

SPECIFICATION

COMPOSITION FOR REMOVING RESIDUE FROM WIRING BOARD AND CLEANING METHOD

Technical Field

[0001]

The present invention relates to a composition for removing a residue to be used for manufacturing a wiring board of a semiconductor integrated circuit, a liquid crystal panel, an organic electroluminescence (hereinafter abbreviated as "EL") panel, a printed board or the like and a cleaning method and in detail, to a composition for removing a residue from a wiring board containing titanium or a titanium alloy and a cleaning method.

Background art

[0002]

In a manufacturing step of a wiring board of a semiconductor integrated circuit, a liquid crystal panel, an organic EL panel, a printed board or the like, in fabricating a circuit on the board surface, a wiring is fabricated by coating a resist and a photomask on the board surface, developing the resist and then performing a dry etching step. A residue derived from the resist or a residue derived from

members used in the integrated circuit is deposited on a pattern side part or a bottom part after the dry etching step, and therefore, the removal of this residue is necessary.

[0003]

As a method for removing this residue deposited on the board after the drying etching step, a wet process is studied, and for example, there are proposed a method for using a removing composition composed of hydroxylamine, an alcoholamine and a gallic acid compound (Patent Document 1), a method for using a resist removing composition composed of a fluorine compound and an organic solvent (Patent Document 2), a method for using a resist removing composition composed of hydrogen peroxide, a quaternary ammonium salt and an anticorrosive (Patent Document 3) and a method for using a resist removing composition composed of hydrogen peroxide ammonium sulfate, a fluorine compound and a chelating agent (Patent Document 4).

[0004]

These resist removing compositions to be used in the residue removal step by a wet process are required to have low corrosiveness against wiring materials such as copper, aluminum, titanium and alloys thereof, insulating film materials and diffusion-preventing film materials. In particular, following the miniaturization of a semiconductor integrated circuit or the like in recent years, a tolerable

level of corrosiveness has become extremely severe.

However, the foregoing methods by a wet process are large in corrosiveness against titanium or titanium alloys and hardly applicable to the residue removal step in the manufacture of a wiring board using titanium or a titanium alloy.

[0005]

Patent Document 1: JP-A-9-296200

Patent Document 2: JP-A-11-67632

Patent Document 3: JP-A-2002-202617

Patent Document 4: JP-A-2004-325918

Disclosure of the Invention

Problems that the Invention is to Solve

[0006]

An object of the present invention is to provide a composition for removing a residue, which in manufacturing a wiring board, is able to effectively remove residues remaining after dry etching which are derived from a resist or metals without corroding titanium or titanium alloys with high corrosiveness and a cleaning method.

Means for Solving the Problems

[0007]

The present inventors made extensive and intensive

investigations regarding the foregoing problems. As a result, it has been found that a composition containing an oxidizing agent and an azole compound and having a pH of from 1 to 7 is able to effectively remove a resist residue or a residue derived from a metal which is a wiring material such as copper, aluminum and titanium after dry etching without corroding titanium or titanium alloys, leading to accomplishment of the present invention.

[0008]

Specifically, the present invention provides a composition for removing a residue from a wiring board and a cleaning method.

1. A composition for removing a residue from a wiring board comprising an oxidizing agent and an azole compound and having a pH of from 1 to 7.

2. The composition for removing a residue from a wiring board as set forth above in 1, wherein the oxidizing agent is at least one member selected among hydrogen peroxide, ozone, potassium permanganate, percarbonic acid and salts thereof, perphosphoric acid and salts thereof, persulfuric acid and salts thereof, iodic acid and salts thereof, bromic acid and salts thereof, perchloric acid and salts thereof, chloric acid and salts thereof, and hypochlorous acid and salts thereof.

3. The composition for removing a residue from a wiring board as set forth above in 2, wherein the oxidizing agent is hydrogen

peroxide.

4. The composition for removing a residue from a wiring board as set forth above in any one of 1 to 3, wherein the azole compound is a triazole compound and/or a tetrazole compound.

5. The composition for removing a residue from a wiring board as set forth above in any one of 1 to 4, wherein the azole compound is from 0.0001 to 5 % by mass.

6. The composition for removing a residue from a wiring board as set forth above in any one of 3 to 5, wherein hydrogen peroxide is from 0.01 to 20 % by mass.

7. A cleaning method of a wiring board comprising removing a residue from a wiring board after dry etching by using the composition for removing a residue from a wiring board as set forth above in any one of 1 to 6.

8. The cleaning method of a wiring board as set forth above in 7, wherein the wiring board contains titanium and/or a titanium alloy.

Advantages of the Invention

[0009]

By using the composition for removing a residue from a wiring board according to the present invention, residues remaining after dry etching which are derived from a resist or metals such as copper, aluminum and titanium in a wiring board of a semiconductor integrated circuit, a liquid crystal

panel, an organic EL panel, a printed board or the like, especially a titanium-containing wiring board can be effectively removed without corroding titanium or titanium alloys; and a semiconductor device using such a wiring board can be efficiently manufactured.

Brief Description of the Drawings

[0010]

Fig. 1 is a cross-sectional view of a silicon wafer board used in the Examples and Comparative Examples, in which a via structure and a trench structure are prepared by an etching treatment. In the drawing, though a via and a trench are precisely prepared on copper wirings, in fact, there may be the case where the via or trench deviates. In that case, a titanium portion is exposed.

Description of Reference Numerals and Signs

[0011]

1: Silicon substrate, 2: Carbon-doped silicon oxide, 3: Resist, 4: Copper, 5: Titanium, 6: Dry etching residue

Best Modes for Carrying Out the Invention

[0012]

The present invention is hereunder described in detail.

Examples of the oxidizing agent to be used in the

composition for removing a residue from a wiring board (hereinafter also referred to simply as "composition for removing a residue") of the present invention include hydrogen peroxide, ozone, potassium permanganate, percarbonic acid and salts thereof, perphosphoric acid and salts thereof, persulfuric acid and salts thereof, iodic acid and salts thereof, bromic acid and salts thereof, perchloric acid and salts thereof, chloric acid and salts thereof, and hypochlorous acid and salts thereof. These can be used singly or in admixture, and hydrogen peroxide is especially preferable.

In the case where hydrogen peroxide is used as the oxidizing agent, the concentration of hydrogen peroxide in the cleaning liquid is preferably from 0.01 % by mass to 20 % by mass, more preferably from 0.05 % by mass to 5 % by mass, and especially preferably from 0.1 % by mass to 3 % by mass. When the concentration of hydrogen peroxide is 0.01 % by mass or more, the residue removal properties are enhanced, and when it is not more than 20 % by mass, an increase of the solubility of titanium is avoided.

[0013]

Examples of the azole compound which is used in the composition for removing a residue of the present invention include imidazole, pyrazole, thiazole, isoxazole, benzotriazole, 1H-1,2,3-triazole, 1H-1,2,4-triazole,

1H-tetrazole, 1-methylimidazole, benzimidazole, 3-methylpyrazole, 4-methylpyrazole, 3,5-dimethylpyrazole, 3-aminopyrazole, 3-amino-5-methylpyrazole, 4-methylthiazole, 5-methylisoxazole, 3-amino-5-methylisoxazole, 2-aminothiazole, 1,2,3-triazole-4,5-dicarboxylic acid, 3,5-diamino-1,2,4-triazole, 3-amino-1,2,4-triazole, 1H-4,5-methylbenzotriazole, 2-(3,5-di-t-butyl-2-hydroxyphenyl)benzotriazole and 5-amino-1H-tetrazole. Above all, triazole compounds or tetrazole compounds are favorable, and 5-amino-1H-tetrazole, benzotriazole, 1H-1,2,4-triazole and 3,5-diamino-1,2,4-triazole are more preferable. These azole compounds are an anticorrosive of titanium or titanium alloys and can be used singly or in admixture.

[0014]

In the composition for removing a resin of the present invention, in addition to the foregoing azole compound, pyrroles, pyridines, quinolines, morpholines and the like may be used in combination as the anticorrosive.

Examples of the pyrroles include pyrrole, 2H-pyrrole, 1-methylpyrrole, 2-ethylpyrrole, 2,4-dimethylpyrrole, 2,5-dimethylpyrrole and 1,2,5-trimethylpyrrole. Examples of the pyridines include pyridine, 2-picoline, 3-picoline, 4-picoline, 2-ethylpyridine, 3-ethylpyridine, 4-ethylpyridine, 2,3-lutidine, 2,4-lutidine, 3,5-lutidine, 4-t-butylpyridine, 2-aminopyridine, 3-aminopyridine and

4-aminopyridine. Examples of the quinolines include quinoline, isoquinoline, quinaldine, 3-methylquinoline, 2-hydroxyquinoline, 3-hydroxyquinoline, 5-hydroxyquinoline, 3-aminoquinoline, 5-aminoquinoline, 8-aminoquinoline, 5-nitroquinoline, 6-nitroquinoline, 8-nitroquinoline, 8-methyl-5-nitroquinoline and 8-hydroxy-5-nitroquinoline. Examples of the morpholines include morpholine, 1-methylmorpholine, 1-ethylmorpholine, hydroxyethylmorpholine, hydroxypropylmorpholine, aminoethylmorpholine and aminopropylmorpholine.

[0015]

The concentration of the azole compound which is used in the composition for removing a residue of the present invention is preferably from 0.0001 % by mass to 5 % by mass, more preferably 0.01 % by mass to 3 % by mass, and especially preferably from 0.1 % by mass to 1 % by mass. When the concentration of the azole compound is 0.0001 % by mass or more, an anticorrosion effect against titanium or titanium alloys is obtained, and from the viewpoints of economy and practicality, the concentration of the azole compound is preferably not more than 5 % by mass.

[0016]

Since hydrogen peroxide is instable against metals, the composition for removing a residue of the present invention preferably contains a stabilizer of hydrogen peroxide. Though

known stabilizers can be used as the stabilizer of hydrogen peroxide, specific examples thereof include chelating stabilizers such as aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetra(methylenephosphonic acid), diethylenetriamine-penta(methylenephosphonic acid) and ethylenediamine. In the present invention, these stabilizers can be used without particular limitations. The concentration of the stabilizer is preferably 0.0001 % by mass to 0.1 % by mass. When the concentration of the stabilizer is 0.0001 % by mass or more, an effect for stabilizing hydrogen peroxide is obtained, and from the viewpoints of economy and practicality, the concentration of the stabilizer is preferably not more than 0.1 % by mass.

[0017]

The pH of the composition for removing a residue of the present invention is from 1 to 7, and preferably from 2 to 6. When the pH is 1 or more, the residue removal properties are enhanced, and when the pH is not more than 7, the dissolution of titanium or titanium alloys is suppressed. A substance which is used for adjusting the pH is not particularly limited, and general acids including inorganic acids such as sulfuric acid, phosphoric acid and hydrochloric acid and organic acids such as formic acid and acetic acid can be used.

[0018]

By using the composition for removing a residue of the present invention singly in a step of removing a residue after dry etching in a semiconductor manufacturing apparatus, a residue derived from a resist on a wiring board of a semiconductor integrated circuit, a liquid crystal panel, an organic EL panel, a printed board or the like and a residue derived from a metal which is a wiring material such as copper, aluminum and titanium after the dry etching step can be effectively removed.

Even when a wiring board is treated with other resist removing composition before and after treating the wiring board with the composition for removing a residue of the present invention, there is no problem at all. On that occasion, though known resist removing compositions can be used, an organic alkaline composition is especially favorable.

[0019]

Examples of the wiring board which is used in the cleaning method of the invention include semiconductor boards using a semiconductor wiring material (for example, silicon, amorphous silicon, polysilicon, silicon oxide, silicon nitride, copper, titanium, titanium nitride, titanium-tungsten, tungsten, tantalum, tantalum alloys, cobalt, cobalt alloys, chromium, chromium oxide and chromium alloys) or a compound semiconductor (for example, gallium-arsenic, gallium-phosphorus and indium-phosphorus);

printed boards such as polyimide resins; and glass boards to be used in LCD or the like. These wiring boards are not corroded with the composition for removing a residue of the present invention.

Examples

[0020]

The present invention is hereunder more specifically described with reference to the following Examples and Comparative Examples. However, it should be construed that the present invention is not at all limited to these Examples.

In the following Examples and Comparative Examples, the measurement and evaluation methods of the composition for removing a residue are as follows.

[0021]

1. Preparation of specimen A:

On a silicon wafer substrate in which a wiring layer composed of copper and titanium and an insulating layer composed of carbon-doped silicon oxide were stacked, a resist pattern was formed, and dry etching was performed using this resist pattern as a mask to form a pattern composed of copper, titanium and carbon-doped silicon oxide, thereby obtaining a specimen A. A schematic view of a cross-section of the specimen A is shown in Fig. 1.

[0022]

2. Measurement of titanium dissolution rate (Ti E/R):

The composition for removing a residue was heated at 40 °C; a silicon wafer having a 1,000 angstrom-thick titanium film prepared on the surface thereof was dipped therein for a prescribed time and then rinsed with ultra pure water; and a difference in thickness of the titanium film before and after the treatment was measured by a fluorescent X-ray unit. The dipping time of the wafer was adjusted to a degree that the titanium film did not disappear. A titanium dissolution rate (Ti E/R) per minute was calculated from the obtained difference in film thickness.

[0023]

3. Evaluation of corrosiveness of wiring layer and residue removal properties:

The specimen A was subjected to a dipping treatment with the composition for removing a residue at 40 °C for 3 minutes, rinsed with ultra pure water and then blow dried by a nitrogen gas, and the presence or absence of corrosion of the wiring layer and the presence or absence of a residue were confirmed through observation by a scanning electron microscope (SEM).

The corrosiveness of wiring layer and the residue removal properties were evaluated as follows.

(Corrosiveness of wiring layer)

O: Corrosion of the wiring layer is not observed at all.

△: Corrosion of the wiring layer is partially observed.

×: Corrosion of the wiring layer is entirely observed.

(Residue removal properties)

O: Remaining of a residue is not observed at all.

△: Remaining of a residue is partially observed.

×: Remaining of a residue is entirely observed.

[0024]

Examples 1 to 5

Compositions for removing a residue as shown in Table 1 were prepared and measured for the titanium dissolution rate and evaluated for the corrosiveness of wiring layer and the residue removal properties relative to the specimen A.

In Tables 1 and 2, DTPP expresses diethylenetriaminepenta(methylenephosphonic acid). Also, all of concentrations (%) shown in the composition in the tables are % by mass, and the remainders not reaching 100 % by mass are all water.

In these Examples, the residue could be removed without causing corrosion of the wiring layer, and the dissolution of titanium could be suppressed.

[0025]

[Table 1]

	Composition		pH	Ti E/R [angstrom/min]	Corrosiveness of wiring layer	Residue removal properties
	Compound	Concentration				
Example 1	Hydrogen peroxide Benzotriazole DTPP	3 % 0.1 % 1 ppm	4.7	1.2	○	○
Example 2	Hydrogen peroxide Sulfuric acid 5-Amino-1H-tetrazole DTPP	3 % 0.05 % 0.5 % 1 ppm	2	0.8	○	○
Example 3	Hydrogen peroxide 1,2,4-Triazole DTPP	3 % 1 % 1 ppm	5.9	1	○	○
Example 4	Hydrogen peroxide 1,2,4-Triazole DTPP	1 % 1 % 1 ppm	5.9	0.3	○	○
Example 5	Hydrogen Peroxide 1,2,4-Triazole	1 % 1 %	6	0.3	○	○

[0026]

Comparative Examples 1 to 9

Compositions for removing a residue as shown in Table 2 were prepared and measured for the titanium dissolution rate and evaluated for the corrosiveness of wiring layer and the residue removal properties relative to the specimen A. Also, the titanium dissolution rate (Ti E/R) was measured.

[0027]

[Table 2]

	Composition		pH	Ti E/R [angstrom/min]	Corrosive ness of wiring layer	Residue removal properties
	Compound	Concentration				
Comparative Example 1	Hydrogen peroxide DTPP	3 % 1 ppm	5.2	10	×	○
Comparative Example 2	Hydrogen peroxide DTPP	15 % 1 ppm	4.1	25	×	○
Comparative Example 3	Hydrogen peroxide Sulfuric acid DTPP	15 % 0.4 % 1 ppm	3	46	×	○
Comparative Example 4	Hydrogen peroxide 1,2,4-Triazole Tetrabutylammonium hydroxide DTPP	3 % 1 % 0.25 % 1 ppm	8	2.9	△	○
Comparative Example 5	Hydrogen peroxide Ammonium acetate	3 % 2 %	6.5	5.2	×	○
Comparative Example 6	Hydrogen peroxide Ammonium sulfate Ammonium hexafluorosilicate Ethylene glycol	3 % 5 % 0.5 % 5 %	3.5	14	×	○
Comparative Example 7	Hydrogen peroxide Sulfuric acid Acetic acid Ammonium fluoride	3 % 10 % 2 % 0.05 %	0.8	26	×	○
Comparative Example 8	Ammonium fluoride Dimethylformamide	1 % 70 %	9.6	1.7	△	△
Comparative Example 9	Hydroxylamine Ethanolamine Gallic acid	35 % 60 % 5 %	12	< 0.1	×	○

[0028]

In Comparative Examples 1 to 7, the titanium dissolution rate was large, and the corrosion of the wiring was observed. Also, in Comparative Examples 8 and 9, though the titanium dissolution rate was small, the corrosion of the wiring was observed.

Industrial Applicability

[0029]

By using the composition for removing a residue of the present invention, in manufacturing a wiring board, residues

remaining after dry etching which are derived from a resist or metals can be effectively removed without corroding titanium or titanium alloys with high corrosiveness, and in particular, a semiconductor device using a wiring board containing titanium or titanium alloys can be efficiently manufactured.

CLAIMS

[1] A composition for removing a residue from a wiring board comprising an oxidizing agent and an azole compound and having a pH of from 1 to 7.

[2] The composition for removing a residue from a wiring board according to claim 1, wherein the oxidizing agent is at least one member selected among hydrogen peroxide, ozone, potassium permanganate, percarbonic acid and salts thereof, perphosphoric acid and salts thereof, persulfuric acid and salts thereof, iodic acid and salts thereof, bromic acid and salts thereof, perchloric acid and salts thereof, chloric acid and salts thereof, and hypochlorous acid and salts thereof.

[3] The composition for removing a residue from a wiring board according to claim 2, wherein the oxidizing agent is hydrogen peroxide.

[4] The composition for removing a residue from a wiring board according to any one of claims 1 to 3, wherein the azole compound is a triazole compound and/or a tetrazole compound.

[5] The composition for removing a residue from a wiring board according to any one of claims 1 to 4, wherein the azole compound is from 0.0001 to 5 % by mass.

[6] The composition for removing a residue from a wiring board according to any one of claims 3 to 5, wherein hydrogen peroxide is from 0.01 to 20 % by mass.

[7] A cleaning method of a wiring board comprising removing

a residue from a wiring board after dry etching by using the composition for removing a residue from a wiring board according to any one of claims 1 to 6.

[8] The cleaning method of a wiring board according to claim 7, wherein the wiring board contains titanium and/or a titanium alloy.