[0003]

However, the hydrogen peroxide solution not only has a problem that when a metal such as, for example, copper, silver, gold is contained, decomposition of hydrogen peroxide is promoted and lifetime of the etching liquid is shortened, but also has such problems that it is difficult to control a concentration of hydrogen peroxide in the etching liquid and that etching rate is slow, and the like.

[0004]

In addition, for example, the ~~fluorine~~ hydrofluoric acid-hydrogen peroxide mixed liquid has such problems that, for example, etching rate is slow and that corrosion of underlying metal or metal on a substrate is significant, and the like, and the phosphoric acid - hydrogen peroxide mixed liquid has such problems, for example, that etching residue is generated and that corrosion of underlying metal or metal on a substrate is significant, and the like.

[0005]

Under such circumstance, as an etching method for a Ti-based metal film such as Ti film, TiW alloy film without generating etching residue, an etching method for a Ti-based film on a semiconductor substrate using a solution containing hydrogen peroxide and a chelating agent has been proposed (see, JP-A-2002-155382).

[0006]

However, depending on a kind of underlying metal or metal on a semiconductor substrate, such problems occur that etching selectivity is poor because, for example, corrosion of other metals

the etching agent for a W-based metal film on a semiconductor substrate, on which a metal bump or a metal wiring having lower ionization tendency than that of tungsten has been formed, relevant to the present invention, that is, the etching agent relevant to the present invention <2>, not only W-based metal film can be rapidly etched, but also etching of a W-based metal film directly beneath relevant metal bump or metal wiring, so-called side-etching caused by bimetallic corrosion (Galvanic corrosion) by a metal bump or a metal wiring having lower ionization tendency than that of tungsten and tungsten can be inhibited.

[**0111**]

In the etching agent for a W-based metal film on a semiconductor substrate, on which a metal bump or a metal wiring having lower ionization tendency than that of tungsten has been formed, relevant to the present invention, that is, the etching agent relevant to the present invention <2>, in particular, by using sodium hydroxide or ~~tetra-ammonium-~~tetramethylammonium hydroxide as (C) at least one or more kinds of basic compound selected from (c-1) inorganic alkalis and (c-2) organic amines, such advantages that bimetallic corrosion (Galvanic corrosion) can be inhibited, and the like, can be obtained, because electron transfer, in which the cation species such as sodium ion, quaternary ammonium ion generated from these basic compounds is one cause of the bimetallic corrosion (Galvanic corrosion), is inhibited, and electric influence can be dispersed in a wide range while electric double layer can be maintained due to existence of a small amount of a specific anion species such as a sulfate ion, a citrate ion, and the like.

	Dipping ~~30~~10 min.	Dipping ~~60~~ 20min.	Dipping ~~90~~30 min.
Example 7	1%	2%	3%
Example 8	4%	17%	28%

[**0133**]

It has been known that stability of hydrogen peroxide is decreased under high pH condition. However, as obvious from the results of Table 4, it was found that when ammonia was used as an inorganic alkali (Example 8, pH: 8.5), hydrogen peroxide decomposition rate was higher and lifetime of the etching agent was shorter, even though pH was lower, as compared with the case when potassium hydroxide was used (Example 7, pH: 9.0). From the above description, it could be understood that, as an inorganic alkali to be used in the present invention, hydroxides of alkali metals such as potassium hydroxide, and the like are preferable.

[**0134**]

Reference Example 1 and Examples 9 to Example 14

(1) Preparation of etching agents

An etching agent composed of the following composition was prepared. (The details of component are described in Table 5)

Hydrogen peroxide	28.0% by weight
Phosphonic acid chelating agent (HEDPO)	0.34% by weight
Basic compound (sodium hydroxide)	0.58% by weight
Citric acid (buffering agent)	0.07% by weight
Sodium sulfate	0.0 to 0.2% by weight
Water	Remainder
pH	7.8

* HEDPO = 1-hydroxyethylidene-1,1'-diphosphonic acid

~~WHAT IS CLAIMED IS~~Claims:

1. An etching agent for a semiconductor substrate on which copper wiring has been formed on a titanium (Ti)-based metal film composed of a solution comprising at least the following (A), (B), (C) and ~~(C), and~~ (D-1) ~~and/or (D-2)~~:

(A) hydrogen peroxide;

(B) a phosphonic acid chelating agent having a hydroxyl group and not having a nitrogen atom;

(C) ~~a basic compound~~an inorganic alkali;

(D-1) a copper anticorrosive selected from the group consisting of epihalohydrin-modified polyamide, benzotriazole compound, hydroxycarboxylic acid, or nitrogen-containing cyclic compound~~;~~

~~(D-2) 0.01 to 3% by weight of two or more kinds of anion species other than phosphonic acid chelating agents having a hydroxyl group, in which anion species have no oxidizing power~~.

~~2. The etching agent according to claim 1, wherein the semiconductor substrate is the one on which copper wiring has been formed, and wherein the etching agent comprises at least the above-described (A), (B), (C) and (D-1).~~

~~3. The etching agent according to claim 2, wherein the semiconductor substrate, on which the copper wiring has been formed, is the semiconductor substrate, in which copper wiring has been formed on a titanium (Ti)-based metal film.~~

2. The etching agent according to claim 1, wherein the (C) inorganic alkali is (c-1) a hydroxide of an alkali metal.

~~4.~~3. The etching agent according to claim ~~2~~1, wherein the copper

wiring is the one for forming a lead (Pb)-free solder bump.

~~5.~~4. The etching agent according to claim ~~2~~1, wherein ~~it~~the etching agent is the one to be used in a Pb-free solder bump forming step.

~~6.~~5. The etching agent according to claim ~~2~~1, wherein pH of the solution is 7 to 10.

~~7.~~6. The etching agent according to claim ~~2~~1, wherein ~~the~~ (B) ~~a~~the phosphonic acid chelating agent having a hydroxyl group and not having a nitrogen atom is the one to be selected from the group consisting of 1-hydroxyethylidene-1,1'-diphosphonic acid, 1-hydroxypropylidene-1,1'-diphosphonic acid, and 1-hydroxybutylidene-1,1'-diphosphonic acid.

~~8. The etching agent according to claim 2, wherein the (C) basic compound is (c-1) an inorganic alkali.~~

~~9. The etching agent according to claim 8, wherein the (c-1) inorganic alkali is an alkali metal hydroxide or ammonia.~~

~~10.~~7. The etching agent according to claim ~~8~~2, wherein ~~the~~ (c-1) ~~inorganic~~the hydroxide of an alkali metal is ~~a~~ potassium hydroxide or ~~a~~ sodium hydroxide.

~~11. The etching agent according to claim 2, wherein the (D-1) copper anticorrosive is epihalohydrin-modified polyamide, benzotriazole compound, hydroxycarboxylic acid, or nitrogen-containing cyclic compound.~~

~~12.~~8. The etching agent according to claim ~~8~~7, comprising (A) 10 to 35% by weight of hydrogen peroxide, (B) 0.1 to 3% by weight of the phosphonic acid chelating agent having a hydroxyl group and not having a nitrogen atom, (~~c-1~~C) 0.2 to 12% by weight of the inorganic alkali, and (D-1) 0.05 to 5% by weight of the copper anticorrosive

selected from the group consisting of epihalohydrin-modified polyamide, benzotriazole compound, hydroxycarboxylic acid, or nitrogen-containing cyclic compound.

~~13.~~9. The etching agent according to claim ~~8~~7, wherein the etching agent is prepared from a solution comprising hydrogen peroxide and a liquid for preparing etching agent composed of a solution comprising the phosphonic acid chelating agent having a hydroxyl group and not having a nitrogen atom, the inorganic alkali and the copper anticorrosive selected from the group consisting of epihalohydrin-modified polyamide, benzotriazole compound, hydroxycarboxylic acid, or nitrogen-containing cyclic compound.

~~14.~~10. The etching agent according to claim ~~13~~9, wherein (i) a mixing ratio of the solution comprising hydrogen peroxide and the liquid for preparing etching agent is 1:9 to 98:2, and/or (ii) pH of the solution comprising hydrogen peroxide and pH of the liquid for preparing etching agent are adjusted so that final pH of the mixed solution of these solutions falls in a range of 7 to 10.

~~15. The etching agent according to claim 13, wherein pH of the solution comprising hydrogen peroxide and pH of the liquid for preparing etching agent are adjusted so that final pH of the mixed solution of these solutions falls in a range of 7 to 10.~~

~~16.~~11. The etching agent according to claim ~~13~~9, wherein (i) final concentrations in the etching agent obtained by mixing ~~mixed solution of~~ the solution comprising hydrogen peroxide and the liquid for preparing etching agent are (A) 10 to 35% by weight of hydrogen peroxide, (B) 0.1 to 3% by weight of the phosphonic acid chelating agent having a hydroxyl group and not having a nitrogen atom, (~~c-1~~C) 0.2 to 12% by weight of the inorganic alkali, and (D-1) 0.05 to

5% by weight of the copper anticorrosive selected from the group consisting of epihalohydrin-modified polyamide, benzotriazole compound, hydroxycarboxylic acid, or nitrogen-containing cyclic compound, and/or (ii) the etching agent is prepared by mixing the solution comprising 15 to 30% by weight of hydrogen peroxide and the liquid for preparing etching solution composed of the solution comprising 0.2 to 2% by weight of the phosphonic acid chelating agent having a hydroxyl group and not having a nitrogen atom, 0.5 to 10% by weight of the inorganic alkali, and 0.05 to 2% by weight of the copper anticorrosive selected from the group consisting of epihalohydrin-modified polyamide, benzotriazole compound, hydroxycarboxylic acid, or nitrogen-containing cyclic compound, in a mixing ratio of 4:6 to 9:1.

~~17. The etching agent according to claim 13, wherein the etching agent is prepared by mixing the solution comprising 15 to 30% by weight of hydrogen peroxide and the liquid for preparing etching solution composed of the solution comprising 0.2 to 2% by weight of the phosphonic acid chelating agent having a hydroxyl group, 0.5 to 10% by weight of the inorganic alkali, and 0.05 to 2% by weight of the copper anticorrosive, in a mixing ratio of 4:6 to 9:1.~~

~~18.~~12. An etching method, characterized in that selective etching of a titanium (Ti)-based metal film on a semiconductor substrate is performed using the etching agent according to claim ~~21~~.

~~19.~~13. The etching method according to claim ~~18~~12, wherein the etching agent is prepared by mixing a solution comprising hydrogen peroxide and a liquid for preparing etching agent composed of a solution comprising ~~a~~the phosphonic acid chelating agent having a hydroxyl group and not having a nitrogen atom, ~~a basic~~

~~compound~~the inorganic alkali and ~~a~~the copper anticorrosive selected from the group consisting of epihalohydrin-modified polyamide, benzotriazole compound, hydroxycarboxylic acid, or nitrogen-containing cyclic compound, preferably wherein a mixing ratio of the solution comprising hydrogen peroxide and the liquid for preparing etching agent is 1:9 to 98:2.

~~20. The etching method according to claim 19, wherein a mixing ratio of the solution comprising hydrogen peroxide and the liquid for preparing etching agent is 1:9 to 98:2.~~

~~21. The etching agent according to claim 1, wherein the semiconductor substrate is the one on which a metal bump or a metal wiring having lower ionization tendency than that of tungsten has been formed, and wherein the etching agent comprises at least the above-described (A), (B), (C) and (D-2).~~

~~22. The etching agent according to claim 21, wherein the metal bump or metal wiring having lower ionization tendency than that of tungsten is composed of gold, silver, palladium, tin or an alloy thereof.~~

~~23. The etching agent according to claim 21, wherein the semiconductor substrate on which metal bump or metal wiring having lower ionization tendency than that of tungsten has been formed is a semiconductor substrate in which relevant metal bump or metal wiring has been formed on the upper part of a tungsten (W) -based metal film.~~

~~24. The etching agent according to claim 23, wherein the metal bump or metal wiring having lower ionization tendency than that of tungsten is a metal bump, and a copper wiring has been formed between relevant metal bump and the W-based metal film.~~

~~25. The etching agent according to claim 23, wherein the W-based metal film is a titanium-tungsten (TiW) alloy film.~~

~~26. The etching agent according to claim 21, wherein pH of the solution is 6 to 10.~~

~~27. The etching agent according to claim 21, wherein the (B) phosphonic acid chelating agent having a hydroxyl group is the one of at least one or more kinds selected from 1-hydroxyethylidene-1,1'-diphosphonic acid, 1-hydroxypropylidene-1,1'-diphosphonic acid, and 1-hydroxybutylidene-1,1'-diphosphonic acid.~~

~~28. The etching agent according to claim 21, wherein the (C) basic compound is the one of at least one or more kinds selected from inorganic alkalis and organic amines.~~

~~29. The etching agent according to claim 21, wherein the (C) basic compound is either a sodium hydroxide or a tetramethylammonium hydroxide.~~

~~30. The etching agent according to claim 21, wherein the (D-2) 0.01 to 3% by weight of two or more kinds of anion species other than phosphonic acid chelating agents having a hydroxyl group, in which anion species have no oxidizing power, are a combination of 0.0001 to 0.5% by weight of at least one or more kinds of anion species derived from an inorganic acid selected from a sulfate ion, a sulfite ion, a chloride ion, a phosphate ion a phosphite ion and a hypophosphite ion and 0.0099 to 2.5% by weight of at least one or more kinds of anion species derived from an organic acid selected from a citrate ion and a malate ion.~~

~~31. The etching agent according to claim 21, wherein the (D-2) 0.01 to 3% by weight of two or more kinds of anion species other~~

than phosphonic acid chelating agents having a hydroxyl group, in which anion species have no oxidizing power, are a combination of 0.0001 to 0.5% by weight of any one kind of anion species derived from an inorganic acid selected from a sulfate ion, a sulfite ion, a chloride ion or a phosphate ion and 0.0099 to 2.5% by weight of any one kind of anion species derived from an organic acid selected from a citrate ion or a malate ion.

32. The etching agent according to claim 21, wherein the (D-2) 0.01 to 3% by weight of two or more kinds of anion species other than phosphonic acid chelating agents having a hydroxyl group, in which anion species have no oxidizing power, are a combination of 0.0001 to 0.5% by weight of any one kind of anion species derived from an organic acid selected from a carbonate ion, an acetate ion, a citrate ion or a malate ion and 0.0099 to 2.5% by weight of an anion species derived from an organic acid selected from a citrate ion or a malate ion other than the anion species derived from the organic acid selected above.

33. The etching agent according to claim 21, wherein the (D-2) 0.01 to 3% by weight of two or more kinds of anion species other than phosphonic acid chelating agents having a hydroxyl group, in which anion species have no oxidizing power, are a combination of 0.0001 to 0.5% by weight of at least one or more kinds of anion species derived from an inorganic acid selected from a sulfate ion, a sulfite ion and chloride ion and 0.0099 to 2.5% by weight of at least one or more kinds of anion species derived from an inorganic acid selected from a phosphate ion, a phosphate ion and a hypophosphite ion.

34. The etching agent according to claim 21, comprising (A) 10 to

~~35% by weight of hydrogen peroxide, (B) 0.1 to 3% by weight of the phosphonic acid chelating agent having a hydroxyl group, (C) 0.1 to 5% by weight of the basic compound, and (D-2) 0.01 to 3% by weight of two or more kinds of anion species other than phosphonic acid chelating agents having a hydroxyl group, in which anion species have no oxidizing power.~~

~~35. The etching agent according to claim 21, prepared from a solution comprising hydrogen peroxide and a liquid for preparing etching agent composed of a solution comprising the phosphonic acid chelating agent having a hydroxyl group, the basic compound and two or more kinds of anion species other than phosphonic acid chelating agents having a hydroxyl group, in which anion species have no oxidizing power.~~

~~36. An etching method, characterized by etching a W-based metal film on a semiconductor substrate using the etching agent according to claim 21.~~

~~37. The etching method according to claim 36, wherein the etching agent is prepared by mixing a solution comprising hydrogen peroxide and a liquid for preparing etching agent composed of a solution comprising a phosphonic acid chelating agent having a hydroxyl group, a basic compound and two or more kinds of anion species other than phosphonic acid chelating agents having a hydroxyl group, which anionic species have no oxidizing power.~~

~~38. The etching method according to claim 37, wherein mixing ratio of the solution comprising hydrogen peroxide and the liquid for preparing the etching agent is 30:70 to 99:1.~~

~~39.~~14. A liquid for preparing the etching agent of any one of claims 1 to 11 for a semiconductor substrate on which copper wiring has

been formed on a titanium (Ti)-based metal film composed of a solution comprising at least the following (B), ~~and~~ (C), and (D-1) ~~and/or (D-2)~~:

(B) a phosphonic acid chelating agent having a hydroxyl group and not having a nitrogen atom;

(C) ~~a basic compound~~an inorganic alkali;

(D-1) a copper anticorrosive selected from the group consisting of epihalohydrin-modified polyamide, benzotriazole compound, hydroxycarboxylic acid, or nitrogen-containing cyclic compound;

~~(D-2) two or more kinds of anion species other than phosphonic acid chelating agents having a hydroxyl group, in which anion species have no oxidizing power~~.

~~40. The liquid for preparing etching agent according to claim 39, wherein the (C) basic compound is (c-1) an inorganic alkali, and wherein the liquid comprises at least the (B), relevant (c-1) and the (D-1).~~

~~41.~~15. The liquid for preparing the etching agent according to claim ~~40~~14, wherein the liquid is used ~~to be used~~ for preparing etching agent by mixing with a solution comprising hydrogen peroxide; preferably (i) a mixing ratio of the liquid and the solution comprising hydrogen peroxide is 1:9 to 98:2, and/or (ii) pH of the liquid is adjusted so that final pH of the etching agent after mixing with the solution comprising hydrogen peroxide falls in a range of 7 to 10, and/or (iii) final concentrations in the etching agent obtained by mixing the liquid and the solution comprising hydrogen peroxide are (A) 10 to 35% by weight of hydrogen peroxide, (B) 0.1 to 3% by weight of the phosphonic acid chelating agent having a hydroxyl group and

not having a nitrogen atom, (c-1) 0.2 to 12% by weight of the inorganic alkali, and (D-1) 0.05 to 5% by weight of the copper anticorrosive selected from the group consisting of epihalohydrin-modified polyamide, benzotriazole compound, hydroxycarboxylic acid, or nitrogen-containing cyclic compound.

~~42. The liquid for preparing etching agent according to claim 41, wherein mixing ratio of the liquid and the solution comprising hydrogen peroxide is 1:9 to 98:2.~~

~~43. The liquid for preparing etching agent according to claim 41, wherein pH of the liquid is adjusted so that final pH of the etching agent after mixing with the solution comprising hydrogen peroxide falls in a range of 7 to 10.~~

~~44. The liquid for preparing etching agent according to claim 41, to be used for preparing the etching agent having final concentrations after mixing with the solution comprising hydrogen peroxide of (A) 10 to 35% by weight of hydrogen peroxide, (B) 0.1 to 3% by weight of the phosphonic acid chelating agent having a hydroxyl group, (c-1) 0.2 to 12% by weight of the inorganic alkali, and (D-1) 0.05 to 5% by weight of the copper anticorrosive.~~

~~45. The liquid for preparing etching agent according to claim 39, comprising at least the (B), (C) and (D-2).~~

~~46. The liquid for preparing etching agent according to claim 45, to be used for preparing etching agent by mixing with a solution comprising hydrogen peroxide.~~

~~47. The liquid for preparing etching agent according to claim 46, wherein mixing ratio of the liquid and the solution comprising hydrogen peroxide is 30:70 to 99:1.~~

~~48. The liquid for preparing etching agent according to claim 46,~~

~~wherein pH of the liquid is adjusted so that final pH of the etching agent after mixing with the solution comprising hydrogen peroxide falls in a range of 6 to 10.~~

~~49. The liquid for preparing etching agent according to claim 46, to be used for preparing the etching agent having final concentrations after mixing with the solution comprising hydrogen peroxide of (A) 10 to 35% by weight of hydrogen peroxide, (B) 0.1 to 3% by weight of the phosphonic acid chelating agent having a hydroxyl group, (C) 0.1 to 5% by weight of the inorganic alkali, and (D-2) 0.01 to 3% by weight of two or more kinds of anion species other than phosphonic acid chelating agents having a hydroxyl group, in which anion species have no oxidizing power.~~