

DESCRIPTION

Title of Invention: ETCHING SOLUTION

5 Technical Field

[0001] The present disclosure relates to an etching solution and an etching method using the same.

Background Art

10 [0002] A process for manufacturing a semiconductor device includes, for example, a step of etching a layer being etched to form a predetermined pattern, where the layer being etched contains at least one metal selected from tungsten, tantalum, zirconium, hafnium, molybdenum, niobium, ruthenium, osmium, rhenium, rhodium, copper, nickel, cobalt, titanium, titanium nitride, alumina, aluminum, iridium or the like.

15 Recently, in the field of semiconductor, wiring has been required to be finer and more complicated due to a high level of integration. Also, the levels required for patterning techniques and etching solutions are increased, and various etching methods have been proposed.

[0003] For example, JP 2013-237873 A (Patent Document 1) proposes an etching
20 solution to be used for etching a metal film having at least one layer of a metal thin film made of molybdenum or a molybdenum alloy, and the etching solution contains phosphoric acid, nitric acid, and polyalkylene polyamine having three or more amino groups in a molecule.

JP 2021-114569 A (Patent Document 2) proposes a substrate processing
25 method including a step of supplying a first etching solution to a substrate having a laminated film including a molybdenum film, the first etching solution containing an oxidizing agent (for example, nitric acid), a catalyst (for example, phosphoric acid), and a moisture adjusting agent (for example, organic acid) and having a ratio of the moisture adjusting agent higher than a total ratio of the oxidizing agent and the
30 catalyst, and a step of supplying a second etching solution to the substrate after supplying the first etching solution to the substrate, the second etching solution having the ratio of the moisture adjusting agent higher than that of the first etching solution.

JP 2022-502835 A (Patent Document 3) proposes, as an etching solution for selectively etching aluminum oxide, tungsten and/or titanium nitride, an etching solution containing phosphoric acid of approximately 65 to 90% by weight, acetic acid of approximately 0.01 to 4% by weight, nitric acid of 0.01 to 5% by weight, and water.

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Disclosure of Invention

[0004] In one aspect, the present disclosure relates to an etching solution for etching a layer being etched containing at least one metal, the etching solution obtainable by blending: a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and an acid containing an organic acid, nitric acid, and phosphoric acid, in which a blending amount of the organic acid in the etching solution is 50% by mass or more.

[0005] In one aspect, the present disclosure relates to an etching method including a step of etching a layer being etched containing at least one metal by use of the etching solution of the present disclosure, wherein the temperature of the etching solution during etching is 20°C or higher and 50°C or lower.

[0006] In one aspect, the present disclosure relates to an etching solution for etching a layer being etched containing at least one metal, the etching solution containing a salt of a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more, and an acid containing an organic acid, nitric acid, and phosphoric acid, in which a blending amount of the organic acid in the etching solution is 50% by mass or more.

[0007] In one aspect, the present disclosure relates to an etching solution for etching a layer being etched containing at least one metal, the etching solution obtainable by blending: a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and an acid containing an organic acid, nitric acid, and phosphoric acid, in which a blending amount of the organic acid in the etching solution is 80% by mass or more.

[0008] In one aspect, the present disclosure relates to an etching solution for etching a layer being etched containing molybdenum, the etching solution obtainable by blending: at least one nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more;

and an acid containing an organic acid, nitric acid, and phosphoric acid, in which a blending amount of the organic acid in the etching solution is 50% by mass or more.

[0009] In one aspect, the present disclosure relates to a method for manufacturing an electronic component, including a step of etching a layer being etched containing at least one metal by use of the etching solution of the present disclosure.

Description of the Invention

[0010] As the etching solution, a mixed acid aqueous solution (strongly acidic aqueous solution) containing phosphoric acid, nitric acid, and an organic acid (for example, acetic acid) is typically used. To the etching solution, a nitrogen-containing compound may be added as an etching inhibitor to prevent deterioration or the like in the quality of the surface of the layer being etched (the surface of the metal film) after etching. Patent Document 1 proposes addition of polyalkylene polyamine to an etching solution in which acetic acid is not an essential component. However, addition of an auxiliary agent such as polyalkylene polyamine to the mixed acid aqueous solution may cause a problem that turbidity occurs to degrade the storage stability of the etching solution.

[0011] Therefore, in one aspect, the present disclosure provides an etching solution excellent in storage stability and capable of inhibiting etching and improving the quality of the surface of a layer being etched after etching, and an etching method using the same.

[0012] As a result of intensive studies, the present inventors have found that, use of an etching solution containing or obtainable by blending a specific nitrogen-containing compound and an acid including an organic acid of 50% by mass or more serves to improve storage stability while inhibiting etching and improving the quality of the surface of a layer being etched after etching (uniform etching of the layer being etched).

[0013] In one aspect, the present disclosure relates to an etching solution for etching a layer being etched containing at least one metal, the etching solution obtainable by blending: a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and an acid containing an organic acid, nitric acid, and phosphoric acid, in which a blending

amount of the organic acid in the etching solution is 50% by mass or more (hereinafter, also referred to as “etching solution of the present disclosure”).

[0014] In one aspect, the present disclosure can provide an etching solution excellent in storage stability and capable of inhibiting etching and improving the quality of the surface of a layer being etched after etching.

[0015] The mechanism by which the effects of this disclosure are realized is presumed to be as follows, though the details have not been clarified.

An example of etching solutions commonly used is a mixed acid aqueous solution (strongly acidic aqueous solution) containing phosphoric acid, nitric acid, and an organic acid (for example, acetic acid). When a nitrogen-containing compound such as a polyvalent amine is mixed, as an etching inhibitor, into such a mixed acid aqueous solution, the polyvalent amine can form a salt with the acid in the mixed acid aqueous solution. In particular, for example, in the case of a polyvalent amine having a large number of nitrogen atoms as hydrophilic groups in its molecule, a salt of a hydrophilic polyvalent amine and an acid is likely to be dissolved in an aqueous solvent. In the case of a polyvalent amine containing a large number of methylene groups, as hydrophobic groups in the molecule, a salt of a hydrophobic polyvalent amine and an acid is unlikely to be dissolved in an aqueous solvent.

In the meantime, the organic acid is not dissociated in the mixed acid aqueous solution having a low pH (strongly acidic aqueous solution), and the hydrophobicity of the mixed acid aqueous solution increases as the blending amount of the organic acid increases. Therefore, although the salt of the hydrophobic polyvalent amine and the acid can be dissolved, the solubility of the salt of the hydrophilic polyvalent amine and the acid is extremely lowered, causing white turbidity.

In the present disclosure, the etching inhibitor used is a specific nitrogen-containing compound having high hydrophobicity or amphiphilicity (a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more). A combination of the nitrogen-containing compound and a mixed acid containing 50% by mass or more of an organic acid is considered to improve the solubility of a salt of the nitrogen-containing compound and the acid, thereby improving the storage stability of the etching solution.

It is also known that a nitrogen-containing compound used as an etching

inhibitor acts on a metal surface to inhibit etching by an acid. In the present disclosure, it is considered that the high-concentration organic acid reduces the viscosity of the mixed acid aqueous solution, thereby improving the diffusion property of the acid itself and the nitrogen-containing compound and achieving uniform etching of the surface, and as a result, etching can be inhibited and the quality of the surface of the layer being etched after etching can be improved.

However, the present disclosure is not interpreted as being limited to these mechanisms.

[0016] [Nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more (component A)]

The etching solution of the present disclosure contains or is obtainable by blending a nitrogen-containing compound (hereinafter, also referred to as “component A”) having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more.

The number of carbon atoms (C) in one molecule of the component A is preferably 4 or more, and more preferably 8 or more, from the viewpoint of storage stability and etching inhibition, and is preferably 24 or less, and more preferably 18 or less, from the viewpoint of improving the quality of the layer being etched. From the same viewpoint, the number of carbon atoms in one molecule of the component A is preferably 4 or more and 24 or less, and more preferably 8 or more and 18 or less.

The number of nitrogen atoms (N) in one molecule of the component A is preferably 1 or more and more preferably 2 or more from the viewpoint of storage stability and etching inhibition, and is preferably 3 or less from the viewpoint of improving the quality of the layer being etched. From the same viewpoint, the number of nitrogen atoms in one molecule of the component A is preferably 1 or more and 3 or less.

In one or more embodiments, the ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of the component A is 2.2 or more, preferably 2.3 or more, more preferably 4 or more, and still more preferably 8 or more from the viewpoint of storage stability and etching inhibition, and is preferably 20 or less and more preferably 18 or less from the viewpoint of improving the quality of the

layer being etched. More specifically, the ratio C/N of the component A is preferably 2.2 or more and 20 or less, more preferably 4 or more and 18 or less, and still more preferably 8 or more and 18 or less.

In one or more embodiments, the component A contained or to be blended in
5 the etching solution of the present disclosure is at least one nitrogen-containing compound selected from an aliphatic amine, an aromatic amine, and an amino alcohol.

The component A may be one kind or a combination of two or more kinds.
[0017] In one or more embodiments, the component A may be in the form of a salt of
the nitrogen-containing compound. In one or more embodiments, the component A
10 can form a salt with an acid in the etching solution.

Therefore, in another aspect, the present disclosure relates to an etching
solution for etching a layer being etched containing at least one metal, the etching
solution containing: a salt of component A; and an acid containing an organic acid,
nitric acid, and phosphoric acid, in which a blending amount of the organic acid in the
15 etching solution is 50% by mass or more.

[0018] (Aliphatic amine)

In one or more embodiments, the component A may be an aliphatic amine.
Examples of the aliphatic amine include primary, secondary, and tertiary aliphatic
amines. The aliphatic amine may be one kind or a combination of two or more kinds.
20 In the present disclosure, the primary, secondary, or tertiary aliphatic amine is
a compound in which at least one hydrogen atom of ammonia (NH_3) is substituted
with a hydrocarbon group. In one or more embodiments, the primary aliphatic amine
is obtained by substituting one hydrogen atom of ammonia with a hydrocarbon group,
the secondary aliphatic amine is obtained by substituting two hydrogen atoms of
25 ammonia with hydrocarbon groups, and the tertiary aliphatic amine is obtained by
substituting three hydrogen atoms of ammonia with hydrocarbon groups. Examples
of the hydrocarbon group include hydrocarbon groups having 1 or more and 24 or less
carbon atoms. The hydrocarbon group may be linear, branched or cyclic. The
hydrocarbon group may contain an unsaturated bond. The hydrocarbon group may
30 be partially substituted with an oxygen atom or the like.

The carbon number of the aliphatic amine is preferably 4 or more, and more
preferably 8 or more, from the viewpoint of storage stability and etching inhibition,

and is preferably 24 or less, and more preferably 18 or less, from the viewpoint of improving the quality of the layer being etched. From the same viewpoint, the number of carbon atoms of the primary, secondary, or tertiary aliphatic amine is preferably 4 or more and 24 or less, and more preferably 8 or more and 18 or less.

5 The ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of the aliphatic amine is preferably 4 or more, and more preferably 6 or more from the viewpoint of storage stability, and is preferably 24 or less, more preferably 20 or less, and still more preferably 18 or less from the viewpoint of improving the quality of the layer being etched. From the same viewpoint, the
10 ratio C/N of the number of carbon atoms to the number of nitrogen atoms in one molecule of the aliphatic amine is preferably 4 or more and 24 or less, more preferably 6 or more and 20 or less, and still more preferably 6 or more and 18 or less.

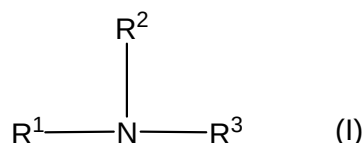
 Examples of the primary aliphatic amine include oleylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, 2-ethylhexylamine, nonylamine,
15 aminodecane, aminoundecane, aminododecane (dodecylamine), aminotridecane, tetradecylamine, aminopentadecane, hexadecylamine, aminoheptadecane, stearylamine (octadecylamine), aminononadecane, and 2-ethylhexylamine.

 Examples of the secondary aliphatic amine include methylhexylamine, methylpentylamine, methyloctylamine, methylnonylamine, methyldecylamine,
20 methylundecylamine, methyldodecylamine, methyloctadecylamine, cyclohexylamine, bis (hexamethylene) triamine, and N-butylethylenediamine.

 Examples of the tertiary aliphatic amine include dimethylbutylamine, dimethylpentylamine, dimethylhexylamine, methylpentylamine, methyloctylamine, methylnonylamine, methyldecylamine, methylundecylamine, methyldodecylamine,
25 and dimethyloctadecylamine.

 In one or more embodiments, the aliphatic amine may be one or more compounds represented by the following formula (I).

[Chemical Formula 1]



30 In the formula (I), R¹ is a linear or branched alkyl group having 1 or more and

18 or less carbon atoms, a linear or branched alkenyl group having 1 or more and 18 or less carbon atoms, or a cyclic hydrocarbon group having 1 or more and 18 or less carbon atoms. The alkyl group, the alkenyl group, and the cyclic hydrocarbon group may contain an amino group or an ether bond.

5 R² and R³ each independently represent a hydrogen atom, a linear or branched alkyl group having 1 or more and 8 or less carbon atoms, a linear or branched alkenyl group having 1 or more and 8 or less carbon atoms, or a cyclic hydrocarbon group having 1 or more and 8 or less carbon atoms. The alkyl group, the alkenyl group, and the cyclic hydrocarbon group may contain an amino group or an
10 ether bond.

In the formula (I), from the viewpoint of inhibiting etching and improving the quality of the layer being etched, R¹ is preferably a linear alkyl group having 1 or more and 18 or less carbon atoms, a linear alkyl group having 1 or more and 18 or less carbon atoms and an amino group, or a branched alkenyl group having 1 or more and
15 18 or less carbon atoms. Preferably, R² and R³ each independently represent a hydrogen atom, a methyl group, or a linear alkyl group having 1 or more and 8 or less carbon atoms and having an amino group.

[0019] (Aromatic amine)

In one or more embodiments, the component A may be an aromatic amine.
20 The aromatic amine may be one kind or a combination of two or more kinds.

In the present disclosure, the aromatic amine is a compound in which at least one hydrogen atom of ammonia (NH₃) is substituted with an aromatic ring. From the viewpoint of inhibiting etching and improving the quality of the layer being etched, the aromatic amine is preferably a primary aromatic amine in which one hydrogen atom
25 of ammonia is substituted with an aromatic ring. Examples of the aromatic ring include a benzene ring. The aromatic ring may have a substituent. Examples of the substituent include an alkyl group having 1 or more and 12 or less carbon atoms. The alkyl group may be linear or branched. Examples of branched alkyl groups include an isopropyl group.

30 From the viewpoint of etching inhibition and storage stability, examples of the aromatic amine include aniline derivatives (for example, aniline, and 2,6-diisopropylaniline), triazole derivatives (for example, benzotriazole, and 5-

methylbenzotriazole), imidazole derivatives, and quinoline derivatives (for example, isoquinoline).

[0020] (Amino alcohols)

In one or more embodiments, the component A may be an amino alcohol.

5 The amino alcohol may be one kind or a combination of two or more kinds.

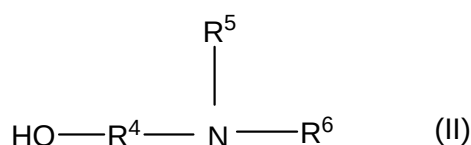
In the present disclosure, the amino alcohol (alkanolamine) is a compound having a hydroxyl group and an amino group. Examples of the amino group include a primary, secondary, or tertiary amino group, and a primary amino group is preferable from the viewpoint of inhibiting etching and improving the quality of the layer being etched.

10 The number of carbon atoms of the amino alcohol is preferably 2 or more and 24 or less, more preferably 4 or more and 18 or less, and still more preferably 4 or more and 12 or less, from the viewpoint of storage stability.

Examples of the amino alcohol include 2-(2-aminoethoxy) ethanol and triethanolamine.

In one or more embodiments, the amino alcohol (component A) may be one or more compounds represented by the following formula (II).

[Chemical Formula 2]



20 In the formula (II), R⁴ is a linear or branched alkyl group having 2 or more and 6 or less carbon atoms, and the alkyl group may have an ether group.

R⁵ and R⁶ each independently represent a hydrogen atom or a linear or branched alkyl group having 2 or more and 6 or less carbon atoms, and the alkyl group may have an amino group, a hydroxy group, or an ether group.

25 In the formula (II), the alkyl group of R⁴ is preferably linear from the viewpoint of inhibiting etching and improving the quality of the layer being etched. From the same viewpoint, R⁴ is preferably a linear alkyl group having an ether group and having 2 or more and 6 or less carbon atoms, and R⁵ and R⁶ are each independently a hydrogen atom.

30 [0021] In one or more embodiments, from the viewpoint of inhibiting etching and

improving the quality of the layer being etched, the component A is preferably at least one selected from butylamine, octylamine, dodecylamine, octadecylamine, methyloctadecylamine, dimethyloctadecylamine, oleylamine, 2-ethylhexylamine, bis(hexamethylene) triamine, aniline, 2,6-diisopropylaniline, 5-methylbenzotriazole, and 2-(2-aminoethoxy) ethanol, and more preferably at least one selected from dodecylamine, octadecylamine, methyloctadecylamine, dimethyloctadecylamine, oleylamine, bis(hexamethylene) triamine, aniline, 2,6-diisopropylaniline, 5-methylbenzotriazole, and 2-(2-aminoethoxy) ethanol.

[0022] The molecular weight of the component A contained in the etching solution of the present disclosure is preferably 70 or more, more preferably 120 or more, and still more preferably 150 or more, from the viewpoint of inhibiting etching and improving the quality of the layer being etched, and is preferably 350 or less, more preferably 300 or less, and still more preferably 250 or less, from the viewpoint of improving the quality of the layer being etched. More specifically, the molecular weight of the component A is preferably 70 or more and 350 or less, more preferably 120 or more and 300 or less, and still more preferably 150 or more and 250 or less.

[0023] The blending amount of the component A in the etching solution of the present disclosure is preferably 0.01% by mass or more, more preferably 0.1% by mass or more, and still more preferably 0.5% by mass or more from the viewpoint of inhibiting etching and improving the quality of a layer being etched, and is preferably 5% by mass or less, more preferably 3% by mass or less, and still more preferably 2% by mass or less from the viewpoint of storage stability. From the same viewpoint, the blending amount of the component A in the etching solution of the present disclosure is preferably 0.01% by mass or more and 5% by mass or less, more preferably 0.1% by mass or more and 3% by mass or less, and still more preferably 0.5% by mass or more and 2% by mass or less. In the case where the component A is a combination of two or more kinds, the blending amount of component A is the total blending amount thereof.

[0024] [Acid]

The acid contained or to be blended in the etching solution of the present disclosure is an acid containing an organic acid, nitric acid, and phosphoric acid. In one or more embodiments, examples of the acid contained or to be blended in the etching solution of the present disclosure include an acid (mixed acid) composed of an

organic acid, nitric acid, and phosphoric acid, from the viewpoint of storage stability.

The blending amount of the acid in the etching solution of the present disclosure is preferably 70% by mass or more, more preferably 80% by mass or more, and still more preferably 90% by mass or more, from the viewpoint of etching inhibition and storage stability.

[0025] (Organic acid)

From the viewpoint of storage stability, examples of the organic acid include at least one selected from acetic acid, acetic anhydride, methoxyacetic acid, ethoxyacetic acid, propionic acid, butanoic acid, citric acid, formic acid, gluconic acid, glycolic acid, malonic acid, oxalic acid, lactic acid, and pentanoic acid. Among these, from the same viewpoint, the organic acid is preferably at least one selected from acetic acid, acetic anhydride, methoxyacetic acid, and ethoxyacetic acid, and more preferably acetic acid. The organic acids may be one kind or a combination of two or more kinds. In the case where acetic anhydride is used as the organic acid in the preparation of the etching solution of the present disclosure, the acetic anhydride reacts with water in the etching solution to be converted into acetic acid and water, so that the amount of water in the etching solution can be reduced.

The blending amount of the organic acid in the etching solution of the present disclosure is 50% by mass or more, preferably 70% by mass or more, and more preferably 80% by mass or more or 85% by mass or more, and is preferably 95% by mass or less, and more preferably 90% by mass or less, from the viewpoint of improving the quality and storage stability of the layer being etched, and from the viewpoint of reducing the viscosity of the etching solution. More specifically, the blending amount of the organic acid in the etching solution of the present disclosure is preferably 50% by mass or more and 95% by mass or less, and more preferably 70% by mass or more and 90% by mass or less or 80% by mass or more and 90% by mass or less. In the case where the organic acid is a combination of two or more kinds, the blending amount of the organic acid is the total blending amount thereof.

Therefore, in another aspect, the present disclosure relates to an etching solution for etching a layer being etched containing at least one metal, the etching solution obtainable by blending the component A and an acid containing an organic acid, nitric acid, and phosphoric acid, in which a blending amount of the organic acid in

the etching solution is 80% by mass or more.

[0026] (Nitric acid)

The blending amount of nitric acid in the etching solution of the present disclosure is preferably 0.1% by mass or more, more preferably 0.5% by mass or more, and still more preferably 1% by mass or more, from the viewpoint of improving the quality of the layer being etched, and is preferably 10% by mass or less, more preferably 8% by mass or less, and still more preferably 5% by mass or less, from the viewpoint of improving the quality of the layer being etched and storage stability. More specifically, the blending amount of the nitric acid in the etching solution of the present disclosure is preferably 0.1% by mass or more and 10% by mass or less, more preferably 0.5% by mass or more and 8% by mass or less, and still more preferably 1% by mass or more and 5% by mass or less.

[0027] (Phosphoric acid)

The blending amount of the phosphoric acid in the etching solution of the present disclosure is preferably 0.1% by mass or more, more preferably 0.5% by mass or more, and still more preferably 1% by mass or more, from the viewpoint of improving the quality of the layer being etched, and is preferably 40% by mass or less, more preferably 20% by mass or less, and still more preferably 10% by mass or less, from the viewpoint of improving the quality of the layer being etched and storage stability. More specifically, the blending amount of the phosphoric acid in the etching solution of the present disclosure is preferably 0.1% by mass or more and 40% by mass or less, more preferably 0.5% by mass or more and 20% by mass or less, and still more preferably 1% by mass or more and 10% by mass or less.

[0028] The mass ratio of the blending amount of the organic acid to the phosphoric acid (organic acid / phosphoric acid) in the etching solution of the present disclosure is preferably 1.2 or more, and more preferably 3.5 or more, 5 or more, or 6 or more, from the viewpoint of etching inhibition, and is preferably 950 or less, and more preferably 100 or less, 50 or less, or 20 or less, from the same viewpoint of etching inhibition.

More specifically, the mass ratio (organic acid / phosphoric acid) in the etching solution of the present disclosure is preferably 1.2 or more and 950 or less, and more preferably 3.5 or more and 100 or less, 5 or more and 50 or less, or 6 or more and 20 or less.

[0029] The mass ratio of the blending amount of the organic acid to the blending

amount of the nitrogen-containing compound (component A) (organic acid / nitrogen-containing compound) in the etching solution of the present disclosure is preferably 10 or more, more preferably 20 or more, still more preferably 30 or more, even more preferably 40 or more, and even still more preferably 50 or more, from the viewpoint of etching inhibition and from the viewpoint of reducing the viscosity of the etching solution, and is preferably 10,000 or less, more preferably 5,000 or less, further preferably 2,500 or less, still more preferably 1,000 or less, even more preferably 500 or less, and even still more preferably 100 or less, from the same viewpoints. More specifically, the mass ratio (organic acid / nitrogen-containing compound) in the etching solution of the present disclosure is preferably 10 or more and 10,000 or less, more preferably 20 or more and 5,000 or less, further more preferably 30 or more and 2,500 or less, still more preferably 40 or more and 1,000 or less, even more preferably 50 or more and 500 or less, and even still more preferably 50 or more and 100 or less.

[0030] (Other acids)

The acid contained or to be blended in the etching solution of the present disclosure may further contain an acid other than nitric acid, phosphoric acid, and an organic acid. Examples of other acids include inorganic acids other than nitric acid and phosphoric acid. Examples of the inorganic acid include hydrochloric acid, sulfuric acid, and hydrofluoric acid.

[0031] [Water]

In one or more embodiments, the etching solution of the present disclosure further contains or is obtainable by blending with water. Examples of the water contained or to be blended in the etching solution of the present disclosure include distilled water, ion-exchanged water, pure water, and ultrapure water.

[0032] The blending amount of water in the etching solution of the present disclosure is preferably 10% by mass or less, more preferably 8% by mass or less, and still more preferably 5% by mass or less, from the viewpoint of improving the quality of the layer being etched.

[0033] [Other components]

The etching solution of the present disclosure may be obtained by further blending other components as long as the effects of the present disclosure are not impaired. Examples of the other components include a chelating agent, a surfactant,

a solubilizing agent, a preservative, a rust inhibitor, a bactericide, an antibacterial agent, and an antioxidant.

[0034] In one or more embodiments, the etching solution of the present disclosure can be substantially free of polyalkyleneimine and polyalkylene polyamine. Examples of the polyalkyleneimine include polyethyleneimine. Examples of the polyalkylenepolyamine include polyalkylenepolyamines containing three or more amino groups in one molecule, such as triethylenetetramine.

The content of the polyalkyleneimine and the polyalkylene polyamine in the etching solution of the present disclosure is preferably less than 0.01% by mass, more preferably 0.001% by mass or less, and still more preferably 0% by mass (that is, the etching solution is free of the polyalkyleneimine and the polyalkylene polyamine).

[0035] [Method for producing etching solution]

In one aspect, the etching solution of the present disclosure is obtained by blending the component A, an acid, water, and, if desired, the optional component described above by a known method, where the acid includes an organic acid, nitric acid, and phosphoric acid. Therefore, in one aspect, the present disclosure relates to a method for producing an etching solution, the method including a step of blending at least the component A, an organic acid, nitric acid, phosphoric acid, and water (hereinafter, also referred to as “the method for producing an etching solution of the present disclosure”).

In the present disclosure, in one or more embodiments, “blending at least the component A, an organic acid, nitric acid, phosphoric acid, and water” includes mixing the component A, the organic acid, the nitric acid, the phosphoric acid, the water, and the optional component described above as necessary simultaneously or sequentially. The order of mixing may not be particularly limited. The blending can be performed using, for example, a mixer such as a propeller stirrer, liquid circulation stirring by a pump, a homomixer, a homogenizer, an ultrasonic disperser, or a wet ball mill.

The preferred blending amount of each component in the etching solution production method of the present disclosure can be the same as the preferred blending amount of each component in the etching solution of the present disclosure described above.

[0036] In one or more embodiments of the present disclosure, the “blending amount

of each component in the etching solution” refers to the blending amount of each component of the etching solution used in an etching step, that is, at the time of starting the use in an etching process (at the time of use).

5 In one or more embodiments, the blending amount of each component in the etching solution of the present disclosure can be regarded as the content of each component in the etching solution of the present disclosure. However, in the case of being affected by neutralization, the blending amount and the content may be different.

[0037] An embodiment of the etching solution of the present disclosure may be a so-called one-liquid type in which all components are supplied to the market in a state of being mixed in advance, or may be a so-called two-liquid type in which all components are mixed at the time of use. An example of an embodiment of the two-liquid type etching solution is an etching solution composed of a solution containing the component A (first liquid) and an acid aqueous solution containing an organic acid, 10 nitric acid, and phosphoric acid (second liquid), in which the first liquid and the second liquid are mixed at the time of use. After the first liquid and the second liquid are mixed, the mixture may be diluted with water or an acid aqueous solution as necessary. The first liquid or the second liquid may contain all or a part of water to be used for preparing the etching solution. The first liquid and the second liquid may 15 each contain the optional components described above as necessary.

[0038] The pH of the etching solution of the present disclosure is preferably 2 or less and more preferably 1 or less from the viewpoint of storage stability. The pH of the etching solution of the present disclosure can be preferably -2.5 or more, and more preferably -2 or more. In the present disclosure, the pH of the etching solution is a 20 value at 25°C and can be measured using a pH meter, and specifically, can be measured by a method described in Examples.

[0039] The viscosity at 25°C of the etching solution of the present disclosure is preferably $1\text{ mPa}\cdot\text{s}$ or more and more preferably $2\text{ mPa}\cdot\text{s}$ or more from the viewpoint of improving the quality of the layer being etched, and is preferably $40\text{ mPa}\cdot\text{s}$ or less, 30 more preferably $25\text{ mPa}\cdot\text{s}$ or less, and still more preferably $10\text{ mPa}\cdot\text{s}$ or less from the viewpoint of improving the quality of the layer being etched. More specifically, the viscosity of the etching solution of the present disclosure is preferably $1\text{ mPa}\cdot\text{s}$ or more

and 25 mPa·s or less, and more preferably 2 mPa·s or more and 10 mPa·s or less.

In the present disclosure, the viscosity of the etching solution can be measured using a general-purpose viscometer such as a B-type viscometer or an Ubbelohde viscometer, and specifically, can be measured by a method described in Examples. The viscosity
5 of the etching solution at 25°C can be adjusted with, for example, water or an organic solvent.

[0040] The etching solution of the present disclosure may be stored and supplied in a concentrated state as long as its stability is not impaired. This case is preferable in that the production and transportation costs can be reduced. This concentrated
10 solution can be appropriately diluted with water or an acid aqueous solution as necessary and used in the etching step. The dilution ratio can be, for example, 5 to 100 times.

[0041] [Kit]

In another aspect, the present disclosure relates to a kit for producing the
15 etching solution of the present disclosure (hereinafter, also referred to as “kit of the present disclosure”).

Examples of the kit of the present disclosure include a kit (two-liquid type etching solution) that includes a solution (first liquid) containing the component A and an acid aqueous solution (second liquid) containing an organic acid, nitric acid, and
20 phosphoric acid in a state of not being mixed with each other, and these are mixed at the time of use. After the first liquid and the second liquid are mixed, the mixture may be diluted with water or an acid aqueous solution as necessary. The first liquid or the second liquid may contain all or a part of water used for preparing the etching solution. The first liquid and the second liquid may each contain the optional
25 components described above as necessary. According to the kit of the present disclosure, an etching solution with excellent storage stability can be prepared.

[0042] [Layer being etched]

In one or more embodiments, the layer being etched to be etched with the etching solution of the present disclosure is a layer being etched containing at least one
30 metal. Here, the metal is not particularly limited as long as the effects of the present disclosure are exhibited, and examples thereof include at least one metal selected from tungsten, tantalum, zirconium, hafnium, molybdenum, niobium, ruthenium, osmium,

rhodium, copper, nickel, cobalt, titanium, titanium nitride, alumina, aluminum, and iridium. Among these, in one or more embodiments, the etching solution of the present disclosure is preferably used for etching a layer being etched containing at least one metal selected from tungsten, molybdenum, niobium, 5 tantalum, and zirconium, and in one or more embodiments, is suitably used for etching a molybdenum film. That is, in one or more embodiments, the layer being etched may be a molybdenum film.

Therefore, in another aspect, the present disclosure relates to an etching solution for etching a layer being etched containing molybdenum, the etching solution 10 obtainable by blending a component A and an acid containing an organic acid, nitric acid, and phosphoric acid, in which a blending amount of the organic acid in the etching solution is 50% by mass or more.

In one or more embodiments, the layer being etched is a layer being etched formed on a substrate. Examples of the substrate include at least one substrate 15 selected from a semiconductor wafer (semiconductor substrate), a substrate for a liquid crystal display device, a substrate for a plasma display, a substrate for a field emission display (FED), a substrate for an optical disk, a substrate for a magnetic disk, a substrate for a magneto-optical disk, a substrate for a photomask, a ceramic substrate, and a substrate for a solar cell.

20 [0043] [Etching method]

In one aspect, the present disclosure relates to an etching method (hereinafter, also referred to as “etching method of the present disclosure”) including a step of etching a layer being etched containing at least one metal by use of an etching solution of the present disclosure (hereinafter, also referred to as “etching step of the present 25 disclosure”), in which the temperature of the etching solution during etching is 20°C or higher and 50°C or lower. According to the etching method of the present disclosure, in one or more embodiments, the productivity of a semiconductor substrate can be improved by using an etching solution having excellent storage stability.

[0044] In the etching step of the present disclosure, examples of the etching process 30 include immersion etching and single-wafer etching.

[0045] The temperature of the etching solution during etching (etching temperature) in the etching step of the present disclosure is preferably 20°C or higher, more

preferably 25°C or higher, and still more preferably 30°C or higher, from the viewpoint of improving the quality of the layer being etched, and is preferably 50°C or lower, more preferably 45°C or lower, and still more preferably 40°C or lower, from the viewpoint of improving the quality of the layer being etched. More specifically, the
5 etching temperature is preferably 20°C or higher and 50°C or lower, more preferably 25°C or higher and 45°C or lower, and still more preferably 30°C or higher and 40°C or lower.

[0046] In the etching step of the present disclosure, the etching time can be set to, for example, 1 minute or more and 180 minutes or less. From the viewpoint of
10 improving the quality of the layer being etched, it is preferably 15 minutes or more and 90 minutes or less, and more preferably 30 minutes or more and 60 minutes or less.

[0047] In one or more embodiments, the etching solution of the present disclosure and the etching method of the present disclosure can be used for etching a metal in a process of manufacturing an electronic device, particularly a semiconductor wafer
15 (semiconductor substrate). Examples of the metal include the metals described above.

In one or more embodiments, the etching solution of the present disclosure and the etching method of the present disclosure can be suitably used for producing at least one substrate selected from a semiconductor wafer (semiconductor substrate), a
20 substrate for a liquid crystal display device, a substrate for a plasma display, a substrate for a field emission display (FED), a substrate for an optical disk, a substrate for a magnetic disk, a substrate for a magneto-optical disk, a substrate for a photomask, a ceramic substrate, and a substrate for a solar cell. Accordingly, uniform etching of the layer being etched can be realized, and productivity and yield can be
25 improved.

In one or more embodiments, the etching solution of the present disclosure and the etching method of the present disclosure can be used for etching an electrode in a process of manufacturing an electronic device, particularly, a semiconductor memory such as a nonvolatile memory including a NAND flash memory.

30 In one or more embodiments, the etching solution of the present disclosure and the etching method of the present disclosure can be suitably used for producing a pattern having a three-dimensional structure. As a result, an advanced device such

as a large-capacity memory can be obtained.

The etching solution of the present disclosure and the etching method of the present disclosure can be used in an etching method as disclosed in, for example, JP 2020-145412 A.

5 [0048] [Method for manufacturing electronic component]

In one aspect, the present disclosure relates to a method for manufacturing an electronic component, the method including a step of etching a layer being etched containing at least one metal by use of an etching solution of the present disclosure (etching step) (hereinafter, also referred to as “method for manufacturing an electronic component of the present disclosure”). Examples of the electronic component include at least one substrate selected from a semiconductor wafer (semiconductor substrate), a substrate for a liquid crystal display device, a substrate for a plasma display, a substrate for an FED (field emission display), a substrate for an optical disk, a substrate for a magnetic disk, a substrate for a magneto-optical disk, a substrate for a photomask, a ceramic substrate, and a substrate for a solar cell., and further semiconductor memories such as nonvolatile memory including NAND flash memory, and the like. Examples of the etching process and the etching conditions in the etching step of the electronic component manufacturing method of the present disclosure include the same etching process and etching conditions as those in the etching step of the etching method of the present disclosure described above. An example of the layer being etched is the above-described layer being etched.

[0049] The present disclosure further relates to one or more of the following embodiments.

<1> An etching solution for etching a layer being etched containing at least one metal, the etching solution obtainable by blending:

a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and
an acid comprising an organic acid, nitric acid, and phosphoric acid,
wherein a blending amount of the organic acid in the etching solution is 50%

30 by mass or more.

<2> An etching solution for etching a layer being etched containing at least one metal, comprising:

a salt of a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and

an acid comprising an organic acid, nitric acid, and phosphoric acid,
 5 wherein a blending amount of an organic acid in the etching solution is 50% by mass or more.

<3> An etching solution for etching a layer being etched containing at least one metal, the etching solution obtainable by blending:

a nitrogen-containing compound having a ratio C/N of the number of carbon
 10 atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and
 an acid comprising an organic acid, nitric acid, and phosphoric acid,
 wherein a blending amount of an organic acid in the etching solution is 80% by mass or more.

<4> An etching solution for etching a layer being etched containing molybdenum,
 15 the etching solution obtainable by blending:

at least one nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and

an acid comprising an organic acid, nitric acid, and phosphoric acid,
 20 wherein a blending amount of an organic acid in the etching solution is 50% by mass or more.

<5> The etching solution according to any one of <1> to <4>, wherein the nitrogen-containing compound is at least one selected from an aliphatic amine, an aromatic amine, and an amino alcohol.

25 <6> The etching solution according to <5>, wherein the aliphatic amine has a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 4 or more.

<7> The etching solution according to any one of <1> to <6>, wherein the nitrogen-containing compound is a primary, secondary, or tertiary aliphatic amine.

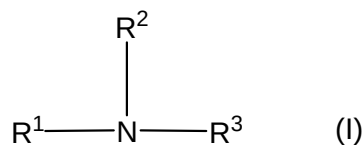
30 <8> The etching solution according to <7>, wherein the primary aliphatic amine is one or more selected from oleylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, 2-ethylhexylamine, nonylamine, aminodecane,

aminoundecane, aminododecane (dodecylamine), aminotridecane, tetradecylamine, aminopentadecane, hexadecylamine, aminoheptadecane, stearylamine (octadecylamine), aminononadecane, and 2-ethylhexylamine.

<9> The etching solution according to <7> or <8>, wherein the secondary aliphatic amine is one or more selected from methylhexylamine, methylpentylamine, methyloctylamine, methylnonylamine, methyldecylamine, methylundecylamine, methyldodecylamine, methyloctadecylamine, cyclohexylamine, bis(hexamethylene) triamine, and N-butylethylenediamine.

<10> The etching solution according to any one of <7> to <9>, wherein the tertiary aliphatic amine is one or more selected from dimethylbutylamine, dimethylpentylamine, dimethylhexylamine, methylpentylamine, methyloctylamine, methylnonylamine, methyldecylamine, methylundecylamine, methyldodecylamine, and dimethyloctadecylamine.

<11> The etching solution according to any one of <5> to <10>, wherein the aliphatic amine is one or more compounds represented by the following formula (I):
[Chemical Formula 3]



In the formula (I), R¹ is a linear or branched alkyl group having 1 or more and 18 or less carbon atoms, a linear or branched alkenyl group having 1 or more and 18 or less carbon atoms, or a cyclic hydrocarbon group having 1 or more and 18 or less carbon atoms, where the alkyl group, the alkenyl group, and the cyclic hydrocarbon group may contain an amino group or an ether bond.

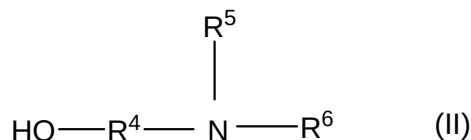
R² and R³ each independently represent a hydrogen atom, a linear or branched alkyl group having 1 or more and 8 or less carbon atoms, a linear or branched alkenyl group having 1 or more and 8 or less carbon atoms, or a cyclic hydrocarbon group having 1 or more and 8 or less carbon atoms, where the alkyl group, the alkenyl group, and the cyclic hydrocarbon group may contain an amino group or an ether bond.

<12> The etching solution according to any one of <5> to <11>, wherein the aromatic amine is at least one selected from an aniline derivative (for example, aniline,

and 2,6-diisopropylaniline), triazole derivatives (for example, benzotriazole, and 5-methylbenzotriazole), imidazole derivatives, and quinoline derivatives (for example, isoquinoline).

- <13> The etching solution according to any one of <5> to <12>, wherein the amino alcohol is one or more compounds represented by the following formula (II):

[Chemical Formula 4]



In the formula (II), R⁴ is a linear or branched alkyl group having 2 or more and 6 or less carbon atoms, and the alkyl group may have an ether group.

- 10 R⁵ and R⁶ each independently represent a hydrogen atom or a linear or branched alkyl group having 2 or more and 6 or less carbon atoms, and the alkyl group may have an amino group, a hydroxy group, or an ether group.

- <14> The etching solution according to any one of <1> to <13>, wherein the organic acid is at least one selected from acetic acid, acetic anhydride, methoxyacetic acid, ethoxyacetic acid, propionic acid, butanoic acid, citric acid, formic acid, gluconic acid, glycolic acid, malonic acid, oxalic acid, lactic acid, and pentanoic acid.

- <15> The etching solution according to any one of <1> to <14>, wherein a blending amount of the nitrogen-containing compound is 0.01% by mass or more and 5% by mass or less, 0.1% by mass or more and 3% by mass or less, or 0.5% by mass or more and 2% by mass or less.

<16> The etching solution according to any one of <1> to <15>, wherein a blending amount or a content of the organic acid is 50% by mass or more and 95% by mass or less, or 70% by mass or more and 90% by mass or less.

- <17> The etching solution according to any one of <1> to <16>, wherein a blending amount or a content of the nitric acid is 0.1% by mass or more and 10% by mass or less, 0.5% by mass or more and 8% by mass or less, or 1% by mass or more and 5% by mass or less.

- <18> The etching solution according to any one of <1> to <17>, wherein a blending amount or a content of the phosphoric acid is 0.1% by mass or more and 40% by mass or less, 0.5% by mass or more and 20% by mass or less, or 1% by mass or more and

- 10% by mass or less.
- <19> The etching solution according to any one of <1> to <18>, wherein a mass ratio (organic acid / phosphoric acid) of a blending amount or a content of the organic acid to the phosphoric acid is 1.2 or more and 950 or less, 3.5 or more and 100 or less, 5 or
 5 more and 50 or less, or 6 or more and 20 or less.
- <20> The etching solution according to any one of <1> to <19>, wherein a mass ratio of a blending amount or a content of the organic acid to the nitrogen-containing compound (organic acid / nitrogen-containing compound) is 10 or more and 10,000 or less, 20 or more and 5,000 or less, 30 or more and 2,500 or less, 40 or more and 1,000 or
 10 less, 50 or more and 500 or less, or 50 or more and 100 or less.
- <21> The etching solution according to any one of <1> to <20>, obtainable by further blending water.
- <22> The etching solution according to any one of <1> to <21>, wherein a pH of the etching solution is 2 or less, or 1 or less.
- 15 <23> The etching solution according to any one of <1> to <22>, wherein a pH of the etching solution is -2.5 or more, or -2 or more.
- <24> The etching solution according to any one of <1> to <23>, wherein a viscosity of the etching solution at 25°C is 1 mPa·s or more and 25 mPa·s or less, or 2 mPa·s or more and 10 mPa·s or less.
- 20 <25> An etching method comprising a step of etching a layer being etched containing at least one metal by use of the etching solution according to any one of <1> to <24>, wherein a temperature of the etching solution during etching is 20°C or higher and 50°C or lower.
- <26> An etching solution for etching a layer being etched containing at least one
 25 metal, the etching solution obtainable by blending:
- a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and
 - an acid comprising an organic acid, nitric acid, and phosphoric acid,
- wherein the nitrogen-containing compound is at least one selected from
 30 butylamine, octylamine, dodecylamine, octadecylamine, methyloctadecylamine, dimethyloctadecylamine, oleylamine, 2-ethylhexylamine, bis(hexamethylene) triamine, aniline, 2,6-diisopropylaniline, 5-methylbenzotriazole, and 2-(2-aminoethoxy)

ethanol,

a blending amount of the organic acid in the etching solution is 50% by mass or more, and

a mass ratio of a blending amount of the organic acid to a blending amount of the nitrogen-containing compound in the etching solution (organic acid / nitrogen-containing compound) is 10 or more and 10,000 or less.

<27> A method for manufacturing an electronic component, comprising a step of etching a layer being etched containing at least one metal by use of the etching solution according to any one of <1> to <24> and <26>.

10

Examples

[0050] Hereinafter, the present disclosure will be specifically described with reference to Examples, though the present disclosure is not limited to these Examples.

[0051] 1. Preparation of etching solutions (Examples 1 to 15, Comparative Examples 1 to 9)

Nitric acid, phosphoric acid, and acetic acid shown in Table 1, nitrogen-containing compounds shown in Table 1, and water were blended to obtain etching solutions (pH: -2.0 to -1.5) of Examples 1 to 15 and Comparative Examples 1 to 9.

The blending amount (% by mass, effective component) of each component is shown in Table 1. The blending amount of water is the balance excluding the acid and the nitrogen-containing compound. The blending amount of water includes the blending amount of water contained in the acid aqueous solution or the like.

[0052] The following components were used to prepare the etching solution.

<Acid>

25 Acetic acid [FUJIFILM Wako Pure Chemical Corporation, concentration: 100%]

Nitric acid [FUJIFILM Wako Pure Chemical Corporation, concentration: 70%]

Phosphoric acid (manufactured by Rin Kagaku Kogyo Co., Ltd., concentration: 85%)

<Nitrogen-containing compound>

(Aliphatic amine)

30 Butylamine [Tokyo Chemical Industry Co., Ltd.]

Octylamine [Tokyo Chemical Industry Co., Ltd.]

Dodecylamine [Tokyo Chemical Industry Co., Ltd.]

- Octadecylamine [Tokyo Chemical Industry Co., Ltd.]
 Methyloctadecylamine [Tokyo Chemical Industry Co., Ltd.]
 Dimethyloctadecylamine [Tokyo Chemical Industry Co., Ltd.]
 Oleylamine [Tokyo Chemical Industry Co., Ltd.]
- 5 2-Ethylhexylamine [Tokyo Chemical Industry Co., Ltd.]
 Bis(hexamethylene) triamine [Tokyo Chemical Industry Co., Ltd.]
 (Aromatic amine)
 Aniline [Tokyo Chemical Industry Co., Ltd.]
 2,6-Diisopropylaniline [Tokyo Chemical Industry Co., Ltd.]
- 10 5-Methylbenzotriazole [Tokyo Chemical Industry Co., Ltd.]
 (Amino alcohol)
 2-(2-Aminoethoxy) ethanol [Tokyo Chemical Industry Co., Ltd.]
 (Phenols)
 Catechol [Tokyo Chemical Industry Co., Ltd.]
- 15 (Polyalkylenepolyamine)
 Triethylenetetramine [molecular weight: 146.23, Tosoh Corporation]
 (Polyalkyleneimine)
 Polyethyleneimine (PEI) [number average molecular weight: 1,800, “EPOMIN SP-018” manufactured by Nippon Shokubai Co., Ltd.]
- 20 <Water>
 Water [ultrapure water produced using a continuous water purifying apparatus (Pureconti-2000VRL type) and a subsystem (Makuace KC-05H type) manufactured by Kurita Water Industries Ltd.]
 [0053] [pH of etching solution]
- 25 The pH value of the etching solution at 25°C is a value measured using a pH meter (manufactured by DKK-TOA CORPORATION), and is a numerical value 1 minute after an electrode of the pH meter is immersed in the etching solution.
 [0054] [Viscosity of etching solution]
 The viscosity (unit: mPa・s) of the etching solution was measured using the
- 30 following viscometer under the following conditions.
 Apparatus name: TVB-10 viscometer (equipped with a constant temperature bath) manufactured by Toki Sangyo Co., Ltd.

Rotor: Spindle No. M1, Cord No. 20

Rotation speed: 100 rpm, viscosity value after 60 seconds measured

Measurement temperature: 25°C

The viscosity was measured 30 minutes after the temperature in the thermostatic
 5 chamber indicated by the apparatus reached 25°C.

[0055] 2. Evaluation of etching solution

[Solubility (storage stability)]

A mixed acid and a nitrogen-containing compound shown in Table 1 were
 mixed in the blending amounts (% by mass) shown in Table 1 to prepare an etching
 10 solution of 20 mL. After stirring for 10 minutes, the solubility was visually confirmed.
 The evaluation criteria of the solubility are indicated as A, B and C in Table 1, namely,
 'A' is the case where there is no undissolved residue in the temperature range of 0°C to
 40°C and the etching solution is colorless-transparent or pale yellow-transparent; B is
 the case where there is an undissolved residue in the temperature range of 0°C to 40°C
 15 but the etching solution is colorless-transparent or pale yellow-transparent; and C is
 the case where the etching solution is cloudy or in another state (for example,
 blackened) in the temperature range of 0°C to 40°C. Points to be specifically noted
 are also described in the same column.

[0056] [Evaluation of etching inhibition rate]

20 A specific etching solution is exemplified here. When the etching rate of the
 mixed acid alone constituting the etching solution is α and the etching rate of the
 etching solution obtained by mixing the mixed acid and the nitrogen-containing
 compound is β , the etching inhibition rate is calculated by the following formula. The
 results are shown in Table 1.

25 Etching inhibition rate (%) = $100 \times (\alpha - \beta) / \alpha$

[0057] [State of substrate surface]

A molybdenum plate having a length of 2 cm, a width of 2 cm, and a thickness
 of 0.1 mm, the weight of which had been measured in advance, was immersed in an
 etching solution (Examples 1 to 15 and Comparative Examples 1 to 5 and 9) prepared
 30 to have each composition shown in Table 1, and the molybdenum plate was etched at
 each temperature for each treatment time. However, the etching solution containing
 the mixed acid alone and the nitrogen-containing compound is tested under the same

etching conditions. Then, after washing with water, the surface of the molybdenum plate was observed again using a shape measurement laser microscope VK-9710 (lens magnification: 150 times) manufactured by KEYENCE CORPORATION, and the photograph was analyzed in the surface roughness mode of the same instrument.

- 5 And then, the profile irregularity serving as an index of etching unevenness was obtained by the following formula. The etching unevenness of the molybdenum plate was evaluated based on the following evaluation criteria. Table 1 shows the results.
- Profile irregularity (%) = Surface roughness after etching / surface roughness before etching $\times$ 100

10 <Evaluation criteria>

4: Profile irregularity of less than 150%

3: Profile irregularity of 150% or more and less than 200%

2: Profile irregularity of 200% or more and less than 300%

1: Profile irregularity of 300% or more

15 [0058] [Table 1]

- [0059] As shown in Table 1, the etching solutions of Examples 1 to 15 had favorable solubility and excellent storage stability as compared with the etching solution of Comparative Example 6 and the etching solutions of Comparative Examples 7 and 8. Here, the etching solutions of Examples 1 to 15 each contain a nitrogen-containing compound having a ratio C/N of 2.2 or more as the nitrogen-containing compound, while the etching solution of Comparative Example 6 contain catechol (phenols) instead of the nitrogen-containing compound, and the etching solutions of Comparative Examples 7 and 8 each contain a nitrogen-containing compound having a ratio C/N of less than 2.2 as the nitrogen-containing compound.
- Furthermore, the etching solutions of Examples 1 to 15 were excellent in etching inhibition and the states of the substrate surface were favorable as compared with the etching solutions of Comparative Examples 2 to 4 and the etching solution of Comparative Example 5, where the etching solutions of Examples 1 to 15 each have a blending amount of acetic acid of 50% by mass or more and containing a nitrogen-containing compound having a ratio C/N of 2.2 or more, while the etching solutions of Comparative Examples 2 to 4 each have a blending amount of acetic acid of 50% by mass or more and free of a nitrogen-containing compound, and the etching solution of Comparative Example 5 has a blending amount of acetic acid of 30% by mass and free of a nitrogen-containing compound.
- Furthermore, the etching solution of Comparative Example 9 in which the blending amount of acetic acid was less than 50% by mass was not favorable in the state of the substrate surface as compared with the counterparts of Examples 1, 8, and 15 in which the blending amount of acetic acid was 50% by mass or more.
- Industrial Applicability**
- [0060] The etching solution of the present disclosure is excellent in storage stability, capable of inhibiting etching, and capable of improving the quality of the surface of a layer being etched after etching, and thus, is useful in a method for manufacturing a large-capacity semiconductor memory.

CLAIMS

- [Claim 1] An etching solution for etching a layer being etched containing at least one metal, the etching solution obtainable by blending:
- 5 a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and
an acid comprising an organic acid, nitric acid, and phosphoric acid,
wherein a blending amount of the organic acid in the etching solution is 50%
by mass or more.
- 10 [Claim 2] The etching solution according to claim 1, wherein the nitrogen-containing compound is at least one selected from the group consisting of an aliphatic amine, an aromatic amine, and an amino alcohol.
- 15 [Claim 3] The etching solution according to claim 2, wherein the aliphatic amine has a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 4 or more.
- [Claim 4] The etching solution according to any one of claims 1 to 3, wherein the
20 organic acid is at least one selected from the group consisting of acetic acid, acetic anhydride, methoxyacetic acid, ethoxyacetic acid, propionic acid, butanoic acid, citric acid, formic acid, gluconic acid, glycolic acid, malonic acid, oxalic acid, lactic acid, and pentanoic acid.
- 25 [Claim 5] The etching solution according to any one of claims 1 to 4, wherein the blending amount of the nitrogen-containing compound is 0.01% by mass or more and 5% by mass or less.
- [Claim 6] The etching solution according to any one of claims 1 to 5, wherein a
30 mass ratio of a blending amount of the organic acid to a blending amount of the nitrogen-containing compound (organic acid / nitrogen-containing compound) is 10 or more and 10,000 or less.

[Claim 7] The etching solution according to any one of claims 1 to 6, obtainable by further blending water.

- 5 [Claim 8] The etching solution according to any one of claims 1 to 7, wherein a pH of the etching solution is 2 or less.

[Claim 9] An etching method comprising etching a layer being etched containing at least one metal, by use of the etching solution according to any one of
10 claims 1 to 8,
 wherein a temperature of the etching solution during etching is 20°C or higher and 50°C or lower.

[Claim 10] An etching solution for etching a layer being etched containing at
15 least one metal, comprising:
 a salt of a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and
 an acid comprising an organic acid, nitric acid, and phosphoric acid,
20 wherein a blending amount of the organic acid in the etching solution is 50% by mass or more.

[Claim 11] An etching solution for etching a layer being etched containing at least one metal, the etching solution obtainable by blending:
25 a nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and
 an acid comprising an organic acid, nitric acid, and phosphoric acid,
 wherein a blending amount of the organic acid in the etching solution is 80% by mass or more.

30
[Claim 12] An etching solution for etching a layer being etched containing molybdenum, the etching solution obtainable by blending:

at least one nitrogen-containing compound having a ratio C/N of the number of carbon atoms (C) to the number of nitrogen atoms (N) in one molecule of 2.2 or more; and

5 an acid comprising an organic acid, nitric acid, and phosphoric acid, wherein a blending amount of an organic acid in the etching solution is 50% by mass or more.

[Claim 13] A method for manufacturing an electronic component, comprising etching a layer being etched containing at least one metal, by use of the etching
10 solution according to any one of claims 1 to 8, 10, 11 and 12.