascene method, it is possible to obtain a semiconductor integrated circuit surface having excellent and flat surface state.

[0086] Still another component may be added to the polishing composition of the present invention to form a polishing agent for use. In this method, change of polishing composition or polishing mechanism according to polishing process become unnecessary in many cases.

Polishing Composition

[0087] The polishing composition of the present invention contains an oxidizer, a dissolving agent for metal oxide, an agent for forming protection film and water; and is characterized in that increase of dishing amount is at most 10 nm and that the final dishing amount is at most 20 nm, when the polishing composition is used for polishing a copper layer formed on an insulation layer via a barrier layer to form a pattern in which copper buried wirings of each 100 μm wide and insulation layers of each 100 μm are alternately arranged, and when the polishing composition is used to further polish the copper after the barrier layers adjacent to the copper buried wirings are exposed, at the same removal rate as that before the barrier layers are exposed, for a time required to remove 200 nm of copper before the barrier layers are exposed. By this method, it is possible to realize flat surface of copper used as a metal for wiring with high accuracy.

[0088] Here, the dissolving agent for metal oxide corresponds to, in the above explanations, the carboxylic acid (B-1) or the carboxylic acid (B-1a), and the agent for protection film corresponds to, in the explanations, the alicyclic resin acid (A). Further, the polishing composition of the present invention preferably has a pH value of from 7.5 to 12, particularly preferably from 8.5 to 10.5.

[0089] It is more preferred that a polishing time at which the increase of dishing amount is at most 10 nm is a polishing time required for removing 400 nm of the copper. Further, the final dishing amount is preferably at most 15 nm, more preferably at most 10 nm.

[0090] "When the polishing composition is used for polishing a copper layer formed on an insulation layer via a barrier layer to form a pattern in which copper buried wirings of each 100 μm wide and insulation layers of each 100 μm are alternately arranged, and when the polishing composition is used to further polish the copper after the barrier layers adjacent to the copper buried wirings are exposed, at the same removal rate as that before the barrier layers are exposed, for a time required to remove 200 nm of copper before the barrier layers are exposed" is a condition for obtaining the increase of dishing amount, and does not limit the application of the polishing composition according to the present invention.

[0091] The polishing conditions include variable conditions such as removal rate and pressing pressure of polishing pad, but there is no particular limitation to these conditions.

Generally speaking, it is preferred to make the removal rate from 200 to 800 nm/min and make the pressing pressure of polishing pad at most 4 psi (which is converted to 27.6 kPa).

[0092] In the above, the dishing amount is the depth indicated by the reference numeral 7 in FIG. 1(b) to be described later. Meanwhile, the increase of dishing amount means the difference (Y-X) between the dishing amount (X) at a time when the barrier layer is exposed and the dishing amount (Y) when the copper is further polished (i.e. over polishing) at a removal rate of copper before the barrier layer is exposed for a time required to polish 200 nm of copper.

[0093] In a case of determining whether or not the increase of dishing amount is at most 10 nm or whether or not the final dishing amount is at most 20 nm, it is preferred to carry out several times of testing to obtain the average value.

[0094] In the above conditions, the timing when the barrier layers adjacent to the copper-buried wirings are exposed, can be defined as a timing when a part of barrier layer is observed for the first time when actual polishing is carried out and appropriate observation of polishing surface is carried out.

[0095] "The removal rate of copper before the barrier layers are exposed" may be actually obtained under the above conditions, but in this step, since presence or absence of pattern does not affect the removal rate of copper, it may also be obtained by using a polishing sample (e.g. a blanket wafer) whose one surface is covered with copper as an alternative. Here, the covering copper in this case is required to be produced under the same conditions as those of the covering copper in the above-described conditions.

[0096] The following is a specific example of obtaining increase of dishing amount under the above-conditions. First of all, a polishing sample one surface of which is covered with copper, is used to obtain a time required for polishing 200 nm of copper. This value is assumed to be 30 seconds.

[0097] Then, the dishing amount (X) at a time when the barrier layers are exposed, is obtained. X is assumed to be 10 nm. Thereafter, over polishing for 30 seconds is carried out, and the dishing amount (Y) at the end of the over polishing is obtained. Y is assumed to be 17 nm.

[0098] In this case, $17\text{ nm} - 10\text{ nm} = 7\text{ nm}$ is the increase of dishing amount, and the dishing amount at the completion of over polishing is designated as the final dishing amount.

[0099] Here, "the increase of dishing amount when the copper is polished at a removal rate of copper before the barrier layers are exposed for a time required to polish 200 nm of the copper" does not necessarily means the value obtained after the copper is actually polished for the time, but means the incremental speed of dishing amount by over polishing when the over polishing is carried out after the barrier layers adjacent to the copper-buried wirings are exposed. For example, when the time required to polish 200 nm is 50 sec and the increase of dishing amount when the copper is actually polished for 60 sec is 15 nm, the increase of dishing amount converted to the polishing amount by polish of 50 seconds, that is, $15 \times (50/60) = 12.5\text{ nm}$ is the increase of dishing amount "when the copper is polished for a time required to polish 200 nm of the copper" according to the present invention.

[0100] The polishing composition according to the present invention preferably further contains abrasive particles. When the composition contains abrasive particles, it becomes possible to complete polishing in shorter time.

[0101] Further, the polishing composition according to the present invention preferably has a characteristic that the

removal rate of copper before the barrier layers are exposed is at least 100 times of the removal rate of the barrier layers. It becomes further easy to realize flat surface with high precision when copper is used as a wiring metal, in many cases.

Polishing Method

[0102] The polishing composition according to the present invention is suitably usable for a polishing method for polishing a copper layer formed on an insulation layer via a barrier layer to form a pattern in which copper-buried wirings and insulation layers are alternately arranged, wherein the method comprises a first polishing step of polishing with a first polishing composition that is the above polishing composition, and a second polishing step that is the subsequent step in the step of polishing the copper layer formed on the insulation layer via the barrier layer to form a pattern in which the copper-buried wirings and the insulation layers are alternately arranged, which is a step of polishing with a second polishing composition whereby the removal rate of copper before the barrier layers are exposed is within a range of from 0.5 to 2 times of the removal rate of the barrier layer, and the removal rate of the insulation layer is within the range of from 0.5 to 2 times of the removal rate of the barrier layer.

[0103] By this polishing method in which these two types of polishing compositions are selectively used, it is possible to realize excellent flat surface having little dishing or erosion, with good uniformity in the entire wafer when copper is used as a metal for wiring. Accordingly, this polishing method is extremely effective for multi-layer wiring and reduction of pattern size in semiconductor integrated circuits.

[0104] Conditions required for the second polishing composition, specifically, removal rate of copper, removal rate of barrier layer and removal rate of insulation layer may be obtained by using a polishing sample (e.g. a blanket wafer) one surface of which is covered by copper, the same material as the material forming barrier layer or the same material as the material forming insulation layer, in the same manner as the case of obtaining removal rate of copper. However, the covering materials in this case needs to be produced under the same conditions as those of covering materials in the above-described conditions, in the same manner as described above. Whether the conditions satisfy the respective ranges or not, is preferably judged by the averaged values of several times of sampling tests in the same manner as described above.

[0105] With respect to the first polishing step and the second polishing step, it is usually preferred that right after the first polishing step, the second polishing step is carried out to complete polishing, but another step may be included between the first polishing step and the second polishing step, before the first polishing step or after the second polishing step. The finish timing of the first polishing step or the start timing or the finish timing of the second polishing step is not particularly limited, and it is appropriately determined depending on the nature of polishing. However, it is usually preferred that the first polishing step is finished at a timing when the copper layer formed on the insulation layer via the barrier layer is removed except in the wirings, the second polishing step is started and the second polishing step is stopped at a timing when a predetermined surface flatness is obtained. Namely, in the first polishing step, copper portions other than the copper wirings are removed, and in the second polishing step, the barrier layer is removed and in most cases, a part of insulation layer and as the case requires, a part of

copper is slightly polished to form a flat surface constituted by the insulation layer and the copper layer.

[0106] From now, the materials polished in the present invention are described.

Copper Layer

[0107] A copper layer is formed on an insulation layer via a barrier layer. Its film-forming method may, for example, be a method of forming a Cu seed layer of about 100 nm thick on a barrier layer by a sputtering method, and further forming a Cu layer on the Cu seed layer by an electrolytic plating method.

Insulation Layer

[0108] The insulation layer may be a SiO₂ film formed by a plasma-CVD method using tetraethoxysilane or silane, a low-dielectric material film (e.g. SiOF film or an organic SOG film) or a film having a construction that a cap layer is combined with any of these films.

[0109] The material constituting the insulation layer as the object to be polished by the polishing composition of the present invention, may be any one of known films. Silicon dioxide film is an example. As the silicon dioxide film, usually one having a bridging structure of Si and O, in which the ratio of the number of atoms of Si and O is 1:2 is used, but another silicon dioxide film may also be employed. As such a silicon dioxide film, one deposited by a plasma-CVD method by using tetraethoxysilane (TEOS) or silane gas (SiH₄), is commonly known.

[0110] Further, in recent years, besides such a silicon dioxide film, a film made of low-dielectric material having a specific dielectric coefficient of at most 3 has become used as an insulation layer for the purpose of suppressing signal delay. As such a low-dielectric material film, a film made of fluorine-added silicon oxide (SiOF), an organic SOG film (a film containing an organic component obtainable by a spin-on-glass method), a low-dielectric material film such as a porous silica film, or an organic silicon material (generally abbreviated as SiOC) film mainly constituted by Si—O bonds and containing CH₃ bonds, are known. These films also may be suitably used as an insulation layer to which the polishing composition according to the present invention is applicable.

[0111] The organic silicon material belongs to the extension of existing process technique, and it is expected to be easily applicable to wide range of mass-production techniques by carrying out appropriate process tunings. Accordingly, a technique for flattening a film made of low-dielectric material is desired, and the polishing composition according to the present invention can be suitably used for polishing such a film.

[0112] As the organic silicon material being a low-dielectric material, a product name: Black Diamond (specific dielectric coefficient: 2.7, manufactured by APPLIED MATERIALS INC.), product name: Coral (specific dielectric coefficient: 2.7, manufactured by Novellous Systems Inc.) or Aurora 2.7 (specific dielectric coefficient: 2.7, distributed by Japan ASM Inc.) may, for example, be mentioned, and among these, a compound having a Si—CH₃ bond is preferably employed.

[0113] The polishing composition according to the present invention can also be suitably used in a case where a cap layer is formed on an insulation layer. For example, in a multi-layer structure in which on a low-dielectric insulation layer, a cap

layer, a barrier layer and metal wiring layers are laminated in this order, the polishing composition can be applied in a case of completely removing the cap followed by scraping the insulation layer to achieve flattening.

[0114] The cap layer is a layer provided for the purpose of increasing adhesiveness between the insulation layer and the barrier layer in a case of using a low-dielectric material for the insulation layer, or for the purpose of using the cap layer as an etching mask for forming grooves for burring a metal wiring layer in the low-dielectric insulation layer that is chemically mechanically fragile, or for the purpose of preventing quality change of the low-dielectric material.

[0115] As such a cap layer, usually a film constituted by silicon and oxygen is used. As such a film, a silicon dioxide film may, for example, be mentioned. As such a silicon dioxide film, usually one having a bridging structure of Si and O wherein the ratio of numbers of Si and O atoms is 1:2, is used, but a film other than this may also be used. As such a silicon dioxide film, one deposited by a plasma CVD method using tetraethoxysilane (TEOS) or a silane gas (SiH₄), is commonly known.

Barrier Layer

[0116] A barrier layer is a layer made of e.g. Ta, TaN or TiN formed on the insulation layer by e.g. a sputtering method, and it is disposed for the purpose of preventing diffusion of copper from the copper layer to the insulation layer, but in the present invention, the barrier layer also serves as a stopper for finding a timing when the wiring portion appears in the polishing of copper layer.

[0117] According to the present invention, it is possible to realize flattening of a surface with high accuracy when copper is used as a material for wiring. For this reason, it is possible to obtain a semiconductor integrated circuit having excellent and flat surface state having little dishing or erosion, whereby the present invention is extremely effective for multi-layer structure and reduction of pattern size in semiconductor integrated circuits. This feature is described in more detail below.

[0118] Generally speaking, in a case of polishing a wafer of large size, since unevenness of film thickness distribution or unevenness of polishing pressure by a pad in the wafer is inevitable, it is difficult to uniformly polish the entire region of the wafer. Accordingly, when a copper layer formed on an insulation layer via a barrier layer is polished to be removed, a barrier layer adjacent to a copper-buried wiring is exposed in a part of the wafer at first. Subsequently, when an overpolishing is carried out to remove a copper film on the barrier layer in the entire region of the wafer, there occurs a problem that dishings of the copper buried wirings sequentially exposed sequentially progress in a polishing process using a conventional polishing agent. Namely, there have been such problems that the dishing amount at a timing when the barrier layer is exposed is large, the dishing amounts become significantly uneven when the first polishing step is completed and excess copper layer is removed by overpolishing, and that erosion also occurs in some cases. For this reason, in the second polishing step, after the barrier layer is removed by polishing, it has been necessary to further remove a part of insulation layer and copper wirings to finish the copper wirings and the insulation layer to be smooth. When the removal amount in the second polishing step is increased, there is a possibility that the depth of wiring groove becomes insufficient in some portion due to uneven polishing in the wafer, or further dishing of copper wirings occurs.

[0119] On the other hand, when the polishing composition of the present invention is employed, as described in the above examples, since the initial dishing amount at a timing when the barrier layer is exposed is small and the dishing amount does not substantially increase by overpolishing, it is possible to carry out overpolishing with a margin in the first polishing step without increasing dishing or forming erosion. As a result, even if the copper layer on the barrier layer is removed in the entire wafer, it is possible to suppress the increase of dishing amount due to overpolishing to be within 10 nm in the entire region of the wafer. No erosion occurs in this step. This feature provides an effect that even in a large-sized wafer of at least 8 inches, it is possible to remove excessive copper layer smoothly and uniformly in the entire region of the wafer by overpolishing, and to make the dishing amount at the completion of polishing to be within 20 nm.

[0120] Further, since it is not necessary to excessively remove the insulation layer and the copper layer in the second polishing step, it is possible to reduce the thicknesses of the insulation layer and the copper layer and make the trench fabrication shallow, and to reduce the polishing amount. Accordingly, since it is possible to carry out the entire step in shorter time, it is possible to achieve cost down and to obtain a effect of suppressing variation of the depth of grooves for wiring or suppressing dishing of copper wirings.

[0121] Further, according to the present invention, it is possible to realize copper wirings with high precision in which decrease of groove depth for wiring (Cu thinning) is suppressed to be within 10 nm, that is required to produce a semiconductor integrated circuit of 50 nm pitch or smaller design rule.

EXAMPLES

[0122] Now, the present invention will be described with reference to Examples, but the present invention is by no means limited to these Examples. Examples 1 to 10 and Examples 12 to 19 are Examples of the present invention, and Example 11 is a Comparative Example.

[0123] The composition of each of polishing compositions of Examples 1 to 19 is shown in Table 1. The content of each component is shown in the unit of mass % based on the total of mixed polishing composition. The content of pH adjusting agent required for obtaining a desired pH value is determined in advance by a separate test using a polishing composition having the same composition. The pH value is measured by using a pH meter (pH 81-11) manufactured by Yokogawa Electric Corporation.

[0124] With respect to the polishing composition of each of Examples 1 to 10, first of all, a predetermined amount of 2-pyridinecarboxylic acid (Examples 1 to 3, Examples 5 to 10) or oxalic acid (Example 4), that are the carboxylic acids (B-1) contained in the polishing composition other than the alicyclic resin acid (A), is added to an ion-exchanged water, and subsequently, the above-mentioned content of potassium hydroxide being a pH adjusting agent is added, and they are sufficiently stirred. Further, as the stirring is continued, a potassium salt of rosin being the alicyclic resin acid (A) and a colloidal silica being abrasive particles are added, and subsequently, ammonium persulfate (Examples 1 to 7), potassium persulfate (Example 8, 9) or hydrogen peroxide (Example 10), that are oxidizers, is added to produce the polishing composition.

[0125] Here, in each of Examples 9 and 10, a part of potassium hydroxide being a pH adjusting agent is replaced by the

amount of ammonium described in Table 1, so that predetermined pH value is obtained by adding these potassium hydroxide and ammonium.

[0126] As the potassium salt of rosin being the alicyclic resin acid (A), in Examples 1 to 10, Rosin Soap 30K (product name) manufactured by ARAKAWA CHEMICAL INDUSTRIES, LTD. was used. The Rosin Soap 30K is an aqueous solution containing an aliphatic potassium salt and a rosin potassium salt, wherein the amount of aliphatic potassium salt is about 13 mass % based on the total amount of solid content consisting of the rosin potassium salt and the aliphatic potassium salt, and the main content of the aliphatic potassium salt is potassium salts of linolic acid and oleic acid.

[0127] The polishing composition of each of Examples 1 to 5 and Examples 8 to 10 contains abrasive particles made of colloidal silica and having an average primary particle size of 0.02 μm and a specific surface area of 112 m^2/g . In Example 6, the polishing composition contains 0.25 mass % of colloidal silica having an average primary particle size of 0.012 μm and a specific surface area of 195 m^2/g . In Example 6, the polishing composition contains 0.1 mass % of colloidal silica having an average particle size of 0.03 μm and a specific surface area of 80 m^2/g .

[0128] Further, in Example 2, the polishing composition also contains as another raw material a dodecylbenzenesulfonic acid being a surfactant that is neutralized by a pH adjusting agent. The amount of pH adjusting agent used for neutralization is included in the amount of pH adjusting agent in Table 1.

[0129] The polishing composition of Example 11 was prepared in the same manner as Example 2 except that it contains no alicyclic resin acid (A).

[0130] The polishing compositions of Examples 12 to 14 were prepared in the same manner as Example 1 except that potassium dihydroabietate salt, potassium tetrahydroabietate salt and potassium dehydroabietate salt, respectively, were employed instead of Rosin Soap 30K as the alicyclic resin salt.

[0131] The polishing composition of Example 15 was produced in the same manner as Example 1 except that SIZEPINE E (product name, manufactured by ARAKAWA CHEMICAL INDUSTRIES, LTD.) that is a rosin partially modified into maleic acid was employed as the alicyclic resin acid. The SIZEPINE E is a maleic-acid-modified product of rosin containing at least about 60 mass % of abietic acid, and the SIZEPINE E contains a fatty acid containing as the main components linolic acid and oleic acid, wherein the amount of fatty acid is about from 10 to 20 mass % based on the total amount of solid content consisting of the rosin and the fatty acid.

[0132] The polishing compositions of Examples 16, 17, 18 and 19 were prepared in the same manner as Example 3 except that these polishing compositions employ Vandis T-25K, Vandis E-34K and Vandis G-25K, respectively, as the alicyclic resin acid. Here, in Example 17, the pH value was made to 9.0. The Vandis T-25K and Vandis E-34K are product names of potassium salts of modified product of rosin manufactured by Harima Chemicals Inc. produced by a disproportionation process of tall rosin as the raw material. Vandis T-25 typically contains 50.5 mass % of dehydroabietic acid, 24.9 mass % of dihydroabietic acid, 4.1 mass % of isopimaric acid, 5.2 mass % of isopimaric acid isomer, 2.8 mass % of secodehydroabietic acid, 0 mass % of abietic acid, neoabietic acid and parastrinic acid, and 10.4 mass % of other components as

converted as the amount of alicyclic resin acid. Vandis G-25K is a product name of potassium salt of resin manufactured by Harima Chemicals Inc. produced by a disproportionation process of gum rosin as the raw material, and the Vandis G-25K typically contains 62.7 mass % of dehydroabietic acid, 22.6 mass % of dihydroabietic acid, 1.7 mass % of isopimaric acid, 8.9 mass % of isopimaric acid isomer, 0 mass % of secodehydroabietic acid, abietic acid, neoabietic acid and parastrinic acid, and 4.1 mass % of other components as calculated as the amount of alicyclic resin acid.

[0133] The polishing property of the polishing compositions were evaluated by the following method.

OBJECT TO BE POLISHED

[0134] As objects to be polished, blanket wafers and patterned wafers were used. As the blanket wafers, 8-inch wafers (manufactured by Sematech Inc., 000CUR015) each having a copper film formed on a Si substrate by a wet plating method, were used for evaluation of copper-removal rate. For tantalum-removal rate evaluation, 8-inch wafers (manufactured by Yamaichi) each having a tantalum film of 300 nm thick formed on a Si substrate by sputtering, were used.

[0135] As the patterned wafer, a 8-inch wafer (product name: 854CMP208) manufactured by Sematech Inc. FIG. 1(a) schematically shows a cross section of the patterned wafer before polishing. This patterned wafer has a construction that on a Si substrate 1, an insulation film made of SiO₂ on which concave portions for burring copper-buried wirings and convex portions are formed, a barrier layer 3 made of a tantalum film of 25 nm thick formed by sputtering, and a wiring metal layer 4 made of a copper film of predetermined thickness formed by a wet plating method, are laminated, and wiring patterns of various width from 100 μm to 180 nm are formed. The film thickness of the copper film on a surface of the barrier layer 3 made of tantalum on a convex portion of the insulation layer 2 is the initial film thickness 8, and the stepheight between the portions of copper film formed on a convex portion and a concave portion of the insulation layer 2 is the initial stepheight 9.

Evaluation of Polishing Property

[0136] As a polishing machine, a full-automatic CMP apparatus MIRRA manufactured by APPLIED MATERIALS INC., was used. As a polishing pad, 2-layer pad IC1400 with K-groove (manufactured by Nitta Haars Corp.) was used and its conditioning was carried out by using MEC100-PH3. 5L (manufactured by Mitsubishi Materials Corporation).

[0137] Polishing was carried out under the conditions that the supply speed of the polishing composition was 200 cm³/min, rotation speeds of the polishing head and a polishing table were 117 rpm and 123 rpm respectively, and the polishing pressure was 1 psi that was 6.89 kPa.

[0138] Measurements of copper-removal rate and tantalum-removal rate by using blanket wafers, were carried out by using a film-thickness meter RS-75 (manufactured by KLA-Tencor Inc.). Namely, with respect to each of blanket wafers with copper and blanket wafers with tantalum, the film thickness before polishing and the film thickness after 1 minute of polishing were measured, and from the difference, the copper-removal rate or the tantalum-removal rate (nm/min) was obtained. Further, by dividing the copper-removal rate by the tantalum-removal rate, the removal rate ratio (Cu/Ta ratio) between copper and tantalum was obtained. Further, the SiO₂

removal rate by using a blanket wafer was measured by using UV1280SE (manufactured by KLA-Tencor Corp.).

[0139] Polishing of each patterned wafer was carried out while the endpoint of polishing was monitored by using an optical polishing endpoint detector (manufactured by AMAT, MIRRA ISRM Endpoint Detecting System). Namely, as the polishing progress, the barrier layer made of tantalum became exposed, the reflectivity started to drop, and an endpoint was detected when the drop substantially finished and the reflectivity became constant, and thereafter, overpolishing was carried out for 30 sec, 60 sec or 25 sec. At the endpoint of polishing, the copper film on the barrier layer was removed except for a part of entire wafer, and by carrying out overpolishing, the residual copper film in such a portion is removed. The polishing time described in Table 2 to be described later, is a polishing time including such an overpolishing time.

[0140] After the polishing, with respect to a pattern in which the wiring width and spacing with were each 100 μm, the surface stepheight between a tantalum film surface and a copper film surface, namely a dishing amount, was measured by using a profiler HRP-100 apparatus (KLA-Tencor Corp.), to evaluate the degree that the copper wiring pattern surface is concaved from the tantalum film surface by polishing. The lower limit of the surface stepheight measurable by this apparatus is 10 nm. The increase of dishing amount was calculated from the dishing amounts of a patterned wafer when overpolishing was carried out for 30 sec, 60 sec or 25 sec.

[0141] FIG. 1(a) shows a schematic cross sectional view of a patterned wafer after polishing. In FIG. 1(b), the wiring metal layer 4 made of copper film was completely removed on convex portions of the insulation film 2, and surfaces of the barrier layer 3 made of a tantalum film were exposed. Further, on the concave portions of the insulation layer 2, the wiring copper layer 4 was concaved by the amount of reference numeral 7 from the barrier layer 3 surface by polishing. This surface stepheight was designated as a dishing amount 7. On the other hand, FIG. 1(c) is a schematic cross sectional view of a patterned wafer ideally polished, in which copper-buried wirings 6 are formed without forming such a surface step, that is, dishing.

[0142] Patterned wafers used for evaluation of polishing with the polishing compositions of Examples 1 and 10 each had a copper film having an initial film thickness of 650 nm and an initial stepheight of 150 nm (Example 1 and 10 in the evaluation result), and the patterned wafers employed for evaluation of polishing with polishing compositions of Examples 2, 3, 4 to 6 and 12 to 15 each had a copper film having an initial film thickness of 550 nm and an initial stepheight of 100 nm that corresponds to pattern grooves (evaluation result of Examples 2, 3a, 4 to 6 and 12 to 15). With respect to the polishing composition of Example 3, polishing evaluation of copper film by using a patterned wafer having an initial film thickness of 900 nm and an initial stepheight of 350 nm, was also carried out (evaluation result of Example 3b). A patterned wafer employed for polishing evaluation of the polishing composition of Example 7 has a copper film having an initial film thickness of 400 nm and an initial stepheight of 80 nm that corresponds to pattern grooves (evaluation result of Example 7), patterned wafers employed for polishing evaluation of the polishing compositions of Examples 8 and 9 each has a copper film having an initial film thickness of 230 nm and an initial stepheight of 50 nm that corresponds to pattern grooves (evaluation results of Examples 8 and 9), a patterned wafer employed for polishing

evaluation of the polishing composition of Example 11 has a copper film having an initial film thickness of 1,000 nm and an initial stepheight of 500 nm that corresponds to pattern grooves (evaluation result of Example 11), and patterned wafers employed for polishing evaluation of polishing compositions of Examples 16 to 19 each had a copper film having an initial film thickness of 900 nm and an initial stepheight of 350 nm that corresponds to pattern grooves (evaluation result of Examples 16 to 19).

[0143] As evident from the polishing evaluation result of these Examples, by using the polishing composition of the present invention, it is possible to polish a patterned wafer while dishing amount is suppressed. Further, it is also evident that by using the polishing composition of the present invention, the copper removal rate is at least 60 nm/min and that the

removal rate ratio between copper and tantal is at least 40 that is sufficiently large, and thus, it is possible to polish a copper film at high speed and to suppress removal of tantal film being a barrier layer.

[0144] Particularly, by employing the polishing composition of any one of Examples 1 to 10 or Example 15 in which Losin Soap 30K or SIZEPINE E is employed as the alicyclic resin acid (A), it is possible to polish a patterned wafer while the dishing amount is suppressed to be within 10 nm. Further, by employing a polishing composition of any one of Examples 1 to 7 and Example 15 in which ammonium persulfate is employed as an oxidizer, it is possible to polish a copper at a high removal rate more than 290 nm/min while the dishing amount is suppressed to be within 10 nm.

TABLE 1

Example	Alicyclic resin acid (A) and its salt	Content mass %	Carboxylic acid (B-1)	Content mass %	Oxidizer	Content mass %
Ex. 1	Rosin Soap 30K	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 2	Rosin Soap 30K	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 3	Rosin Soap 30K	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 4	Rosin Soap 30K	0.1	Oxalic acid	1	APS	1
Ex. 5	Rosin Soap 30K	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 6	Rosin Soap 30K	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 7	Rosin Soap 30K	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 8	Rosin Soap 30K	0.1	2-pyridinecarboxylic acid	1	KPS	1
Ex. 9	Rosin Soap 30K	0.1	2-pyridinecarboxylic acid	1	KPS	1.2
Ex. 10	Rosin Soap 30K	0.075	2-pyridinecarboxylic acid	1	H ₂ O ₂	0.15
Ex. 11	None		2-pyridinecarboxylic acid	0.75	APS	1
Ex. 12	Potassium dihydroabietate	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 13	Potassium tetrahydroabietate	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 14	Potassium dehydroabietate	0.1	2-pyridinecarboxylic acid	1		1
Ex. 15	Sizepine E	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 16	Vandis T-25K	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 17	Vandis T-25K	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 18	Vandis E-34K	0.1	2-pyridinecarboxylic acid	1	APS	1
Ex. 19	Vandis G-25K	0.12	2-pyridinecarboxylic acid	1	APS	1

Example	Abrasive particles	Average primary particle size nm	Content mass %	Surfactant	Content mass %	pH-adjusting agent	Content of ammonium	pH value
Ex. 1	Colloidal silica	20	0.5	None	—	KOH	0	9.2
Ex. 2	Colloidal silica	20	0.5	DBS	0.03	KOH	0	9.2
Ex. 3	Colloidal silica	20	0.25	None	—	KOH	0	9.2
Ex. 4	Colloidal silica	20	0.25	None	—	KOH	0	9.2
Ex. 5	Colloidal silica	20	0.1	None	—	KOH	0	9.2
Ex. 6	Colloidal silica	12	0.25	None	—	KOH	0	9.2
Ex. 7	Colloidal silica	30	0.1	None	—	KOH	0	9.2
Ex. 8	Colloidal silica	20	0.15	None	—	KOH	0	9.2
Ex. 9	Colloidal silica	20	0.1	None	—	KOH	0.15	9.2
Ex. 10	Colloidal silica	20	0.1	None	—	KOH	0.15	9.2
Ex. 11	Colloidal silica	20	1.2	DBS	0.03	KOH	0	9.2
Ex. 12	Colloidal silica	20	0.1	None	—	KOH	0	9.2
Ex. 13	Colloidal silica	20	0.1	None	—	KOH	0	9.2
Ex. 14	Colloidal silica	20	0.1	None	—	KOH	0	9.2
Ex. 15	Colloidal silica	20	0.1	None	—	KOH	0	9.2
Ex. 16	Colloidal silica	20	0.25	None	—	KOH	0	9.2
Ex. 17	Colloidal silica	20	0.25	None	—	KOH	0	9.0
Ex. 18	Colloidal silica	20	0.25	None	—	KOH	0	9.2
Ex. 19	Colloidal silica	20	0.25	None	—	KOH	0	9.2

Note;

APS: ammonium persulfate

KPS: potassium persulfate

DBS: potassium dodecylbenzene sulfonate

H₂O₂: hydrogen peroxide water

TABLE 2

Example	Copper removal rate (nm/min)	Tantalum removal rate (nm/min)	Cu/Ta ratio	Initial film thickness (nm)	Initial stepheight (nm)	Polishing time (s)	Dishing amount (nm)
Ex. 1	426	2.9	147	650	150	135	<10
Ex. 2	353	—	—	550	100	130	<10
Ex. 3a	415	1.7	238	550	100	125	<10
EX. 3b	415	1.7	238	900	350	190	<10
Ex. 4	293	6.3	46	550	100	152	<10
Ex. 5	413	0.6	688	550	100	135	<10
Ex. 6	376	0.8	470	550	100	158	<10
Ex. 7	421	1.2	351	400	80	106	<10
Ex. 8	66	0.6	110	230	50	240	<10
Ex. 9	281	—	—	230	50	70	<10
Ex. 10	351	—	—	650	150	146	<10
Ex. 11	436	4.4	99	1,100	500	206	250
Ex. 12	440	0.5	880	550	100	110	35
Ex. 13	294	0.5	588	550	100	160	50
Ex. 14	359	0.5	718	550	100	141	15
Ex. 15	406	0.6	677	550	100	131	<10
Ex. 16	349	1.5	233	900	350	230	25
Ex. 17	300	—	—	900	350	285	35
Ex. 18	336	1.5	224	900	350	250	40
Ex. 19	368	—	—	900	350	199	40

[0145] The compositions, pH values and results of polishing evaluation of polishing compositions of Examples 20 to 32, are summarized in Table 3. In these Examples, the content of 2-pyridinecarboxylic acid being a carboxylic acid (B-1) was 1 mass %, the content of ammonium persulfate being an oxidizer was 1 mass %; the average primary particle size of colloidal silica being abrasive particles was 20 nm, and its content was constantly 0.25 mass %, and no surfactant was contained and thus, description as to surfactant is omitted in

the Table. The pH values were adjusted to the pH values described in the Table by using KOH. Here, a content means mass % of a component based on the total amount of polishing composition being a mixed product. A polishing composition in each Example was prepared in the same manner as Example 1 except that the aliphatic carboxylic acid (B-2) was blended at the same time with the alicyclic resin acid (A). The polishing evaluations were carried out in the same manner as those of Examples 1 to 19.

TABLE 3

Example	Alicyclic resin acid (A)-1	Concentration mass %	Alicyclic resin acid (A)-2	Concentration mass %	Aliphatic carboxylic acid (B-2)	Concentration mass %	pH
20	Abietic acid	0.095	None		Linolic acid	0.005	9.3
21	Dehydroabietic acid	0.095	None		Linolic acid	0.005	9.3
22	Dihydroabietic acid	0.095	None		Linolic acid	0.005	9.3
23	Sizepine GF	0.09	None		Linolic acid	0.01	9.3
24	Sizepine GF	0.085	None		Linolic acid	0.015	9.3
25	Pine crystal KR614	0.095	None		Linolic acid	0.005	9.3
26	Sizepine GF	0.0475	Pine crystal KR614	0.0475	Linolic acid	0.005	9.3
27	Sizepine GF	0.0675	Pine crystal KR614	0.0225	Alkenyl succinic acid	0.01	9.3
28	Gum rosin RX	0.095	None		Linolic acid	0.005	9.3
29	Hartall RWW	0.095	None		Linolic acid	0.005	9.3
30	Vandis G25K	0.095	None		Linolic acid	0.005	9.3
31	Vandis T25K	0.095	None		Linolic acid	0.005	9.3
32	Vandis E34K	0.095	None		Linolic acid	0.005	9.3

Example	Copper removal rate nm/min	Tantalum removal rate nm/min	Cu/Ta ratio	Initial film thickness (nm)	Initial stepheight (nm)	Polishing time (s)	Dishing at center nm	Dishing at edge nm
20	441	1.2	368	900	350	190	<10	15
21	300	1.1	273	900	350	254	<10	<10
22	334	1.1	303	900	350	288	<10	<10
23	471	1.3	362	900	350	175	25	37
24	416	1.1	378	900	350	199	20	30

TABLE 3-continued

25	317	1.1	288	900	350	246	<10	<10
26	458	1.9	241	900	350	178	<10	<10
27	430	1.9	226	900	350	255	<10	30
28	418	1.5	279	900	350	167	16	27
29	433	1.4	309	900	350	175	14	25
30	352	1.1	320	900	350	224	<10	<10
31	411	1.1	374	900	350	195	<10	<10
32	414	1.2	345	900	350	192	<10	<10

[0146] Polishing compositions of Examples 20, 21 and 22 employ as the alicyclic resin acids (A), abietic acid, dehydroabietic acid and dihydroabietic acid (all manufactured by Wako), respectively, and further contain linolic acid as the aliphatic carboxylic acid (B-2).

[0147] Polishing compositions of Examples 33 to 59 have the compositions and pH values summarized in Table 4, and produced in the same manner as Examples 20 to 32. In each of these Examples, the content of 2-pyridinecarboxylic acid being the carboxylic acid (B-1) was 1 mass %; the content of ammonium persulfate being an oxidizer was 1 mass %; the average primary particle size of colloidal silica being abrasive

particles was 20 nm and its content was 0.25 mass %; a pH adjusting agent employed was constantly KOH, and the description of pH adjusting agent is omitted in the Table. A content amount means a mass % of component based on the total amount of polishing composition being a mixture. In each of Examples 41 and 42, the polishing composition contained as another raw material, dodecylbenzenesulfonic acid being a surfactant in a state that it was neutralized by a pH adjusting agent. The pH adjusting agent used for neutralization is included in the pH adjusting agent in the Table. Polishing evaluation was carried out in the same manner as those of Examples 1 to 19.

TABLE 4

Ex. (A)	Alicyclic resin acid Concentration mass %	Aliphatic carboxylic acid (B-2)	Concentration mass %	Surfactant	Concentration mass %	pH
33 Rosin A	0.09	Maleic acid	0.01	None		9.3
34 Rosin A	0.09	Myristoleic acid	0.01	None		9.3
35 Rosin A	0.095	Linolic acid	0.005	None		9.3
36 Rosin A	0.09	Linolic acid	0.01	None		9.3
37 Rosin A	0.09	Oleic acid	0.01	None		9.3
38 Rosin A	0.085	Oleic acid	0.015	None		9.3
39 Rosin A	0.085	Eladic acid	0.015	None		9.3
40 Rosin A	0.09	Alkenyl succinic acid	0.01	None		9.3
41 Rosin A	0.094	None	None	DBS	0.05	9.3
42 Rosin A	0.094	None	None	DBS	0.1	9.3
43 Rosin B	0.095	Linolic acid	0.005	None		9.3
44 Rosin B	0.095	Oleic acid	0.005	None		9.3
45 Rosin B	0.095	Oleic acid + Linolic acid	0.0025 + 0.0025	None		9.3
46 Rosin B	0.09	Alkenyl succinic acid	0.01	None		9.3
47 Rosin B	0.085	Alkenyl succinic acid	0.015	None		9.3
48 Rosin C	0.095	Linolic acid	0.005	None		9.3
49 Rosin D	0.095	Linolic acid	0.005	None		9.3
50 Rosin A	0.09	Linolenic acid	0.01	None		9.3
51 Rosin A	0.09	Docosahexaenoic acid	0.01	None		9.3
52 Rosin A	0.09	Nervonic acid	0.01	None		9.3
53 Rosin A	0.09	Decanoic acid	0.01	None		9.3
54 Rosin A	0.09	Lauric acid	0.01	None		9.3
55 Rosin A	0.09	Myristic acid	0.01	None		9.3
56 Rosin A	0.0925	Myristic acid	0.0075	None		9.3
57 Rosin A	0.095	Myristic acid	0.005	None		9.3
58 Rosin A	0.09	Palmitinic acid	0.01	None		9.3
59 Rosin A	0.09	Stearic acid	0.01	None		9.3

Ex.	Copper removal rate nm/min	Tantalum removal rate nm/min	Cu/Ta ratio	Initial film thickness (nm)	Initial stepheight (nm)	Polishing time (s)	Dishing at center nm	Dishing at edge nm
33	479	0.5	959	900	350	171	40	100
34	429	2.0	215	900	350	180	<10	<10
35	467	1.4	333	900	350	176	10	25
36	397	1.1	361	900	350	208	10	<10
37	408	2.1	194	900	350	181		<10
38	413	1.7	243	900	350	189	20	35
39	432	2.1	206	900	350	186	20	20
40	397	1.1	361	900	350	185	30	25
41	336	—	—	900	350	222	30	35

TABLE 4-continued

42	320	—	—	900	350	265	20	32
43	412	1.2	343	900	350	181	<10	20
44	432	1.4	309	900	350	183	15	25
45	417	1.5	278	900	350	173	<10	25
46	366	2.1	174	900	350	192	<10	40
47	353	1.8	196	900	350	200	23	30
48	441	1.2	367	900	350	187	10	20
49	452	1.1	411	900	350	185	<10	23
50	388	2.0	194	900	350	210	<10	<10
51	455	2.1	217	900	350	178	<10	12
52	483	1.9	254	900	350	174	75	110
53	395	2.1	188	900	350	164	120	110
54	400	1.9	210	900	350	197	15	15
55	291	2.8	104	900	350	309	<10	<10
56	246	2.0	123	900	350	260	<10	<10
57	395	2.1	188	900	350	185	<10	<10
58	395	1.9	208	900	350	188	<10	<10
59	479	2.0	240	900	350	174	50	80

DBS: docecylbenzenesulfonic acid

[0148] Examples 62 to 72 and Examples 74 and 75 are Examples of the present invention, and Example 73 is a Conventional Example.

[0149] The polishing composition of each of the Examples 60 to 75 was prepared in the following manner by using the amount of raw materials shown in Table 5. First of all, a predetermined amount of carboxylic acid (B-1) was added to an ion-exchanged water, and KOH as a pH adjusting agent was added and they were sufficiently stirred. Further, as the stirring was continued, alicyclic resin acid (A), its salt, as the case requires, aliphatic carboxylic acid (B-2), and further, ammonium persulfate as an oxidizer were added, and colloidal silica as adhesive particles were added to prepare the polishing composition. Here, the content amount described in the Table each means a mass % based on the total amount of polishing composition as a mixture.

[0150] Each of the polishing compositions of Examples 60, 61, 65 to 70 and 72 whose aliphatic carboxylic acid (B-2) in Table 5 is noted as "note", employed Pine crystal E or Rosin Soap 30K being an alicyclic resin acid (A) and its salt, respectively, each containing linolic acid and oleic acid that are aliphatic carboxylic acids (B-2).

[0151] Further, the content of pH adjusting agent was adjusted so that the polishing composition finally had the pH value described in the Table. In Examples 67 and 69, ammonium (NH₃) and tetramethylammonium hydroxide (TMAH) were employed respectively, as pH adjusting agents instead of KOH, and in Example 70, KOH and 0.4 mass % of ethanolamine were employed, and the composition of these Examples were adjusted so as to have the pH values described in the Table. For the abrasive particles, a colloidal silica having an average primary particle size of 0.02 μm and a specific surface area of 112 m²/g was employed.

[0152] In Examples 65 and 73, quinaldic acid was employed as carboxylic acid (B-1), in Examples 66 and 67, glycine was employed as carboxylic acid (B-1), and in Example 68, alanine was employed as carboxylic acid (B-1).

[0153] In Example 71, EXTRA OLEIN 90 (product name) manufactured by NOF Corporation and having an oleic acid purity of at least 90%, was contained in a state that it was neutralized by a pH adjusting agent. The pH adjusting agent used for neutralization is included in the pH adjusting agent in Table 1.

[0154] In Example 64, ammonium dodecylsulfonate (ADS) was employed as a surfactant, and in Examples 72 and 73, dodecylbenzenesulfonic acid was employed as a surfactant.

[0155] In Example 68, a polishing composition was prepared in the same manner as Example 4 of JP-A-2002-12854 without containing alicyclic resin acid (A) and its salt.

[0156] Table 6 shows evaluation results.

[0157] Polishing evaluation of each of Examples 60 to 75 was carried out in the same manner as Examples 1 to 19 except that a patterned wafer was prepared in the following manner.

[0158] Patterned wafers employed for polishing evaluation of polishing compositions of Examples 60, 62 to 64, 70, 71, 74 and 75 (Examples 60, 62 to 64, 70, 71a to 71d, 74a, 74b, 75a and 75b in Table 6 of test result), each had a copper film having an initial film thickness of 800 nm and an initial stepheight of 400 nm. Patterned wafers employed for polishing evaluation of the polishing composition of Example 61 (Example 61 in Table 6 of test result) each had a copper film having an initial film thickness of 550 nm and an initial stepheight of 100 nm. Patterned wafers employed for polishing evaluation of the polishing compositions of Examples 65 and 68 (Examples 65 and 68 in Table 6 of test result) each had a copper film having an initial film thickness of 350 nm and an initial stepheight of 100 nm. Patterned wafers employed for polishing evaluation of the polishing composition of Example 66 (Example 66 in Table 6 of test result) each had a copper film having an initial film thickness of 180 nm and an initial stepheight of 55 nm. Patterned wafers employed for polishing evaluation of the polishing compositions of Examples 67 and 69 (Examples 67 and 69 in Table 1 of test results) each had a copper film having an initial film thickness of 500 nm and an initial stepheight of 100 nm that corresponds to pattern grooves. Patterned wafers employed for polishing evaluation of the polishing compositions of Examples 72 and 73 (Examples 72a, 72b, 73a and 73b in Table 6 of test results) each had a copper film having an initial film thickness of 500 nm and an initial stepheight of 80 nm that corresponds to pattern grooves. Further, patterned wafers employed for additional polishing evaluation of the polishing composition of Example 3 (Example 3c in Table 6 of test results) each had a copper film having an initial film thickness of 800 nm and an initial stepheight of 400 nm.

[0159] In Table 6, “polishing endpoint” means a polishing time to reach the above mentioned point at which a copper film on a barrier layer is removed except for a part and the barrier layer is exposed”, and an overpolishing time means a polishing time after the endpoint. A total polishing time is the total of polishing endpoint and overpolishing time. Measurements of dishing was carried out separately at the central portion (center) and the peripheral portion (edge) in Table 6, a flat rate means a removal rate of a blanket wafer.

[0160] An increase of dishing amount is a value converted to an increase of dishing amount produced by polishing a wafer after a barrier layer adjacent to a copper buried wiring is exposed, at a removal rate of copper before the barrier layer is exposed, for a time required to remove 200 nm of copper before the barrier layer is exposed. For example, at central portion of wafers of Examples 73a and 73b, it is $(50-48) \times (60/25) \times (200/256) = 3.8$ nm.

[0161] Dishing is considered to increase as the polishing time increases. Considering this point, in Examples 71a to 71d, the increase of dishing amount defined in this specification is not considered to be 10 nm or more when the increase of dishing amount is calculated from the difference between

a dishing amount at 0 second of overpolishing time and a dishing amount at 30 seconds of overpolishing time, or calculated from the differences among dishing amounts at 0 second, 60 seconds and 120 seconds of overpolishing times.

[0162] In Examples 72a and 72b, only dishing amounts at 30 seconds and 60 seconds overpolishing time were evaluated, but since dishing increases as polishing time increases, increase of dishing amount in these cases is not considered to be 10 nm or more. Examples 74a, 74b, 75a and 75b are the same in this respect. On the other hand, in Examples 73a and 73b, the dishing amount is large and its variation is also large already at the endpoint.

[0163] In Example 3c, the increase of dishing amount “when a wafer was overpolished at a removal rate of copper before the barrier layer is exposed” for a time required to remove 622 nm of the copper before the barrier layer is exposed, was at most 10 nm, and in Examples 71a to 71d, 72a, 72b, 74a, 74b, 75a and 75b, the increase of dishing amount “when a wafer was overpolished at a removal rate of copper before the barrier layer is exposed” for a time required to remove 128 to 629 nm of the copper before the barrier layer is exposed, was at most 10 nm.

TABLE 5

	Abrasive particles	Content Wt %	Alicyclic resin acid (A) and its salt	Content wt %	Carboxylic acid (B-1)	Content wt %		
Ex. 60	Colloidal silica	0.25	Sizepine E	0.10	2-Pyridinecarboxylic acid	1.0		
Ex. 61	Colloidal silica	0.10	Sizepine E	0.10	2-Pyridinecarboxylic acid	1.0		
Ex. 62	Colloidal silica	1.0	Pine crystal KE604	0.10	2-Pyridinecarboxylic acid	1.0		
Ex. 63	Colloidal silica	1.0	Pine crystal KE604B	0.10	2-Pyridinecarboxylic acid	1.0		
Ex. 64	Colloidal silica	1.0	Pine crystal KR614	0.094	2-Pyridinecarboxylic acid	1.0		
Ex. 65	Colloidal silica	1.0	Rosin Soap 30K	0.10	Quinaldic acid	1.0		
Ex. 66	Colloidal silica	1.0	Rosin Soap 30K	0.10	Glycine	1.5		
Ex. 67	Colloidal silica	0.25	Rosin Soap 30K	0.10	Glycine	2.0		
Ex. 68	Colloidal silica	0.50	Rosin Soap 30K	0.07	Alanine	1.0		
Ex. 69	Colloidal silica	0.25	Rosin Soap 30K	0.01	2-Pyridinecarboxylic acid	1.0		
Ex. 70	Colloidal silica	0.25	Rosin Soap 30K	0.01	2-Pyridinecarboxylic acid	1.0		
Ex. 71a to d	Colloidal silica	0.25	Pine crystal KR614	0.06	2-Pyridinecarboxylic acid	1.0		
Ex. 72a, b	Colloidal silica	0.50	Rosin Soap 30K	0.20	2-Pyridinecarboxylic acid	1.0		
Ex. 73a, b	Colloidal silica	1.2	None	—	Quinaldic acid	0.5		
Ex. 74a, b	Colloidal silica	0.25	Rosin C	0.08	2-Pyridinecarboxylic acid	1.0		
Ex. 75a, b	Colloidal silica	0.25	Rosin C	0.08	2-Pyridinecarboxylic acid	1.0		
	Aliphatic carboxylic acid (B-2)	Content wt %	Oxidizer	Content wt %	Surfactant	Content wt %	pH adjusting agent	pH
Ex. 60	Note	—	APS	1.0	None	—	KOH	9.2
Ex. 61	Note	—	APS	1.0	None	—	KOH	9.2
Ex. 62	Linolic acid	0.01	APS	1.0	None	—	KOH	9.2
Ex. 63	Linolic acid	0.015	APS	1.0	None	—	KOH	9.2
Ex. 64	None	—	APS	1.0	ADS	0.03	KOH	9.2
Ex. 65	Note	—	APS	1.0	None	—	KOH	9.2
Ex. 66	Note	—	APS	1.0	None	—	KOH	9.2
Ex. 67	Note	—	APS	1.5	None	—	NH3	9.2
Ex. 68	Note	—	APS	1.1	None	—	KOH	9.2
Ex. 69	Note	—	APS	1.2	None	—	TMAH	9.2
Ex. 70	Note	—	APS	1.0	None	—	KOH, ethanolamine	9.2
Ex. 71a to d	Extra olein 90	0.05	APS	1.1	None	—	KOH	9.2
Ex. 72a, b	Note	—	APS	1.0	DBS	0.03	KOH	9.2
Ex. 73a, b	None	—	APS	1.0	DBS	0.03	KOH	9.2

TABLE 5-continued

Ex. 74a, b	Oleic acid	0.03	APS	1.0	None	—	KOH	9.2
Ex. 75a, b	Linolic acid	0.02	APS	1.0	None	—	KOH	9.2

ADS: ammonium dodecylsulfonate

TABLE 6

	Initial film thickness nm	Initial stepheight nm	Polishing time		Total polishing time	Overpolished amount (converted to Cu thickness)
			Polishing endpoint	Overpolishing time		
Ex. 3a	550	100	95	30	125	208
Ex. 3b	900	350	160	30	190	208
Ex. 3c	800	400	141	120	261	830
Ex. 60	800	400	131	120	251	812
Ex. 61	550	100	101	30	131	203
Ex. 62	800	400	152	30	182	195
Ex. 63	800	400	172	30	202	168
Ex. 64	800	400	158	30	188	175
Ex. 65	350	100	199	60	259	79
Ex. 66	180	55	118	60	178	62
Ex. 67	500	100	320	30	350	54
Ex. 68	350	100	213	30	243	43
Ex. 69	500	100	79	30	109	222
Ex. 70	800	400	165	30	195	210
Ex. 71a	800	400	130	0	130	0
Ex. 71b	800	400	125	30	155	235
Ex. 71c	800	400	127	60	187	470
Ex. 71d	800	400	128	120	248	940
Ex. 72a	500	80	112	30	142	127
Ex. 72b	500	80	112	60	172	255
Ex. 73a	500	80	107	0	107	0
Ex. 73b	500	80	107	25	132	107
Ex. 74a	800	400	149	35	184	215
Ex. 74b	800	400	151	130	281	800
Ex. 75a	800	400	185	45	230	209
Ex. 75b	800	400	183	180	363	838

	Flat rate			Dishing		Increase of dishing amount	
	Cu removal rate	Ta removal rate	Cu/Ta ratio	Center nm	Edge nm	Center nm/min	Edge nm/min
Ex. 3a	415	1.7	238	<10	—	—	—
Ex. 3b	415	1.7	238	<10	—	—	—
Ex. 3c	415	1.7	238	<10	<10	<10	—
Ex. 60	406	0.6	677	<10	<10	—	—
Ex. 61	406	0.6	677	<10	<10	—	—
Ex. 62	389	—	—	<10	<10	—	—
Ex. 63	335	—	—	<10	<10	—	—
Ex. 64	350	—	—	10	15	—	—
Ex. 65	79	—	—	<10	<10	—	—
Ex. 66	62	—	—	<10	<10	—	—
Ex. 67	108	0.8	133	<10	<10	—	—
Ex. 68	86	1.2	71	<10	<10	—	—
Ex. 69	445	0.9	510	<10	15	—	—
Ex. 70	419	1.0	419	<10	<10	—	—
Ex. 71a	470	2.0	235	<10	<10	—	—
Ex. 71b	470	2.0	235	<10	<10	<10	<10
Ex. 71c	470	2.0	235	<10	<10	<10	<10
Ex. 71d	470	2.0	235	<10	<10	<10	<10
Ex. 72a	255	2.5	102	<10	<10	—	—
Ex. 72b	255	2.5	102	<10	<10	<10	<10
Ex. 73a	256	—	—	48	100	—	—
Ex. 73b	256	—	—	50	90	3.8	-24
Ex. 74a	369	1.9	194	<10	<10	—	—
Ex. 74b	369	1.9	194	<10	<10	<10	<10
Ex. 75a	279	1.8	152	<10	<10	—	—
Ex. 75b	279	1.8	152	<10	<10	<10	<10

[0164] The composition of the alicyclic resin acid (A) was analyzed with respect to samples of plurality of lots by PTAH method by using gas chromatography. Namely, 6 milligram of each sample to be analyzed was dissolved in 0.5 milliliter of PTAH (manufactured by GL Science Inc., Phenyl Trimethyl Ammonium Hydroxide 0.2 mol methanol solution), and put them into a gas chromatography apparatus for which the injection temperature was set to 250° C., so that the sample was instantly turned into methyl ester for measurement. For a column, a capillary column having an inner diameter of 0.25 mm, a length of 25 m and a film thickness of 0.25 μm filled with DEGS, was employed, the oven temperature was set to 180° C., and the injection amount of sample was 4.0 μL. FID was employed for a detector, and from the peak area on the measurement chart obtained, content of each component was obtained.

[0165] Table 7 summarizes analysis results of the composition of alicyclic resin acid (A) used in each example. As a result of analysis by the above GC/MS method, it was understood that Rosin Soap 30K contains as main components 45 to 55 mass % of abietic acid and 20 to 25 mass % of dehydroabietic acid, and contains about 13 mass % of potassium salt of fatty acid containing as the main component potassium salts of linolic acid and oleic acid based on the total solid content amount of potassium salt of rosin and potassium salt of fatty acid contained.

[0166] Sizepine GF is a product name of modified rosin fumarate made from a gum rosin manufactured by ARAKAWA CHEMICAL INDUSTRIES, LTD. Pine crystal KR614 is a product name of dehydrogenated rosin made from a gum rosin manufactured by ARAKAWA CHEMICAL INDUSTRIES, LTD., and it has become clear that its dehydrogenation rate is 80% and contains as the main component 75 to 85 mass % of dehydroabietic acid. For each of the polishing compositions of Examples 26 and 27, two types of alicyclic resin acids that are Sizepine GF and Pine crystal KR614 were employed as a mixture. Gum rosin RX and Hartall RWW employed for the polishing compositions of Examples 28 and 29 respectively, are product names of rosins manufactured by Harima Chemicals Inc. made from gum rosin and tall rosin respectively.

[0167] Rosin A is a rosin made from tall rosin. Rosins B-1, B-2 and B-3 are rosins made from gum rosin, and contain abietic acid with a content of about 40 mass %, 50 mass % and 60 mass % respectively. Further, rosins A, B-1, B-2 and B-3 each contains substantially no aliphatic carboxylic acid (B-2).

[0168] Pine crystal KE604B employed in Example 62 is an acrylic-acid-modified product manufactured by ARAKAWA CHEMICAL INDUSTRIES, LTD. obtained by modifying a rosin raw material into acrylic acid, which contains partial unreacted rosin. Pine crystal KE604 employed in Example 61 is a modified rosin manufactured by ARAKAWA CHEMICAL INDUSTRIES, LTD. obtained by further hydrogenating the acrylic-acid-modified product.

TABLE 7

	Sizepine GF (ARAKAWA CHEMICAL INDUSTRIES, LTD.)	Abietic acid (Wako)	Dehydroabietic acid (Wako)	Dihydroabietic acid (Wako)
Rosin raw material	Gum	Gum	Gum	Gum
Organic acid modification	Fumaric acid modification	None	None	None
Sandaracopimaric acid	13.5	1.2	—	—
Parastrinic acid	11.9	—	—	—
Dehydroabietic acid	14.0	5.3	79.9	34.1
Abietic acid	47.6	89.1	—	3.2
Neoabietic acid	4.7	—	—	—
Pimaric acid	3.1	4.4	—	—
Isopimaric acid	—	—	—	—
Isomer of pimaric acid	—	—	—	—
Dihydroisopimaric acid	—	—	—	2.2
Isomer of iopimaric acid	—	—	14.0	—
Dihydropimaric acid	—	—	—	60.5
Isomer of dihydroisopimaric acid	—	—	6.0	—
Isomer of pimaric acid	—	—	—	—
Isomer of pimaric acid	5.2	—	—	—
Fatty acid	—	—	—	—
Other	—	—	—	—

TABLE 7-continued

	Rosin A	Rosin B	Rosin C	Rosin D	Pine crystal KR614 (ARAKAWA CHEMICAL INDUSTRIES, LTD.)	Gum Rosin RX (Harima Chemicals Inc.)	Hartall RWW (Harima Chemicals Inc.)
Rosin raw material	Tall	Gum	Gum	Gum	Gum	Gum	Tall
Organic acid modification	None	None	None	None	None	None	None
Sandaracopimaric acid	1.8	1.7	1.5	1.5	—	10.4	4.8
Parastrinic acid	9.6	26.8	19.9	12.6	—	19.6	7.5
Dehydroabietic acid	20.9	2.7	2.6	3.7	82.5	7.0	30.1
Abietic acid	49.9	39.0	50.1	60.3	0.4	46.8	43.8
Neoabietic acid	4.5	20.2	17.4	11.8	—	12.1	2.9
Pimaric acid	2.9	8.5	7.5	8.0	—	—	3.3
Isopimaric acid	5.2	1.1	0.7	0.9	—	—	7.6
Isomer of pimaric acid	—	—	—	—	1.4	—	—
Dihydroisopimaric acid	—	—	—	—	4.9	—	—
Isomer of iopimaric acid	—	—	—	—	10.7	—	—
Dihydropimaric acid	—	—	—	—	—	—	—
Isomer of dihydroisopimaric acid	—	—	—	—	—	—	—
Isomer of pimaric acid	—	—	0.3	—	—	—	—
Isomer of pimaric acid	—	—	—	—	—	—	—
Fatty acid	—	—	—	—	—	—	—
Other	5.2	—	—	1.3	—	4.1	—

Example 76

[0169] This example is an example of polishing method in a patterning step of polishing a copper layer formed on an insulation layer via a barrier layer to form alternately arranged copper-buried wirings and insulation layers, wherein the method comprises a first polishing step of polishing the copper layer formed on the insulation layer via the barrier layer by using the polishing composition of the present invention as a first polishing composition, and a second polishing step to be carried out subsequently to the first polishing step.

[0170] A polishing composition for the second polishing step for polishing the barrier layer and the insulation layer was produced in the following manner. Nitric acid, KOH and citric acid were added to a purified water, they were stirred for 10 minutes to obtain an "a" solution. Then, benzotriazole dissolved in ethylene glycol was added to the "a" solution, and pullulan (molecular weight: 2×10^5) was added to the solution and stirred them for 10 minutes to obtain a "b" solution.

[0171] Then, an aqueous dispersed solution of colloidal silica was gradually added to the "b" solution so that the solution had a pH value of pH 2. Further, hydrogen peroxide solution was added to the solution and they were stirred for 30 minutes to obtain a second polishing composition. Here, pullulan is a polysaccharide formed by combining 3 glucose molecules in α -1,4 bond to produce maltotriose and further bonding maltotrioses in α -1,6 bond. The concentrations of these components were such that nitric acid was 0.6 mass %, KOH was 0.5 mass %, citric acid was 0.2 mass %, benzotriazole was 0.1 mass %, ethylene glycol was 1.5 mass %, pullulan was 0.15 mass %, colloidal silica was 5 mass % and hydrogen peroxide was 1.2 mass %.

[0172] The polishing conditions at a time of using this second polishing composition were the same as those described above except that IC1400-K-groove (manufactured by NITTA HAAS INCORPORATED) was employed as a polishing pad, the polishing pressure was set to 2 psi that is 14 kPa and the rotation speeds of polishing head and polishing table were 97 rpm and 103 rpm respectively. The removal rates of copper layer, tantal barrier layer and SiO_2 layer on a blanket wafer were 97 nm/min, 72 nm/min and 66 nm/min respectively.

[0173] A wafer obtained in Example 71 in which excessive copper layer was removed and a tantal surface was exposed, is polished by using this second polishing composition to remove excessive barrier layer (25 nm thick) on the insulation layer, and further 25 nm of insulation layer is removed, whereby excellent flat surface is obtained in the entire region of the wafer in which the total amount of dishing and erosion after the second polishing step is 10 nm in an isolated wiring portion of 100 μm wide, and the total amount is 10 nm in a 90% density wiring portion in which wiring width is 9 μm and insulation layer width is 1 μm .

[0174] Here, erosion tends to occur in a narrow wiring portion or a dense wiring portion, and is a phenomenon that as compared with an insulation layer portion (Global portion) having no wiring pattern, an insulation layer in a wiring portion is excessively removed, whereby the insulation layer partially becomes thin as shown in FIG. 2. Namely, an erosion portion 18 is formed, in which the surface is further removed by polishing than the polished portion 20 of Global portion. Here, in FIG. 2, a barrier layer is omitted.

INDUSTRIAL APPLICABILITY

[0175] The present invention enables to obtain a semiconductor integrated circuit having excellent flat surface state,

and is extremely effective for multi-layer structuring and reduction of pattern size of semiconductor integrated circuits. Further, when the polishing composition of the present invention is employed, it is possible to carry out polishing with low pressure while dishing or erosion is suppressed.

[0176] The entire disclosures of Japanese Patent Application No. 2005-368082 filed on Dec. 21, 2005, Japanese Patent Application No. 2006-125474 filed on Apr. 28, 2006 and Japanese Patent Application No. 2006-277585 filed on Oct. 11, 2006 including specifications, claims, drawings and summaries are incorporated herein by reference in their entireties.

What is claimed is:

1. A polishing composition comprising a neutralized carboxylic acid, an oxidizing agent and water, wherein a part of the carboxylic acid is an alicyclic resin acid (A), and the polishing composition has a pH value of from 7.5 to 12.

2. The polishing composition according to claim 1, wherein the alicyclic resin acid (A) is at least one type of carboxylic acid selected from the group consisting of abietic acid, an isomer of abietic acid, pimaric acid, an isomer of pimaric acid, a rosin and these derivatives.

3. The polishing composition according to claim 1, wherein the alicyclic resin acid (A) is neutralized by a basic potassic compound, an ammonium or an organic amine.

4. The polishing composition according to claim 1, wherein the other part of the carboxylic acid contains at least one type of carboxylic acid (B-1a) selected from the group consisting of: a polycarboxylic acid having at least two carboxylic groups; and a carboxylic acid having at least one carboxylic group and at least one type of group selected from the group consisting of nitrogen-containing heterocyclic group, amino group a hydroxyl group and thiol group.

5. The polishing composition according to claim 4, wherein said the other part of the carboxylic group contains besides at least one type of the carboxylic acid (B-1a), an aliphatic carboxylic acid (B-2) containing total at least 11 carbon atoms and having at least one long-chain hydrocarbon group containing at least 8 carbon atoms and at least one carboxylic group.

6. The polishing composition according to claim 5, wherein the aliphatic carboxylic acid (B-2) is an unsaturated aliphatic carboxylic acid containing total from 12 to 23 carbon atoms and having at least one unsaturated group in its long-chain hydrocarbon portion.

7. The polishing composition according to claim 5, wherein the aliphatic carboxylic acid (B-2) is a saturated aliphatic carboxylic acid wherein the long-chain hydrocarbon group portion has from 11 to 17 carbon atoms in total.

8. The polishing composition according to claim 1, wherein the ratio of the alicyclic resin acid (A) based on the total amount of carboxylic acid is from 0.1 to 70 mass %.

9. The polishing composition according to claim 5, wherein the content of the aliphatic carboxylic acid (B-2) is from 0.001 to 0.5 mass % based on the total amount of the polishing composition.

10. The polishing composition according to claim 1, wherein the oxidizer is at least one type of oxidizer selected from the group consisting of hydrogen peroxide, ammonium persulfate and potassium persulfate.

11. The polishing composition according to claim 1, which further contains abrasive particles.

12. The polishing composition according to claim 1, which contains from 0.11 to 8 mass % of carboxylic acid, 0.1 to 5 mass % of oxidizer and at least 90 mass % of water based on the polishing composition.

13. A polishing composition containing based on the polishing composition:

from 0.01 to 2 mass % of alicyclic resin acid (A);

from 0.1 to 5 mass % of at least one type of carboxylic acid (B-1a) selected from the group consisting of a polycarboxylic acid having at least two carboxylic groups, and a carboxylic acid having at least one carboxylic group and at least one type of group selected from the group consisting of a nitrogen-containing heterocyclic group, an amino group, a hydroxyl group and thiol group;

from 0 to 0.5 mass % of aliphatic carboxylic acid (B-2) having a long-chain hydrocarbon group having at least 10 carbon atoms and at least one carboxylic group, and having at least 11 carbon atoms in total;

from 0.1 to 5 mass % of an oxidizer; and

at least 90 mass % of water;

wherein the alicyclic resin acid (A), the carboxylic acid (B-1a) and the aliphatic carboxylic acid (B-2) are neutralized, and the polishing composition has a pH value of from 8.0 to 11.

14. A polishing composition characterized in that increase of dishing amount is at most 10 nm and that the final dishing amount is at most 20 nm, when the polishing composition is used for polishing a copper layer formed on an insulation layer via a barrier layer to form a pattern in which copper buried wirings of each 100 μm wide and insulation layers of each 100 μm are alternately arranged, and when the polishing composition is used to further polish the copper after the barrier layers adjacent to the copper buried wirings are exposed, at the same removal rate as that before the barrier layers are exposed, for a time required to remove 200 nm of copper before the barrier layers are exposed.

15. The polishing composition according to claim 14, wherein the removal rate of copper before the barrier layers are exposed is at least 100 times of the removal rate of the barrier layer.

16. The polishing composition according to claim 14, which contains an oxidizer, a dissolving agent for metal oxide, an agent for forming protection film and water.

17. The polishing composition according to claim 16, wherein the agent for forming protection film is an alicyclic resin acid (A) and the pH value of the polishing composition is from 7.5 to 12.

18. The polishing composition according to claim 16, wherein the solvent for metal oxide is at least one type of carboxylic acid (B-1a) selected from the group consisting of a polycarboxylic acid having at least two carboxylic groups; and a carboxylic acid having at least one carboxylic group at least one type of group selected from the group consisting of a nitrogen-containing heterocyclic group, an amino group, a hydroxyl group and thiol group.

19. The polishing composition according to claim 17, which further contains an aliphatic carboxylic acid (B-2) having a long-chain hydroxyl group having at least 8 carbon atoms and at least one carboxyl group, the aliphatic carboxylic acid (B-2) having at least 11 carbon atoms.

20. The polishing composition according to claim 16, wherein the oxidizer is at least one type of oxidizer selected from the group consisting of hydrogen peroxide, ammonium persulfate and potassium persulfate.

21. The polishing composition according to claim 16, which further contains abrasive particles.

22. A method for polishing a surface of a semiconductor integrated circuit, which comprises polishing a copper film for wiring formed on a surface having grooves by using the polishing composition as defined in claim 1.

23. A method for polishing a surface of a semiconductor integrated circuit, which comprises polishing a copper film for wiring formed on a surface having grooves by using the polishing composition as defined in claim 13.

24. A method for polishing a surface of a semiconductor integrated circuit, which comprises polishing a copper film for wiring formed on a surface having grooves by using the polishing composition as defined in claim 14.

25. A method for producing a copper wiring for a semiconductor integrated circuit, which comprises polishing a copper film for wiring formed on a surface having grooves by using the polishing composition as defined in claim 1.

26. A method for producing a copper wiring for a semiconductor integrated circuit, which comprises polishing a copper film for wiring formed on a surface having grooves by using the polishing composition as defined in claim 13.

27. A method for producing a copper wiring for a semiconductor integrated circuit, which comprises polishing a copper film for wiring formed on a surface having grooves by using the polishing composition as defined in claim 14.

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