

DESCRIPTION

ETCHING LIQUID

5 Technical Field

[0001] This disclosure relates to an etching liquid for a silicon nitride film, an etching method using the same, and a method for producing a semiconductor substrate.

Background Art

10 [0002] In processes for producing semiconductor devices, a step is performed in which a silicon nitride film (also referred to as "SiN film" hereinafter) is removed from a substrate having the SiN film and a silicon oxide film (also referred to as "SiO₂ film" hereinafter) by selectively etching the SiN film. Conventionally, a method for etching an SiN film, using phosphoric acid in a high temperature of 150°C or more is known as
15 a method for etching an SiN film.

[0003] In recent years, high integration has progressed in the semiconductor field, wiring needs to be complicated and miniaturized, and methods for increasing the ratio of the etch rate of the SiN film to the etch rate of the SiO₂ film have been proposed (e.g., Patent Documents 1 to 6).

20 [0004] Patent Document 1 proposes a method in which an etching liquid for silicon nitride containing a quaternary ammonium, a basic compound, and an acid is used.

Patent Document 2 proposes an etching method in which an etching liquid containing a phosphoric acid compound, a silicon-containing compound, and water is boiled and used.

25 Patent Document 3 proposes a method in which an etching liquid containing an inorganic acid, a silane inorganic acid salt, and a solvent is used.

Patent Document 4 proposes an etching liquid that contains phosphoric acid, an acid having an acid dissociation index that is smaller than the first acid dissociation index pK_a of phosphoric acid, a silicic acid compound, and water, in which the mass
30 ratio of phosphoric acid to the acid (phosphoric acid / acid) is in a range of 0.82 to 725 inclusive.

Patent Document 5 proposes an etching liquid for a semiconductor substrate

that contains fluoric acid in an amount of 3 to 20 wt%, nitric acid in an amount of 5 to 40 wt%, acetic acid in an amount of 10 to 60 wt%, an accelerating agent in an amount of 2 to 20 wt%, and water as the remaining portion, and the accelerating agent is one, or two or more selected from ammonium-based compounds and sulfonic acid compounds.

Patent Document 6 proposes an etching liquid containing a phosphoric acid aqueous solution containing water and phosphoric acid, and a salt of an organic compound that is soluble in the aqueous solution of phosphoric acid.

[0005] Also, with a conventional etching method in which phosphoric acid is used at a high temperature of 150°C or more, there is a problem in that a portion of an SiN film is decomposed into silicic acid ($\text{Si}(\text{OH})_4$) and ammonium phosphate ($(\text{NH}_4)_3\text{PO}_4$), silica (SiO_2) is produced through a dehydration reaction of a portion of silicic acid, and the produced silica precipitates and adheres onto the SiO_2 film. To address this, Patent Document 7 proposes an etching liquid containing a phosphoric acid aqueous solution containing water and phosphoric acid, and a salt of an organic compound that is soluble in the aqueous solution of phosphoric acid, for example.

Prior Art Documents

Patent Document

[0006] [Patent Document 1] JP 2012-33561A
 [Patent Document 2] JP 2014-99480A
 [Patent Document 3] JP 2016-29717A
 [Patent Document 4] WO 2018/168874A
 [Patent Document 5] JP 2015-504247A
 [Patent Document 6] JP 2018-56185A
 [Patent Document 7] JP 2018-56185A

Disclosure of Invention

[0007] In one aspect, this disclosure relates to an etching liquid for use in a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, and the etching liquid is obtained by blending a solution containing silica and an alkali, phosphoric acid, and water together.

[0008] In one aspect, this disclosure relates to an etching method including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid of this disclosure.

[0009] In one aspect, this disclosure relates to a method for producing a
5 semiconductor substrate including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid of this disclosure.

[0010] In one aspect, this disclosure relates to an additive agent to be added to an etching liquid for use in a step of removing a silicon nitride film from a substrate
10 having the silicon nitride film and a silicon oxide film, in which the additive agent is a solution containing silica and an alkali.

[0011] In one aspect, this disclosure relates to a kit for producing an etching liquid for use in a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, the kit including:
15 a solution containing silica and an alkali (a first liquid), and a solution containing phosphoric acid (a second liquid) in a state in which the first liquid and the second liquid are not mixed together, in which the first liquid and the second liquid are mixed together when the kit is used.

20 Description of the Invention

[0012] In recent years, high integration has progressed in the semiconductor field, wiring needs to be complicated and miniaturized, and there is demand for more efficiently removing silicon nitride films. In particular, from the viewpoint of productivity and yields, there is demand for further improvement in the ratio of the
25 etch rate of an SiN film to the etch rate of an SiO₂ film in a process of producing a three-dimensional semiconductor device such as a three-dimensional NAND flash memory.

In view of this, this disclosure provides an etching liquid capable of improving the ratio of the etch rate of a silicon nitride film to the etch rate of a silicon oxide film,
30 an etching method using this etching liquid, and a method for producing a semiconductor substrate.

[0013] That is to say, in one aspect, this disclosure relates to an etching liquid for use

in a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, in which the etching liquid is obtained by blending a solution containing silica and an alkali, phosphoric acid, and water (also referred to as the “etching liquid of Aspect 1”) together. According to the etching liquid of Aspect 1, it is possible to improve the ratio of the etch rate of the silicon nitride film to the etch rate of the silicon oxide film (also referred to as “SiN/SiO₂ selection rate ratio” hereinafter). [0014] Although details of the mechanism of the expression of the effects of Aspect 1 are unclear, the following is inferred.

It is conceivable that, with Aspect 1, dissolution of the silicon oxide film is suppressed, and the SiN / SiO₂ selection rate ratio is improved by using the etching liquid into which a solution containing silica and an alkali is blended.

However, this disclosure need not be interpreted as being limited to these mechanisms.

[0015] In this disclosure, “being obtained by blending a solution containing silica and an alkali, phosphoric acid, and water together” means that not only a solution containing silica and an alkali, phosphoric acid, and water but optional components can also be blended together as needed.

Also, in this disclosure, the amount of each component blended into the etching liquid can be read as the content thereof in the etching liquid.

[0016] Solution containing silica and alkali

In one or more embodiments, a solution containing silica and an alkali is blended into the etching liquid of Aspect 1.

From the viewpoint of improving the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to the SiO₂ film, the solution that contains silica and an alkali and is to be used to prepare the etching liquid of Aspect 1 is preferably a silica solution in which at least a part of silica is dissolved in the alkali (also referred to as the “silica solution of this disclosure” hereinafter). In one or more embodiments, the silica solution of this disclosure is a silica solution in which silica is dissolved to a detection limit or less, the detection limit being the point at which silica can be detected with various particle size measuring devices or where silica can be detected from the external appearance of the silica solution. Note that, as will be described later, the silica solution may contain undissolved silica. The silica solution

of this disclosure can be obtained by mixing silica and an alkali together to dissolve the silica, for example. Examples of a method for dissolving silica include heating treatment, pressurization treatment, and mechanical pulverization treatment, and these treatments may be used in combination. The heating condition can be set to 5 60°C to 100°C, for example. The pressurization condition can be set to 0 to 3 MPa, for example. Mechanical pressurization can be performed using a ball mill or the like, for example. Also, when silica is dissolved in an alkali, ultrasonic vibration may be applied. The state of silica before being mixed with an alkali need not be particular limited, and examples thereof include powder, sol, and gel.

10 [0017] Silica

Examples of silica (the silica before dissolution) used to prepare the silica solution of this disclosure include crystalline silica, amorphous silica, fumed silica, wet silica, colloidal silica, and calcined silica obtained by calcining crystalline silica, amorphous silica, fumed silica, wet silica, and colloidal silica. In particular, at least 15 one selected from fumed silica and colloidal silica is preferable from the viewpoint of improving the SiN/SiO₂ selection rate ratio, suppressing the precipitation and adhesion of silica to an SiO₂ film, and inhibiting the clogging of a filter used in circulation. Colloidal silica may be obtained using a method through particle growth in which an aqueous solution of alkali silicate is used as a raw material (also referred to as a “water glass method” hereinafter), and a method through condensation of a 20 product obtained by hydrolysis of alkoxysilane (also referred to as a “sol-gel method” hereinafter), for example. Silica particles obtained using the water glass method and the sol-gel method can be produced using a conventionally known method. From the viewpoint of improving the SiN/SiO₂ selection rate ratio, the crystallinity of silica is 25 preferably 4% or less, and more preferably 3% or less. The crystallinity can be measured using the method described in Examples, for example. Silica can be used alone or in combination of two or more types thereof.

[0018] Alkali

In one or more embodiments, examples of the alkali used to prepare the silica 30 solution of this disclosure include organic alkalis and inorganic alkalis. Alkalis can be used alone or in combination of two or more types thereof.

An organic alkali used to prepare the silica solution of this disclosure may be

any organic alkali that can dissolve silica, and examples thereof include quaternary ammonium salts such as tetraalkyl ammonium hydroxide. A specific example of the quaternary ammonium salts is at least one selected from tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide (TEAH),
5 trimethylethylammonium hydroxide (ETMAH), benzyltrimethylammonium hydroxide, ethyltrimethylammonium hydroxide, methylbenzyltrimethylammonium hydroxide, and tetraethylammonium hydroxide. In particular, at least one of tetramethylammonium hydroxide (TMAH) and trimethylethylammonium hydroxide (ETMAH) is preferable, and TMAH is more preferable from the viewpoint of improving
10 the SiN/SiO₂ selection rate ratio. Also, TMAH is preferable from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and inhibiting the clogging of a filter used in circulation.

An inorganic alkali used to prepare the silica solution of this disclosure may be any inorganic alkali that can dissolve silica, and examples thereof include sodium
15 hydroxide and potassium hydroxide.

In one or more embodiments, examples of the alkali used to prepare the silica solution of this disclosure may be preferably at least one selected from tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide (TEAH), trimethylethylammonium hydroxide (ETMAH), benzyltrimethylammonium hydroxide,
20 ethyltrimethylammonium hydroxide, methylbenzyltrimethylammonium hydroxide, tetraethylammonium hydroxide, sodium hydroxide, and potassium hydroxide. At least one selected from tetramethylammonium hydroxide (TMAH), trimethylethylammonium hydroxide (ETMAH), sodium hydroxide, and potassium hydroxide is preferable from the viewpoint of improving the SiN/SiO₂ selection rate
25 ratio.

[0019] In one or more embodiments, the silica solution of this disclosure may contain silica that has not been dissolved in an alkali. That is to say, in one or more embodiments, the etching liquid of Aspect 1 may contain undissolved silica. The undissolved silica is preferably minute silica from the viewpoint of inhibiting the
30 clogging of a filter used in circulation of the etching liquid. Minute silica has an average particle size of 0.1 nm to 1000 nm inclusive, for example. In this disclosure, the average particle size of silica is an average particle diameter based on a scattering

intensity distribution measured at a detection angle of 173 degrees in dynamic light scattering. Specifically, the average particle size thereof can be measured using the method described in Examples.

[0020] From the viewpoint of improving the SiN/SiO₂ selection rate ratio and
 5 suppressing precipitation and adhesion of silica to an SiO₂ film, a solution that contains silica and an alkali and is to be used to prepare the etching liquid of Aspect 1 is preferably blended such that the content of silica dissolved in the etching liquid of Aspect 1 is 0.0005 mass% to 1 mass% inclusive. From the viewpoint of improving the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to
 10 the SiO₂ film, the content of silica dissolved in the etching liquid of Aspect 1 (also referred to as “the amount of dissolved silica” hereinafter) is preferably 0.0005 mass% or more, more preferably 0.001 mass% or more, and further preferably 0.01 mass% or more, and from the same viewpoint, preferably 1 mass% or less, more preferably 0.5 mass% or less, and further preferably 0.1 mass% or less. More specifically, the
 15 amount of silica dissolved in the etching liquid of Aspect 1 is preferably 0.0005 mass% to 1 mass% inclusive, more preferably 0.001 mass% to 0.5 mass% inclusive, and further preferably 0.01 mass% to 0.1 mass% inclusive.

[0021] From the viewpoint of improving the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to the SiO₂ film, the content of silica in
 20 the etching liquid of Aspect 1 (the total content of dissolved silica and undissolved silica) is preferably 0.0005 mass% or more, more preferably 0.001 mass% or more, and further preferably 0.01 mass% or more, and from the same viewpoint, preferably 1 mass% or less, more preferably 0.5 mass% or less, and further preferably 0.1 mass% or less. More specifically, the content of silica in the etching liquid of Aspect 1 is
 25 preferably 0.0005 mass% to 1 mass% inclusive, more preferably 0.001 mass% to 0.5 mass% inclusive, and further preferably 0.01 mass% to 0.1 mass% inclusive.

[0022] Phosphoric acid

In one or more embodiments, phosphoric acid is blended into the etching liquid of Aspect 1.

30 From the viewpoint of improving the SiN/SiO₂ selection rate ratio, the amount of phosphoric acid blended into the etching liquid of Aspect 1 is preferably 50 mass% or more, more preferably 70 mass% or more, and further preferably 80 mass% or more,

and from the same viewpoint, preferably 95 mass% or less, more preferably 90 mass% or less, and further preferably 85 mass% or less. More specifically, the amount of phosphoric acid blended into the etching liquid of Aspect 1 is preferably 50 mass% to 95 mass% inclusive, more preferably 70 mass% to 90 mass% inclusive, and further
5 preferably 80 mass% to 85 mass% inclusive.

[0023] Water

In one or more embodiments, water is blended into the etching liquid of Aspect 1.

Examples of water contained in the etching liquid of Aspect 1 include distilled
10 water, ion-exchanged water, pure water, and ultrapure water.

[0024] High-temperature stabilizing agent

In one or more embodiments, from the viewpoint of inhibiting the clogging of a filter used in circulation while maintaining the SiN/SiO₂ selection rate ratio, the etching liquid of Aspect 1 may further contain a high-temperature stabilizing agent.

15 The high-temperature stabilizing agents may be used alone or in combination of two or more types thereof.

[0025] Examples of the high-temperature stabilizing agent include high-temperature stabilizing agents having a pKa value of 2 or less. The pKa value of the high-temperature stabilizing agent is preferably 2 or less, more preferably 1.5 or less,
20 and further preferably 1.0 or less from the viewpoint of inhibiting the clogging of a filter used in circulation while maintaining the SiN/SiO₂ selection rate ratio. The pKa can be obtained using the method described in Examples.

[0026] Examples of the high-temperature stabilizing agents having a pKa value of 2 or less include organic acids having a pKa value of 2 or less. An example of the
25 organic acid having a pKa value of 2 or less is at least one selected from sulfonic acid compounds having a pKa value of 2 or less, maleic acid (having a pKa value of 1.87), and oxalic acid (having a pKa value of 1.27). Examples of the sulfonic acid compound having a pKa value of 2 or less include *p*-toluenesulfonic acid (having a pKa value of -2.8) and benzenesulfonic acid (having a pKa value of 0.7). In particular, the
30 high-temperature stabilizing agent having a pKa value of 2 or less is preferably a sulfonic acid compound having a pKa value of 2 or less, and more preferably at least one of *p*-toluenesulfonic acid and benzenesulfonic acid, from the viewpoint of inhibiting

the clogging of a filter used in circulation while maintaining the SiN/SiO₂ selection rate ratio. These compounds may be used alone or in combination of two or more types thereof.

[0027] If a high-temperature stabilizing agent is blended into the etching liquid of Aspect 1, in one or more embodiments, the ratio of the mass of phosphoric acid (M2) to the mass of the high-temperature stabilizing agent (M1) (mass ratio M2/M1) is preferably 800 or more, more preferably 1000 or more, and further preferably 1500 or more, and preferably 82000 or less, more preferably 41000 or less, and further preferably 27000 or less, from the viewpoint of inhibiting the clogging of a filter used in circulation while maintaining the SiN/SiO₂ selection rate ratio. More specifically, the mass ratio M2/M1 is preferably 800 to 82000 inclusive, more preferably 1000 to 41000 inclusive, and further preferably 1500 to 27000 inclusive.

[0028] If a high-temperature stabilizing agent is blended into the etching liquid of Aspect 1, in one or more embodiments, the ratio of the mole amount of phosphoric acid (m2) to the mole amount of the high-temperature stabilizing agent (m1) (mole ratio m2/m1) is preferably 1000 or more, more preferably 2500 or more, and further preferably 4500 or more, and preferably 140000 or less, more preferably 72000 or less, and further preferably 48000 or less, from the viewpoint of inhibiting the clogging of a filter used in circulation while maintaining the SiN/SiO₂ selection rate ratio. More specifically, the mole ratio m2/m1 is preferably 1000 to 140000 inclusive, more preferably 2500 to 72000 inclusive, and further preferably 4500 to 48000 inclusive.

[0029] If a high-temperature stabilizing agent is blended into the etching liquid of Aspect 1, from the viewpoint of improving the SiN/SiO₂ selection rate ratio, suppressing silica aggregation, and inhibiting the clogging of a filter used in circulation, the amount of the high-temperature stabilizing agent blended into the etching liquid of Aspect 1 is preferably 0.001 mass% or more, more preferably 0.003 mass% or more, and further preferably 0.005 mass% or more, and from the same viewpoint, preferably 1.0 mass% or less, more preferably 0.5 mass% or less, even more preferably 0.1 mass% or less, and further preferably less than 0.1 mass%. More specifically, the amount of the high-temperature stabilizing agent blended into the etching liquid of Aspect 1 is preferably 0.001 mass% to 1.0 mass% inclusive, more preferably 0.003 mass% to 0.5 mass% inclusive, even more preferably 0.005 mass% to 0.1 mass% inclusive, and

further preferably 0.005 mass% or more and less than 0.1 mass%. If two or more types of high-temperature stabilizing agents are used in combination, the amount of blended high-temperature stabilizing agents is the total amount of blended high-temperature stabilizing agents.

5 [0030] Organic phosphonic acid compound

In one or more embodiments, the etching liquid of Aspect 1 may further contain an organic phosphonic acid compound from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and/or suppressing precipitation and adhesion of silica to the SiO₂ film. The organic phosphonic acid compounds may be used alone or in
10 combination of two or more types thereof.

[0031] Examples of the organic phosphonic acid compound include phosphoric acid-based polymers, alkylphosphonic acids, alkenylphosphonic acids, and alkyl ether phosphonic acids from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to the SiO₂ film.

15 An example of the phosphoric acid-based polymer is polyvinylphosphonic acid (PVPA).

From the viewpoint of improving the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to the SiO₂ film, the number of carbon atoms of an alkyl group of an alkylphosphonic acid is preferably 6 or more, and more
20 preferably 8 or more, and from the viewpoint of solubility, the number of carbon atoms thereof is preferably 18 or less, and more preferably 16 or less. The alkyl group of an alkylphosphonic acid may have a linear chain or a branched chain. Specific examples of the alkylphosphonic acid include hexylphosphonic acid, heptylphosphonic acid, octylphosphonic acid, caprylphosphonic acid, dodecylphosphonic acid, and
25 tetradecylphosphonic acid.

From the viewpoint of improving the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to the SiO₂ film, the number of carbon atoms of an alkenyl group of an alkenylphosphonic acid is preferably 6 or more, and more preferably 8 or more, and from the viewpoint of solubility, the number of carbon
30 atoms thereof is preferably 18 or less, and more preferably 16 or less. The alkenyl group of an alkenylphosphonic acid may have a linear chain or a branched chain.

From the viewpoint of improving the SiN/SiO₂ selection rate ratio, and

suppressing precipitation and adhesion of silica to the SiO₂ film, the number of carbon atoms of an alkyl group of an alkyl ether phosphonic acid is preferably 6 or more, and more preferably 8 or more, and from the viewpoint of solubility, the number of carbon atoms thereof is preferably 20 or less, and more preferably 18 or less. The alkyl group
5 of an alkenylphosphonic acid may have a linear chain or a branched chain. Specific examples of the alkyl ether phosphonic acid are polyoxyethylene alkyl ether phosphonic acids.

In particular, at least one selected from polyvinylphosphonic acids, alkylphosphonic acids, and alkyl ether phosphonic acids is preferable as an organic
10 phosphonic acid compound from the viewpoint of improving the SiN/SiO₂ selection rate ratio and suppressing precipitation and adhesion of silica to the SiO₂ film.

[0032] In one or more embodiments, the molecular weight of the organic phosphonic acid compound is preferably 1000 or more, more preferably 5000 or more, and further preferably 7000 or more, and preferably 100000 or less, more preferably 50000 or less,
15 and further preferably 20000 or less from the viewpoint of improving the SiN/SiO₂ selection rate ratio and suppressing precipitation and adhesion of silica to the SiO₂ film. More specifically, the molecular weight of the organic phosphonic acid compound is preferably 1000 to 100000 inclusive, more preferably 5000 to 50000 inclusive, and further preferably 7000 to 20000 inclusive. In another one or more embodiments, the
20 molecular weight of the organic phosphonic acid compound is preferably 150 or more, more preferably 200 or more, and further preferably 300 or more, and preferably 100000 or less, more preferably 50000 or less, and further preferably 20000 or less from the viewpoint of suppressing precipitation and adhesion of silica to the SiO₂ film. More specifically, the molecular weight of the organic phosphonic acid compound is
25 preferably 150 to 100000 inclusive, more preferably 200 to 50000 inclusive, and further preferably 300 to 20000 inclusive.

[0033] If the organic phosphonic acid compound is a phosphoric acid-based polymer, the weight average molecular weight of the organic phosphonic acid compound is preferably 1000 or more, more preferably 5000 or more, and further preferably 7000 or
30 more, and preferably 100000 or less, more preferably 50000 or less, and further preferably 20000 or less from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to the SiO₂ film. More

specifically, the molecular weight of the organic phosphonic acid compound is preferably 1000 to 100000 inclusive, more preferably 5000 to 50000 inclusive, and further preferably 7000 to 20000 inclusive. In this disclosure, the weight average molecular weight can be measured using gel permeation chromatography (GPC) under the following conditions, for example.

Measurement conditions

Column: G4000PWXL+G2500 PWXL (manufactured by Tosoh Corporation)

Eluent: 0.2 M phosphate buffer / CH₃CN = 9 / 1 (volume ratio)

10 Column temperature: 40°C

Flow velocity: 1.0 mL / min

Sample size: 5 mg / mL

Detector: RI

Standard substance: polyethylene glycol

15 [0034] If an organic phosphonic acid compound is blended into the etching liquid of Aspect 1, from the viewpoint of improving the SiN/SiO₂ selection rate ratio and suppressing precipitation and adhesion of silica to the SiO₂ film, the amount of the organic phosphonic acid compound blended into the etching liquid of Aspect 1 is preferably 0.005 mass% or more, more preferably 0.01 mass% or more, and further

20 preferably 0.03 mass% or more, and from the same viewpoint, the amount of the organic phosphonic acid compound blended into the etching liquid of Aspect 1 is preferably 5.0 mass% or less, more preferably 1.0 mass% or less, and further preferably 0.5 mass% or less. More specifically, the amount of the organic phosphonic acid compound blended into the etching liquid of Aspect 1 is preferably 0.005 mass% to

25 5.0 mass% inclusive, more preferably 0.01 mass% to 1.0 mass% inclusive, and further preferably 0.03 mass% to 0.5 mass% inclusive. If two or more types of organic phosphonic acid compounds are used in combination, the amount of blended organic phosphonic acid compounds is the total amount of the blended organic phosphonic acid compounds.

30 [0035] Nonionic surfactant

In one or more embodiments, the etching liquid of Aspect 1 can further contain a nonionic surfactant from the viewpoint of suppressing precipitation and adhesion of

silica to the SiO₂ film. From the viewpoint of suppressing precipitation and adhesion of silica to the SiO₂ film, examples of the nonionic surfactant include polyoxyalkylene alkyl ethers, and specifically, at least one selected from polyoxyethylene lauryl ethers, polyoxyethylene oleyl ethers, and polyoxyethylene polyoxypropylene lauryl myristyl ethers. The nonionic surfactants may be used alone or in combination of two or more types thereof.

[0036] From the viewpoint of suppressing precipitation and adhesion of silica to the SiO₂ film, the HLB value of the nonionic surfactant in the etching liquid of Aspect 1 is preferably 8 or more, more preferably 12 or more, and further preferably 15 or more.

10 Here, HLB is a value obtained by defining an HLB value by “7 + [summation of group numbers of hydrophilic groups] – [summation of group numbers of lipophilic groups]”, using group numbers determined depending on functional groups described in Davis, J. T.; Proc. Intern. Congr. Surface Activity, 2nd, London, 1, 426 (1957).

[0037] If a nonionic surfactant is blended into the etching liquid of Aspect 1, from the viewpoint of suppressing precipitation and adhesion of silica to the SiO₂ film, the amount of the nonionic surfactant blended into the etching liquid of Aspect 1 is preferably 0.001 mass% or more, more preferably 0.01 mass% or more, and further preferably 0.03 mass% or more, and from the same viewpoint, the amount of the nonionic surfactant blended into the etching liquid of Aspect 1 is preferably 10 mass% or less, more preferably 5 mass% or less, and further preferably 1 mass% or less.

More specifically, the amount of the nonionic surfactant blended into the etching liquid of Aspect 1 is preferably 0.001 mass% to 10 mass% inclusive, more preferably 0.01 mass% to 5 mass% inclusive, and further preferably 0.03 mass% to 1 mass% inclusive. If two or more types of nonionic surfactants are used in combination, the amount of blended nonionic surfactants is the total amount of blended nonionic surfactants.

[0038] Other components

The etching liquid of Aspect 1 may further contain other components as long as the effects of this disclosure are not impaired. Examples of the other components include acids other than phosphoric acid, a chelating agent, surfactants other than the above-described nonionic surfactants, a solubilizer, an antiseptic, a rust-preventive agent, a germicide, an antibacterial agent, and an antioxidant.

[0039] In this disclosure, a solution containing silica and an alkali, and the

above-described optional components (organic phosphonic acid compound, high-temperature stabilizing agent, nonionic surfactant, and other components) are additive agents added to the etching liquid. Thus, in one aspect, this disclosure relates to an additive agent (also referred to as the “additive agent of this disclosure” hereinafter) that is to be added to an etching liquid for use in a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, the additive agent containing silica and an alkali. In one or more embodiments, the additive agent of this disclosure can further contain at least one selected from organic phosphonic acid compounds, high-temperature stabilizing agents, and nonionic surfactants. In one or more embodiments, the additive agent of this disclosure can further contain phosphoric acid.

[0040] Method for producing etching liquid

The etching liquid of Aspect 1 can be obtained by blending, using a known method, a solution containing silica and an alkali, phosphoric acid, and water, and the above-described optional components (organic phosphonic acid compounds, high-temperature stabilizing agents, nonionic surfactant, and other components) as desired, for example. Therefore, in one aspect, this disclosure relates to a method for producing an etching liquid (also referred to as the “etching liquid production method of Aspect 1” hereinafter) including a step of blending at least a solution containing silica and an alkali, phosphoric acid, and water together (also referred to as a “blending step” hereinafter). In one or more embodiments, the etching liquid production method of Aspect 1 can further include a step of preparing a silica solution by mixing silica and an alkali together.

In one or more embodiments, “blending at least a solution containing silica and an alkali, phosphoric acid, and water together” in this disclosure includes mixing together a solution containing silica and an alkali, phosphoric acid, and water, and the above-described optional components as needed simultaneously or in order. The order of mixing need not be particularly limited. The blending can be carried out using a mixer such as a homomixer, a homogenizer, an ultrasonic disperser, or a wet ball mill, for example.

[0041] From the viewpoint of improving the SiN/SiO₂ selection rate ratio, in the blending step in the etching liquid production method of Aspect 1, the solution

containing silica and an alkali is preferably obtained through blending such that the content of silica dissolved in the etching liquid of Aspect 1 is in the above-described range.

[0042] From the viewpoint of improving the SiN/SiO₂ selection rate ratio, the pH of the etching liquid of Aspect 1 is preferably 0.1 or more, more preferably 0.2 or more, and further preferably 0.3 or more, and preferably 2 or less, more preferably 1.5 or less, and further preferably 1.0 or less. More specifically, the pH is preferably 0.1 to 2 inclusive, more preferably 0.2 to 1.5 inclusive, and further preferably 0.3 to 1.0 inclusive. In this disclosure, the pH of the etching liquid is a value at 25°C, and can be measured using a pH meter, and specifically, can be measured using the method described in Examples.

[0043] From the viewpoint of inhibiting the clogging of a filter used in circulation, the flow rate of the etching liquid of Aspect 1 flowing through a 0.2 µm-filter is preferably 10 g/3 min or more, more preferably 20 g/3 min or more, and further preferably 25 g/3 min or more. In this disclosure, the 0.2 µm-filter flow rate can be calculated using the method described in Examples.

[0044] The etching liquid of Aspect 1 may be preferably stored or supplied in a concentrated state as long as the stability thereof is not impaired because it is possible to reduce manufacturing and transportation costs. Also, this concentrate can be diluted as appropriate using water, an aqueous solution of phosphoric acid, or the like, as needed, and then the resulting solution can be used in the etching step. The dilution ratio is preferably 1:5 to 1:100.

[0045] Kit

In one aspect, this disclosure relates to a kit for producing the etching liquid of Aspect 1 (also referred to as the “kit of Aspect 1” hereinafter).

As one embodiment of the kit of Aspect 1, the kit (two-component etching liquid) includes a solution containing silica and an alkali (a first liquid) and a solution containing phosphoric acid (a second liquid) in a state in which the first liquid and the second liquid are not mixed together, and the first liquid and the second liquid are mixed together when the kit is used, for example. After the first liquid and the second liquid are mixed together, the resulting mixture may be diluted using water or an aqueous solution of phosphoric acid as needed. The first liquid or the second liquid

may include the total amount or a part of water used to prepare the etching liquid. The amount of phosphoric acid contained in the second liquid may be the total amount or a part of phosphoric acid used to prepare the etching liquid. The first liquid and the second liquid may each contain the above-described optional components as needed.

5 According to the kit of Aspect 1, it is possible to obtain an etching liquid capable of improving the SiN/SiO₂ selection rate ratio.

[0046] Substrate to be processed

In one or more embodiments, a substrate that is to be processed and etched using the etching liquid of Aspect 1 is a substrate having a silicon nitride film and a
10 silicon oxide film. Examples of the substrate include semiconductor substrates and substrates that are to be used for flat panel displays. Examples of the silicon nitride film include nitride films formed using a low-pressure chemical vapor deposition method (LPCVD method), a plasma chemical vapor deposition method (PECVD method), an atomic layer deposition method (ALD method), or the like. Examples of
15 the silicon oxide film include oxide films formed using a thermal oxidation method, the LPCVD method, the PECVD method, the ALD method, or the like.

[0047] Method for producing semiconductor substrate

In one aspect, this disclosure relates to a method for producing a semiconductor substrate (also referred to as the “semiconductor substrate production
20 method of Aspect 1” hereinafter) including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid of Aspect 1 (also referred to as the “etching step of this disclosure” hereinafter). According to the semiconductor substrate production method of Aspect 1, it is possible to improve the SiN/SiO₂ selection rate ratio. Thus, according to the semiconductor
25 substrate production method of Aspect 1, it is possible to achieve the effect that a semiconductor substrate with improved quality can be efficiently produced.

[0048] In the etching step of this disclosure, examples of the etching method include immersion etching and single-wafer etching.

[0049] In the etching step of this disclosure, from the viewpoint of improving the
30 SiN/SiO₂ selection rate ratio, the etching temperature of the etching liquid is preferably 110°C or more, more preferably 120°C or more, even more preferably 140°C or more, and further preferably 150°C or more, and preferably 250°C or less, more

preferably 230°C or less, even more preferably 200°C or less, and further preferably 180°C or less. More specifically, in one or more embodiments, the etching temperature of the etching liquid is preferably 120°C to 250°C inclusive, more preferably 140°C to 230°C inclusive, and further preferably 150°C to 200°C inclusive.

- 5 In another one or more embodiments, the etching temperature of the etching liquid is preferably 110°C to 180°C inclusive.

[0050] In the etching step of this disclosure, the etching time can be set to 30 minutes to 270 minutes inclusive, for example.

- [0051] In the etching step of this disclosure, from the viewpoint of improving
10 productivity, the etch rate of the silicon nitride film is preferably 40 Å/min or more, more preferably 50 Å/min or more, and further preferably 60 Å or more.

[0052] In the etching step of this disclosure, from the viewpoint of improving productivity, the etch rate of the silicon oxide film is preferably 1.0 Å/min or less, more preferably 0.5 Å/min or less, and further preferably 0.3 Å/min or less.

- 15 [0053] In the etching step of this disclosure, from the viewpoint of improving productivity, the SiN/SiO₂ selection rate ratio is preferably 150 or more, more preferably 200 or more, and further preferably 300 or more.

[0054] Etching method

- In one aspect, this disclosure relates to an etching method (also referred to as
20 the “etching method” of Aspect 1 hereinafter) including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid of Aspect 1 (an etching step). Because the SiN/SiO₂ selection rate ratio can be improved by using the etching method of Aspect 1, it is possible to achieve the effect that the productivity of semiconductor substrates with improved
25 quality can be improved.

Specific etching methods and conditions can be the same as the above-described semiconductor substrate production method of Aspect 1 and as those in the above-described semiconductor substrate production method of Aspect 1.

- [0055] Also, in another aspect, this disclosure provides an etching liquid capable of
30 inhibiting the clogging of a filter used in circulation of the etching liquid, an etching method and a method for producing a semiconductor substrate using the etching liquid.

[0056] That is to say, in another aspect, this disclosure relates to an etching liquid for use in a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, in which the etching liquid is obtained by blending a high-temperature stabilizing agent having a pKa value of 2 or less, phosphoric acid, and water together (also referred to as the “etching liquid of Aspect 2” hereinafter). In one or more embodiments, according to the etching liquid of Aspect 2, it is possible to inhibit the clogging of a filter used in circulation of the etching liquid. Also, in one or more embodiments, according to the etching liquid of Aspect 2, it is possible to maintain the ratio of the etch rate of the silicon nitride film to the etch rate of the silicon oxide film (also referred to as the “SiN/SiO₂ selection rate ratio” hereinafter).

[0057] Although details of the mechanism of the expression of the effects of Aspect 2 are unclear, the following is inferred

It is conceivable that, with Aspect 2, in one or more embodiments, as a result of the high-temperature stabilizing agent that has a pKa value of 2 or less and is blended into the etching liquid ionically binding to the surface of precipitates (e.g., silica) derived from silicic acid produced during the etching step, aggregation of precipitates derived from silicic acid is suppressed and thus it is possible to inhibit the clogging of the filter used in circulation of the etching liquid.

However, this disclosure need not be interpreted as being limited to these mechanisms.

[0058] In this disclosure, “being obtained by blending a high-temperature stabilizing agent, phosphoric acid, and water together” means that not only a high-temperature stabilizing agent, phosphoric acid, and water but optional components can also be blended together as needed.

[0059] In one or more embodiments, a high-temperature stabilizing agent is blended into the etching liquid of Aspect 2. An example of the high-temperature stabilizing agent in Aspect 2 is the above-described high-temperature stabilizing agent of Aspect 1. The high-temperature stabilizing agents may be used alone or in combination of two or more types thereof.

In the etching liquid of Aspect 2, it is preferable that the ratio of the mass of phosphoric acid (M2) to the mass of the high-temperature stabilizing agent (M1) (the mass ratio M2 / M1), the ratio of the mole amount of phosphoric acid (m2) to the mole

amount of the high-temperature stabilizing agent (m_1) (the mole ratio m_2 / m_1), and the amount of the high-temperature stabilizing agent blended respectively are in the same ranges as those of the above-described mass ratio M_2 / M_1 , mole ratio m_2 / m_1 , and amount of the high-temperature stabilizing agent blended in Aspect 1, from the viewpoint of inhibiting the clogging of a filter used in circulation while maintaining the SiN/SiO₂ selection rate ratio.

[0060] In one or more embodiments, phosphoric acid is blended into the etching liquid of Aspect 2. It is preferable that the amount of phosphoric acid blended into the etching liquid of Aspect 2 is in the same range as the amount of phosphoric acid blended into the above-described etching liquid of Aspect 1 from the viewpoint of improving the SiN/SiO₂ selection rate ratio.

[0061] In one or more embodiments, water is blended into the etching liquid of Aspect 2. Examples of water in Aspect 2 include the same as those in Aspect 1 above.

[0062] In one or more embodiments, the etching liquid of Aspect 2 may further

contain a solution containing a silicon compound from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and inhibiting the clogging of a filter used in circulation.

Examples of the silicon compound include inorganic silicon compounds containing silicon and organosilicon compounds containing silicon. Examples of the inorganic

silicon compound include silica and inorganic silane compounds. Examples of the

organosilicon compound include organic silane compounds. It is preferable that the

solution containing a silicon compound contains silica and an alkali from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and inhibiting the clogging of a filter

used in circulation. Thus, in one or more embodiments, the etching liquid of Aspect 2 can further contain a solution containing silica and an alkali.

[0063] If the solution containing a silicon compound is a solution containing silica and an alkali in Aspect 2, from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and inhibiting the clogging of a filter used in circulation, the solution that contains silica and an alkali and is used to prepare the etching liquid of Aspect 2 is preferably a silica solution in which at least a part of silica is dissolved in the alkali. An example of the silica solution in Aspect 2 is the above-described silica solution of Aspect 1.

[0064] If the solution containing a silicon compound is a solution containing silica and an alkali in Aspect 2, from the viewpoint of improving the SiN/SiO₂ selection rate ratio,

and inhibiting the clogging of a filter used in circulation, the solution that contains silica and an alkali and is used to prepare the etching liquid of Aspect 2 is preferably blended such that the content of silica dissolved in the etching liquid of Aspect 2 is 0.0005 mass% to 1 mass% inclusive. From the viewpoint of improving the SiN/SiO₂ selection rate ratio, and inhibiting the clogging of a filter used in circulation, the content of silica dissolved in the etching liquid of Aspect 2 (the amount of dissolved silica) is preferably in the same range as the amount of silica dissolved in the above-described etching liquid of Aspect 1.

[0065] If the solution containing a silicon compound is blended into the etching liquid of Aspect 2, from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and inhibiting the clogging of a filter used in circulation, the content of the silicon compound in the etching liquid of Aspect 2 is preferably 0.0005 mass% or more, more preferably 0.001 mass% or more, and further preferably 0.01 mass% or more, and from the same viewpoint, the content of the silicon compound therein is preferably 1 mass% or less, more preferably 0.5 mass% or less, and further preferably 0.1 mass% or less. More specifically, the content of the silicon compound in the etching liquid of Aspect 2 is preferably 0.0005 mass% to 1 mass% inclusive, more preferably 0.001 mass% to 0.5 mass% inclusive, and further preferably 0.01 mass% to 0.1 mass% inclusive.

[0066] In Aspect 2, if the silicon compound is silica, from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and inhibiting the clogging of a filter used in circulation, the content of silica in the etching liquid of Aspect 2 (the total content of dissolved silica and the undissolved silica) is preferably in the same ranges as the content of silica in the above-described etching liquid of Aspect 1.

[0067] In one or more embodiments, the etching liquid of Aspect 2 may further contain an organic phosphonic acid compound. Examples of the organic phosphonic acid compound include the above-described organic phosphonic acid compounds of Aspect 1. The organic phosphonic acid compounds may be used alone or in combination of two or more types thereof.

If an organic phosphonic acid compound is blended into the etching liquid of Aspect 2, the amount of the blended organic phosphonic acid compound in Aspect 2 is preferably in the same range as the amount of the organic phosphonic acid compound blended into the etching liquid of Aspect 1 from the viewpoint of improving the

SiN/SiO₂ selection rate ratio, and suppressing precipitation of silica in the SiO₂ film.

[0068] The etching liquid of Aspect 2 may further contain other components as long as the effects of this disclosure are not impaired. Examples of the other components include acids other than phosphoric acid, a chelating agent, a surfactant, a solubilizer, an antiseptic, a rust-preventive agent, a germicide, an antibacterial agent, and an antioxidant.

[0069] The etching liquid of Aspect 2 can be obtained using a known method by blending a high-temperature stabilizing agent, phosphoric acid, and water, and the above-described optional components as desired, for example. Therefore, in another aspect, this disclosure relates a method for producing an etching liquid (also referred to as the “etching liquid production method of Aspect 2” hereinafter) including a step of blending at least a high-temperature stabilizing agent, phosphoric acid, and water together.

In one or more embodiments, “blending at least a high-temperature stabilizing agent, phosphoric acid, and water together” in this disclosure includes mixing together a high-temperature stabilizing agent, phosphoric acid, and water, and the above-described optional components as needed simultaneously or in order. The order of mixing need not be particularly limited. The blending can be carried out using a mixer such as a homomixer, a homogenizer, an ultrasonic disperser, or a wet ball mill, for example.

[0070] If a solution containing silica and an alkali is blended in the blending step in the etching liquid production method of Aspect 2, from the viewpoint of improving the SiN/SiO₂ selection rate ratio, the solution containing silica and an alkali is preferably obtained such that the content of silica dissolved in the etching liquid of Aspect 2 is in the above-described range.

[0071] From the viewpoint of improving the SiN/SiO₂ selection rate ratio, the pH of the etching liquid of Aspect 2 is preferably in the same range as the pH of the above-described etching liquid of Aspect 1.

[0072] From the viewpoint of inhibiting the clogging of a filter used in circulation, the flow rate of the etching liquid of Aspect 2 flowing through a 0.2 μm-filter is preferably in the same range as Aspect 1 above.

[0073] Similarly to the above-described etching liquid of Aspect 1, the etching liquid

of Aspect 2 may be stored and supplied in a concentrated state as long as the stability thereof is not impaired, and the dilution method and the dilution ratio can be the same as those of Aspect 1 above.

[0074] In another aspect, this disclosure relates to a kit for producing the etching liquid of Aspect 2 (also referred to as the “kit of Aspect 2” hereinafter).

As one embodiment of the kit of Aspect 2, the kit (two-component etching liquid) includes a solution containing a high-temperature stabilizing agent (liquid a) and a solution containing phosphoric acid (liquid b) in a state in which the liquid a and the liquid b are not mixed together, and the liquid a and the liquid b are mixed together when the kit is used, for example. This kit may further contain a solution containing a silicon compound (liquid c) (three-component type), or the liquid c may be blended into either the liquid a or the liquid b. After the liquid a and the liquid b are mixed together, the resulting mixture may be diluted using water or an aqueous solution of phosphoric acid as needed. The liquid a or the liquid b may include the total amount or a part of water used to prepare the etching liquid. The amount of phosphoric acid contained in the liquid b may be the total amount or a part of phosphoric acid used to prepare the etching liquid. The liquid a and the liquid b may each contain the above-described optional components as needed. According to the kit of Aspect 2, it is possible to obtain an etching liquid capable of inhibiting the clogging of a filter used in the circulation of the etching liquid. Also, according to the kit of Aspect 2, it is possible to obtain an etching liquid capable of maintaining the SiN/SiO₂ selection rate ratio.

[0075] A substrate that is to be processed and etched using the etching liquid of Aspect 2 is the above-described substrate to be processed in Aspect 1.

[0076] In another aspect, this disclosure relates to a method for producing a semiconductor substrate (also referred to as the “semiconductor substrate production method of Aspect 2” hereinafter) including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid of Aspect 2 (an etching step). According to the semiconductor substrate production method of Aspect 2, it is possible to inhibit the clogging of a filter used in the circulation of the etching liquid. Also, according to the semiconductor substrate production method of Aspect 2, it is possible to maintain the SiN/SiO₂ selection rate

ratio. Thus, according to the semiconductor substrate production method of Aspect 2, it is possible to achieve the effect that a semiconductor substrate with improved quality can be efficiently produced. Specific etching methods and conditions can be the same as the above-described semiconductor substrate production method of Aspect 1 and as those in the above-described semiconductor substrate production method of Aspect 1.

[0077] In another aspect, this disclosure relates to an etching method (also referred to as the “etching method” of Aspect 2 hereinafter) including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid of Aspect 2 (an etching step). It is possible to inhibit a filter used in the circulation of the etching liquid using the etching method of Aspect 2. Also, it is possible to maintain the SiN/SiO₂ selection rate ratio by using the etching method of Aspect 2. Thus, according to the etching method of Aspect 2, it is possible to achieve the effect that the productivity of semiconductor substrates with improved quality can be improved. Specific etching methods and conditions can be the same as the above-described semiconductor substrate production method of Aspect 1 and as those in the above-described semiconductor substrate production method of Aspect 1.

[0078] Furthermore, in another aspect, this disclosure provides an etching liquid capable of suppressing precipitation and adhesion of silica produced during the etching step to the silicon oxide film, and an etching method and a semiconductor substrate production method using the etching liquid.

[0079] That is to say, in another aspect, this disclosure relates to an etching liquid (also referred to as the “etching liquid of Aspect 3” hereinafter) for use in a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, in which the etching liquid is obtained by blending an organic phosphonic acid compound, phosphoric acid, and water together. In one or more embodiments, according to the etching liquid of Aspect 3, it is possible to suppress precipitation and adhesion of silica produced during the etching step to the SiO₂ film.

[0080] Although details of the mechanism of the expression of the effects of Aspect 3 are unclear, the following is inferred.

It is conceivable that, with Aspect 3, in one or more embodiments, as a result of using the etching liquid into which an organic phosphonic acid compound is blended, the organic phosphonic acid compound is adsorbed on silica produced during the

etching step and the surface of the SiO₂ film, and if the organic phosphonic acid compound has been adsorbed on the surface of the SiO₂ film, precipitation and adhesion of silica thereto can be suppressed due to the effect of a protective film, and if the organic phosphonic acid compound has adhered to silica, adhesion of silica thereto
5 is suppressed due to repulsion with the organic phosphonic acid compound adsorbed on the surface of the SiO₂ film.

However, this disclosure need not be interpreted as being limited to these mechanisms.

[0081] In this disclosure, “being obtained by blending an organic phosphonic acid
10 compound, phosphoric acid, and water together” means that not only an organic phosphonic acid compound, phosphoric acid, and water but optional components can also be blended together as needed.

[0082] In one or more embodiments, an organic phosphonic acid compound is blended into the etching liquid of Aspect 3 from the viewpoint of suppressing precipitation and
15 adhesion of silica to the SiO₂ film. Examples of the organic phosphonic acid compound in Aspect 3 include the above-described organic phosphonic acid compounds of Aspect 1. The organic phosphonic acid compounds may be used alone or in combination of two or more types thereof.

It is preferable that the amount of organic phosphonic acid compounds
20 blended into the etching liquid of Aspect 3 is in the same range as the amount of organic phosphonic acid blended into the above-described etching liquid of Aspect 1 from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to the SiO₂ film.

[0083] In one or more embodiments, phosphoric acid is blended into the etching liquid
25 of Aspect 3. It is preferable that the amount of phosphoric acid blended into the etching liquid of Aspect 3 is in the same range as the amount of phosphoric acid blended into the above-described etching liquid of Aspect 1 from the viewpoint of improving the SiN/SiO₂ selection rate ratio.

[0084] In one or more embodiments, water is blended into the etching liquid of Aspect
30 3. Examples of water in Aspect 3 include the same as those in Aspect 1 above.

[0085] In one or more embodiments, the etching liquid of Aspect 3 can further contain a solution containing silica and an alkali.

It is preferable that the solution that contains silica and an alkali and is used to prepare the etching liquid of Aspect 3 is a silica solution in which at least a part of silica is dissolved in the alkali, from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to the SiO₂ film. An
5 example of the silica solution in Aspect 3 is the above-described silica solution of Aspect 1.

It is preferable that the solution that contains silica and an alkali and is used to prepare the etching liquid of Aspect 3 is blended such that the content of silica dissolved in the etching liquid of Aspect 3 is in a range of 0.0005 mass% to 1 mass%
10 inclusive from the viewpoint of improving the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to the SiO₂ film. The content of silica dissolved in the etching liquid of Aspect 3 (the amount of dissolved silica) is preferably in the same range as the amount of silica dissolved in the above-described etching liquid of Aspect 1 from the viewpoint of improving the SiN/SiO₂ selection rate ratio,
15 and suppressing precipitation and adhesion of silica to the SiO₂ film.

If the solution containing silica and an alkali is blended into the etching liquid of Aspect 3, the content of silica in the etching liquid of Aspect 3 (the total content of dissolved silica and undissolved silica) is preferably in the same range as the content of silica in the above-described etching liquid of Aspect 1 from the viewpoint of improving
20 the SiN/SiO₂ selection rate ratio, and suppressing precipitation and adhesion of silica to the SiO₂ film.

[0086] In one or more embodiments, the etching liquid of Aspect 3 may be obtained by further adding or blending a sulfonic acid compound thereto from the viewpoint of inhibiting the clogging of a filter used in circulation while maintaining the SiN/SiO₂
25 selection rate ratio. Examples of the sulfonic acid compound in Aspect 3 include the above-described sulfonic acid compounds of Aspect 1. The sulfonic acid compounds may be used alone or in combination of two or more types thereof.

If a sulfonic acid compound is blended into the etching liquid of Aspect 3, from the viewpoint of inhibiting the clogging of a filter used in circulation while maintaining
30 the SiN/SiO₂ selection rate ratio, the amount of the sulfonic acid compound blended into the etching liquid of Aspect 3 is preferably 0.001 mass% or more, more preferably 0.003 mass% or more, and further preferably 0.005 mass% or more, and from the same

viewpoint, the amount of the sulfonic acid compound blended into the etching liquid of Aspect 3 is preferably 1.0 mass% or less, more preferably 0.5 mass% or less, and further preferably 0.1 mass% or less. More specifically, the amount of the sulfonic acid compound blended into the etching liquid of this disclosure is preferably 0.001

5 mass% to 1.0 mass% inclusive, more preferably 0.003 mass% to 0.5 mass% inclusive, and further preferably 0.005 mass% to 0.1 mass% inclusive. If two or more types of sulfonic acid compounds are used in combination, the amount of the blended sulfonic acid compounds is the total amount of the blended sulfonic acid compounds.

[0087] The etching liquid of Aspect 3 may further contain other components as long as the effects of this disclosure are not impaired. Examples of the other components include acids other than phosphoric acid, a chelating agent, a surfactant, a solubilizer, an antiseptic, a rust-preventive agent, a germicide, an antibacterial agent, and an antioxidant.

[0088] The etching liquid of Aspect 3 can be obtained by blending an organic phosphonic acid compound, phosphoric acid, and water together, for example. Therefore, in another aspect, this disclosure relates a method for producing an etching liquid (also referred to as the “etching liquid production method of Aspect 3” hereinafter) including a step of blending at least an organic phosphonic acid compound, phosphoric acid, and water together.

20 In one or more embodiments, “blending at least an organic phosphonic acid compound, phosphoric acid, and water together” in this disclosure includes mixing together an organic phosphonic acid compound, phosphoric acid, and water, and the above-described optional components as needed simultaneously or in order. The order of mixing need not be particularly limited. The blending can be carried out using a mixer such as a homomixer, a homogenizer, an ultrasonic disperser, or a wet ball mill, for example.

[0089] If a solution containing silica and an alkali is blended in the blending step in the etching liquid production method of Aspect 3, from the viewpoint of improving the SiN/SiO₂ selection rate ratio, the solution containing silica and an alkali is preferably obtained such that the content of silica dissolved in the etching liquid of Aspect 3 is in the above-described range.

[0090] From the viewpoint of improving the SiN/SiO₂ selection rate ratio, the pH of

the etching liquid of Aspect 3 is preferably in the same range as the pH of the above-described etching liquid of Aspect 1.

[0091] From the viewpoint of inhibiting the clogging of a filter used in circulation, the flow rate of the etching liquid of Aspect 3 flowing through a 0.2 μm -filter is preferably
5 in the same range as Aspect 1 above.

[0092] Similarly to the above-described etching liquid of Aspect 1, the etching liquid of Aspect 3 may be stored and supplied in a concentrated state as long as the stability thereof is not impaired, and the dilution method and the dilution ratio can be the same as those of Aspect 1 above.

10 [0093] In another aspect, this disclosure relates to a kit for producing the etching liquid of Aspect 3 (also referred to as the “kit of Aspect 3” hereinafter).

As one embodiment of the kit of Aspect 3, the kit includes a solution containing an organic phosphonic acid compound (liquid a') and a solution containing phosphoric acid (liquid b') in a state in which the liquid a' and the liquid b' are not mixed together,
15 and the liquid a' and the liquid b' are mixed together when the kit is used (two-component etching liquid), for example. The kit may further include a solution containing silica and an alkali (liquid c') (three-component type), or the liquid c' may be blended into either the liquid a' or the liquid b'. After the liquid a' and the liquid b' are mixed together, the resulting mixture may be diluted using water or an aqueous
20 solution of phosphoric acid as needed. The liquid a' or the liquid b' may include the total amount or a part of water used to prepare the etching liquid. The amount of phosphoric acid contained in the liquid b' may be the total amount or a part of phosphoric acid used to prepare the etching liquid. The liquid a' and the liquid b' may each contain the above-described optional components as needed. According to the kit
25 of Aspect 3, it is possible to obtain an etching liquid capable of suppressing precipitation and adhesion of silica produced during the etching step to the SiO_2 film.

[0094] A substrate that is to be processed and etched using the etching liquid of Aspect 3 is the above-described substrate to be processed in Aspect 1.

[0095] In another aspect, this disclosure relates to a method for producing a
30 semiconductor substrate (also referred to as the “semiconductor substrate production method of Aspect 3” hereinafter) including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching

liquid of Aspect 3 (an etching step). According to the semiconductor substrate production method of Aspect 3, it is possible to suppress precipitation and adhesion of silica produced during the etching step to the SiO₂ film. Thus, according to the semiconductor substrate production method of Aspect 3, it is possible to achieve the effect that a semiconductor substrate with improved quality can be efficiently produced. Specific etching methods and conditions can be the same as the above-described semiconductor substrate production method of Aspect 1 and as those in the above-described semiconductor substrate production method of Aspect 1.

[0096] In another aspect, this disclosure relates to an etching method (also referred to as the “etching method” of Aspect 3 hereinafter) including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid of Aspect 3 (an etching step). As a result of using the etching method of Aspect 3, it is possible to suppress precipitation and adhesion of silica produced during the etching step to the SiO₂ film. Thus, according to the etching method of Aspect 3, it is possible to achieve the effect that the productivity of semiconductor substrates with improved quality can be improved. Specific etching methods and conditions can be the same as the above-described semiconductor substrate production method of Aspect 1 and as those in the above-described semiconductor substrate production method of Aspect 1.

[0097] Furthermore, this disclosure relates to the following one or more embodiments.

(1) An etching liquid for use in a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, in which the etching liquid is obtained by blending a high-temperature stabilizing agent having a pK_a value of 2 or less, phosphoric acid, and water together.

(2) The etching liquid according to (1), in which a ratio of the mass of phosphoric acid (M2) to the mass of the high-temperature stabilizing agent (M1) (a mass ratio M2 / M1) is 800 or more.

(3) The etching liquid according to (1) or (2), in which the etching liquid further contains a solution containing a silicon compound.

(4) The etching liquid according to (3), in which the solution is a solution containing silica and an alkali.

- (5) The etching liquid according to (4), in which the solution is a silica solution in which at least a part of the silica is dissolved in the alkali.
- (6) The etching liquid according to any of (1) to (5), in which the high-temperature stabilizing agent having a pKa value of 2 or less is an organic acid having a pKa value
5 of 2 or less.
- (7) The etching liquid according to any of (1) to (6), in which the etching liquid has a pH of 2 or less at 25°C.
- (8) The etching liquid according to any of (1) to (7), in which the etching liquid has an etching temperature of 110°C to 180°C inclusive.
- 10 (9) The etching liquid according to any of (1) to (8), in which a flow rate of the etching liquid flowing through a filter is 10 g / 3 min or more.
- (10) An etching method including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid according to any of (1) to (9).
- 15 (11) A method for producing a semiconductor substrate, the method including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid according to any of (1) to (9).
- (12) An etching liquid for use in a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film,
20 in which the etching liquid is obtained by blending an organic phosphonic acid compound, phosphoric acid, and water together.
- (13) The etching liquid according to (12), in which the etching liquid further contains a solution containing silica and an alkali.
- (14) The etching liquid according to claim (13), in which the solution is a silica solution
25 in which at least a part of the silica is dissolved in the alkali.
- (15) The etching liquid according to (14), in which silica before being dissolved in the alkali is at least one selected from fumed silica and colloidal silica.
- (16) The etching liquid according to (14) or (15), in which the content of silica dissolved in the etching liquid is 0.0005 mass% to 1 mass% inclusive.
- 30 (17) The etching liquid according to any of (13) to (16), in which the alkali is an organic alkali or an inorganic alkali.
- (18) The etching liquid according to any of (12) to (17), in which the organic phosphonic

acid compound has a molecular weight of 150 or more.

(19) The etching liquid according to any of (12) to (18), in which the organic phosphonic acid compound is at least one selected from polyvinylphosphonic acids, alkylphosphonic acids, and alkyl ether phosphonic acids.

5 (20) The etching liquid according to any of (12) to (19), in which the etching liquid has a pH of 2 or less at 25°C.

(21) The etching liquid according to any of (12) to (20), in which the etching liquid has an etching temperature of 110°C to 180°C inclusive.

(22) An etching method including a step of removing a silicon nitride film from a
10 substrate having the silicon nitride film and a silicon oxide film, using the etching liquid according to any of (12) to (21).

(23) A method for producing a semiconductor substrate, the method including a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid according to any of (12) to (21).

15

Examples

[0098] Although this disclosure will be specifically described below using examples, this disclosure is not limited to these examples.

[0099] 1. Preparation of etching liquids of Examples 1 to 15 and Comparative
20 Examples 1 to 5

Examples 1 to 3

A silica solution was obtained by mixing an aqueous solution of silica (the silica: A1 to A3 shown in Table 1), an aqueous solution of an alkali (the alkali: TMAH),
25 and water together, and heating the resulting mixture at 60°C for 24 hours.

Then, the silica solution and an aqueous solution of phosphoric acid were blended together to obtain the etching liquids (having a pH of 0.45) of Examples 1 to 3. The amounts of blended phosphoric acid and alkali (mass%, active components), and the amounts of dissolved silica (mass%) in the etching liquids of Examples 1 to 3 are
30 shown in Table 1.

Example 4

The same silica solution as in Example 1 was used.

Then, the etching liquid (having a pH of 0.45) of Example 4 was obtained by blending together the silica solution, an aqueous solution of phosphoric acid, an aqueous solution of a phosphoric acid-based polymer (the phosphoric acid-based polymer: PVPA), which is an organic phosphonic acid compound, and an aqueous solution of a sulfonic acid compound (the sulfonic acid compound: PTS), which is a high-temperature stabilizing agent. The amounts of blended phosphoric acid, alkali, PVPA, and PTS (mass%, active components), and the amount of dissolved silica (mass%) in the etching liquid of Example 4 are shown in Table 1.

10

Example 5

The same silica solution as in Example 1 was used.

Then, the etching liquid (having a pH of 0.45) of Example 5 was obtained by blending together the silica solution, an aqueous solution of phosphoric acid, an aqueous solution of a phosphoric acid-based polymer (the phosphoric acid-based polymer: PVPA), which is an organic phosphonic acid compound, and an aqueous solution of a sulfonic acid compound (the sulfonic acid compound: PTS), which is a high-temperature stabilizing agent. The amounts of blended phosphoric acid, alkali, PVPA, and PTS (mass%, active components), and the amount of dissolved silica (mass%) in the etching liquid of Example 5 are shown in Table 1.

15

20

Example 6

The silica solution of Example 6 was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 1), an aqueous solution of an alkali (the alkali: ETMAH), and water together, and heating the resulting mixture at 60°C for 24 hours.

25

The etching liquid (having a pH of 0.45) of Example 6 was obtained in a manner similar to that of Example 1, except that the silica solution of Example 6 was used. The amounts of blended phosphoric acid and alkali (mass%, active components), and the amount of dissolved silica (mass%) in the etching liquid of Example 6 are shown in Table 1.

30

Example 7

The silica solution of Example 7 was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 1), an aqueous solution of an alkali (the alkali: NaOH), and water together, and heating the resulting mixture at 60°C for 24 hours.

5 The etching liquid (having a pH of 0.45) of Example 7 was obtained in a manner similar to that of Example 1, except that the silica solution of Example 7 was used. The amounts of blended phosphoric acid and alkali (mass%, active components), and the amount of dissolved silica (mass%) in the etching liquid of Example 7 are shown in Table 1.

10 Example 8

The silica solution of Example 8 was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 1), an aqueous solution of an alkali (the alkali: KOH), and water together, and heating the resulting mixture at 60°C for 24 hours.

15 The etching liquid (having a pH of 0.45) of Example 8 was obtained in a manner similar to that of Example 1, except that the silica solution of Example 8 was used. The amounts of blended phosphoric acid and alkali (mass%, active components), and the amount of dissolved silica (mass%) in the etching liquid of Example 8 are shown in Table 1.

20 Examples 9 and 10

A silica solution was obtained by mixing an aqueous solution of silica (the silica: A6 and A7 shown in Table 1), an aqueous solution of an alkali (the alkali: TMAH), and water together, and heating the resulting mixture at 60°C for 24 hours.

25 Then, the silica solution and an aqueous solution of phosphoric acid were blended together to obtain the etching liquids (having a pH of 0.45) of Examples 9 and 10. The amounts of blended phosphoric acid and alkali (mass%, active components), and the amounts of dissolved silica (mass%) in the etching liquids of Examples 9 and 10 are shown in Table 1.

30 Examples 11 to 15

The same silica solution as in Example 1 was used.

Then, the silica solution, an aqueous solution of phosphoric acid, and a

nonionic surfactant shown in Table 2 were blended together to obtain the etching liquids (having a pH of 0.45) of Examples 11 to 15. The amounts of blended components (mass%, active components), and the amounts of dissolved silica (mass%) in the etching liquids are shown in Table 2.

5

Comparative Example 1

The etching liquid (having a pH of 0.45) of Comparative Example 1 was obtained by mixing a silane compound (A4 shown in Table 1), an aqueous solution of an alkali (the alkali: TMAH), and an aqueous solution of phosphoric acid together, and heating the resulting mixture at 60°C for 24 hours. The amounts of components blended into the etching liquid of Comparative Example 1 (mass%, active components) were as follows: phosphoric acid was 83 mass%, the silane compound was 1.5 mass%, and TMAH was 0.13 mass%.

15 Comparative Example 2

An aqueous solution of phosphoric acid (manufactured by RIN KAGAKU KOGYO Co., Ltd.) (having a pH of 0.45) was used as the etching liquid of Comparative Example 2. The amount of phosphoric acid blended into the etching liquid of Comparative Example 2 (mass%, active component) was 83 mass%.

20

Comparative Example 3

A liquid mixture (having a pH of 0.45) of an aqueous solution of an alkali (the alkali: tetramethylammonium chloride manufactured by FUJIFILM Wako Pure Chemical Corporation) and an aqueous solution of phosphoric acid was used as the etching liquid of Comparative Example 3. The amounts of components blended into the etching liquid of Comparative Example 3 (mass%, active components) were as follows: phosphoric acid was 83 mass%, and the alkali was 0.13 mass%.

25

Comparative Example 4

A liquid mixture (having a pH of 0.45) of an aqueous solution containing a silane compound (A5 shown in Table 1) and an aqueous solution of phosphoric acid was used as the etching liquid of Comparative Example 4. The amounts of components

30

blended into the etching liquid of Comparative Example 4 (mass%, active components) were as follows: phosphoric acid was 83 mass%, and the silane compound was 0.02 mass%.

5 Comparative Example 5

A liquid mixture (having a pH of 0.45) of the silane compound A5 shown in Table 1, an aqueous solution containing the alkali (tetramethylammonium chloride manufactured by FUJIFILM Wako Pure Chemical Corporation) shown in Table 1, and an aqueous solution of phosphoric acid was used as the etching liquid of Comparative Example 5. The amounts of components blended into the etching liquid of Comparative Example 5 (mass%, active components) were as follows: phosphoric acid was 83 mass%, the silane compound was 0.02 mass%, and the alkali was 0.13 mass%.

[0100] 2. Preparation of etching liquids of Examples 16 to 31 and Comparative Examples 6 and 7

15

Example 16

A silica solution was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 3), an aqueous solution of an alkali (the alkali: TMAH), and water together, and heating the resulting mixture at 60°C for 24 hours.

20

Then, the etching liquid (having a pH of 0.45) of Example 16 was obtained by blending the obtained silica solution, an aqueous solution of phosphoric acid, and an aqueous solution of a sulfonic acid compound, which is a high-temperature stabilizing agent (the sulfonic acid compound: PTS) together. The amounts of blended components (mass%, active components), and the amount of dissolved silica (mass%) in the etching liquid of Example 16 are shown in Table 3.

25

Examples 17 to 19

The etching liquids (having a pH of 0.45) of Examples 17 to 19 were obtained in a manner similar to that of Example 16, except that the amount of the blended high-temperature stabilizing agent was changed such that the mass ratios M2/M1 were the mass ratios shown in Table 3.

30

Examples 20 to 22

The etching liquids (having a pH of 0.45) of Examples 20 to 22 were obtained in a manner similar to that of Example 16, except that the types of high-temperature stabilizing agent were changed to the high-temperature stabilizing agents shown in
5 Table 3.

Example 23

A silica solution was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 3), an aqueous solution of an alkali (the alkali: ETMAH), and
10 water together, and heating the resulting mixture at 60°C for 24 hours.

Then, the etching liquid (having a pH of 0.45) of Example 23 was obtained by blending the obtained silica solution, an aqueous solution of phosphoric acid, and an aqueous solution of a sulfonic acid compound, which is a high-temperature stabilizing agent (the sulfonic acid compound: PTS) together.

15

Example 24

The etching liquid (having a pH of 0.45) of Example 24 was obtained in a manner similar to that of Example 23, except that the amount of the blended high-temperature stabilizing agent was changed such that the mass ratio M2/M1 was
20 the mass ratio shown in Table 3.

Example 25

A silica solution was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 3), an aqueous solution of an alkali (the alkali: NaOH), and
25 water together, and heating the resulting mixture at 60°C for 24 hours.

Then, the etching liquid (having a pH of 0.45) of Example 25 was obtained by blending the obtained silica solution, an aqueous solution of phosphoric acid, and an aqueous solution of a sulfonic acid compound, which is a high-temperature stabilizing agent (the sulfonic acid compound: PTS) together.

30

Example 26

A silica solution was obtained by mixing an aqueous solution of silica (the

silica: A1 shown in Table 3), an aqueous solution of an alkali (the alkali: KOH), and water together, and heating the resulting mixture at 60°C for 24 hours.

Then, the etching liquid (having a pH of 0.45) of Example 26 was obtained by blending the obtained silica solution, an aqueous solution of phosphoric acid, and an aqueous solution of a sulfonic acid compound, which is a high-temperature stabilizing agent (the sulfonic acid compound: PTS) together.

Example 27

A silica solution was obtained by mixing an aqueous solution of silica (the silica: A2 shown in Table 3), an aqueous solution of an alkali (the alkali: TMAH), and water together, and heating the resulting mixture at 60°C for 24 hours.

The etching liquid (having a pH of 0.45) of Example 27 was obtained in a manner similar to that of Example 16, except that the above-described silica solution was used.

15

Examples 28 to 29

The etching liquids (having a pH of 0.45) of Examples 28 and 29 were obtained by blending a solution containing a silicic acid compound (the silicic acid compound: A8 and A9 shown in Table 3), an aqueous solution of phosphoric acid, and an aqueous solution of a sulfonic acid compound, which is a high-temperature stabilizing agent (the sulfonic acid compound: PTS) together.

20

Examples 30 and 31

The etching liquids (having a pH of 0.45) of Examples 30 and 31 were obtained in a manner similar to that of Example 16, except that the types of high-temperature stabilizing agent were changed to the high-temperature stabilizing agents shown in Table 3.

25

Comparative Examples 6 and 7

The etching liquids (having a pH of 0.45) of Comparative Examples 6 and 7 were obtained by blending a solution containing a silicic acid compound (the silicic acid compound: A8 and A9 shown in Table 3), and an aqueous solution of phosphoric acid

30

together.

Table 3 show the amounts of blended components (mass%, active components), the amounts of dissolved silica (mass%), or the content of the silicon compound (mass%), the mass ratios M2/M1, and the mole ratios m2/m1 in the prepared etching liquids of Examples 16 to 31, and Comparative Examples 6 and 7.

[0101] 3. Preparation of etching liquids of Examples 32 to 46

Examples 32 and 33

The etching liquids of Examples 32 and 33 into which phosphoric acid and PVPA were blended in the amounts (mass%, active components) shown in Table 4 were obtained.

Examples 34 to 38

A silica solution was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 5), an aqueous solution of an alkali (the alkali: TMAH), and water together, and heating the resulting mixture at 60°C for 24 hours.

Then, the etching liquids (having a pH of 0.45) of Examples 34 to 38 were obtained by blending together the silica solution, an aqueous solution of phosphoric acid, and an aqueous solution of a phosphoric acid-based polymer (the phosphoric acid-based polymer: PVPA), which is an organic phosphonic acid compound. The amounts of blended components (mass%, active components), and the amounts of dissolved silica in the etching liquids of Examples 34 to 38 are shown in Table 5.

Examples 39 and 40

A silica solution was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 5), an aqueous solution of an alkali (the alkali: ETMAH), and water together, and heating the resulting mixture at 60°C for 24 hours.

Then, the etching liquids (having a pH of 0.45) of Examples 39 and 40 were obtained by blending together the silica solution, an aqueous solution of phosphoric acid, and an aqueous solution of a phosphoric acid-based polymer (the phosphoric acid-based polymer: PVPA), which is an organic phosphonic acid compound. The amounts of blended components (mass%, active components), and the amounts of

dissolved silica in the etching liquids of Examples 39 to 40 are shown in Table 5.

Example 41

5 A silica solution was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 5), an aqueous solution of an alkali (the alkali: NaOH), and water together, and heating the resulting mixture at 60°C for 24 hours.

Then, the etching liquid (having a pH of 0.45) of Example 41 was obtained by blending together the silica solution, an aqueous solution of phosphoric acid, and an aqueous solution of a phosphoric acid-based polymer (the phosphoric acid-based
10 polymer: PVPA), which is an organic phosphonic acid compound. The amounts of blended components (mass%, active components), and the amount of dissolved silica in the etching liquid of Example 41 are shown in Table 5.

Example 42

15 A silica solution was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 5), an aqueous solution of an alkali (the alkali: KOH), and water together, and heating the resulting mixture at 60°C for 24 hours.

Then, the etching liquid (having a pH of 0.45) of Example 42 was obtained by blending together the silica solution, an aqueous solution of phosphoric acid, and an
20 aqueous solution of a phosphoric acid-based polymer (the phosphoric acid-based polymer: PVPA), which is an organic phosphonic acid compound. The amounts of blended components (mass%, active components), and the amount of dissolved silica in the etching liquid of Example 42 are shown in Table 5.

25 Example 43

A silica solution was obtained by mixing an aqueous solution of silica (the silica: A2 shown in Table 5), an aqueous solution of an alkali (the alkali: TMAH), and water together, and heating the resulting mixture at 60°C for 24 hours.

Then, the etching liquid (having a pH of 0.45) of Example 43 was obtained by
30 blending together the silica solution, an aqueous solution of phosphoric acid, and an aqueous solution of a phosphoric acid-based polymer (the phosphoric acid-based polymer: PVPA), which is an organic phosphonic acid compound. The amounts of

blended components (mass%, active components), and the amount of dissolved silica in the etching liquid of Example 43 are shown in Table 5.

Examples 44 and 46

5 A silica solution was obtained by mixing an aqueous solution of silica (the silica: A1 shown in Table 5), an aqueous solution of an alkali (the alkali: TMAH), and water together, and heating the resulting mixture at 60°C for 24 hours.

 Then, the silica solution, an aqueous solution of phosphoric acid, and the organic phosphonic acid compound shown in Table 5 were blended together to obtain
10 the etching liquids (having a pH of 0.45) of Examples 44 to 46. The amounts of blended components (mass%, active components), and the amounts of dissolved silica in the etching liquids of Examples 44 to 46 are shown in Table 5.

[0102] The following components were used to prepare etching liquids.

Silica sources

15 A1: Fumed silica ["QS30" having an average particle size of 5 nm and manufactured by Tokuyama Corporation]

A2: Colloidal silica produced using sol-gel method ["PL-06" having an average particle size of 6 nm and manufactured by FUSO CHEMICAL CO., LTD.]

A3: Colloidal silica produced using water glass method ["SI-550" having an average
20 particle size of 7 nm and manufactured by JGC Catalysts and Chemicals Ltd.]

A6: Silica obtained by drying the colloidal silica A3 and calcining the dried silica at 600°C for 2 hours.

A7: Silica obtained by drying the colloidal silica A3 and calcining the dried silica at 700°C for 2 hours.

25

Silane compound

A4: TEOS (tetraethoxysilane) [tetraethyl orthosilicate manufactured by FUJIFILM Wako Pure Chemical Corporation]

A5: Silane inorganic acid salt [which was synthesized by mixing TEOS to phosphoric
30 acid, and heating the resulting mixture at 90°C for 15 hours]

Silicon compound

A8: Methyl silicate oligomer [manufactured by Mitsubishi Chemical Corporation]

A9: 3-[[3-aminopropyl(dimethyl)silyl]oxy-dimethylsilyl]propane-1-amine
[manufactured by FUJIFILM Wako Pure Chemical Corporation]

5 Phosphoric acid

Aqueous solution of phosphoric acid [having a phosphoric acid concentration of 85%,
and manufactured by RIN KAGAKU KOGYO Co., Ltd.]

High-temperature stabilizing agent

10 Sulfonic acid compound [*p*-toluenesulfonic acid (PTS) manufactured by Meiyusangyo
Co., Ltd.]

Benzenesulfonic acid [manufactured by FUJIFILM Wako Pure Chemical Corporation]

Maleic acid [manufactured by FUJIFILM Wako Pure Chemical Corporation]

Oxalic acid [manufactured by FUJIFILM Wako Pure Chemical Corporation]

15 Toluic acid [manufactured by FUJIFILM Wako Pure Chemical Corporation]

Cresol [manufactured by FUJIFILM Wako Pure Chemical Corporation]

Organic phosphonic acid compound

20 Phosphoric acid-based polymer [polyvinylphosphonic acid (PVPA) having a weight
average molecular weight of 10,000 and manufactured by Maruzen Petrochemical Co.,
Ltd.]

Octylphosphonic acid [having a molecular weight of 190 and manufactured by
FUJIFILM Wako Pure Chemical Corporation]

25 Dodecylphosphonic acid [having a molecular weight of 250 and manufactured by
FUJIFILM Wako Pure Chemical Corporation]

Polyoxyethylene alkyl ether phosphonic acid [Phosphanol RS-610 having a molecular
weight of 372 and manufactured by TOHO Chemical Industry Co., Ltd.]

Nonionic surfactant

30 B1: Polyoxyethylene lauryl ether [EMULGEN 103 with HLB of 8.1 manufactured by
Kao Corporation]

B2: Polyoxyethylene lauryl ether [EMULGEN 108 with HLB of 12.1 manufactured by

Kao Corporation]

B3: Polyoxyethylene lauryl ether [EMULGEN 150 with HLB of 18.4 manufactured by Kao Corporation]

5 B4: Polyoxyethylene oleyl ether [EMULGEN 409PV with HLB of 12 manufactured by Kao Corporation]

B5: Polyoxyethylene polyoxypropylene lauryl myristyl ether [EMULGEN LS-106 with HLB of 12.5 manufactured by Kao Corporation]

[0103] 4. Method for measuring parameters

(1) pH of etching liquid

10 The pH value of an etching liquid at 25°C is a value obtained through measurement using a pH meter (manufactured by DKK-TOA CORPORATION), and is a numerical value obtained 1 minute after the electrode of the pH meter is immersed in the etching liquid.

[0104] (2) Average particle size of silica

15 Silica was diluted with ion-exchanged water to produce a dispersion liquid containing silica particles in an amount of 1 mass%. Then, the dispersion liquid was introduced into the following measuring device to obtain a volume particle size distribution of the silica particles. A particle diameter (Z-average value) at which the cumulative volume frequency of the obtained volume particle size distribution was
20 50% was used as a secondary particle diameter.

Measuring device: ZETASIZER NANO “Nano S” available from Malvern Panalytical Ltd.

Measurement conditions: Amount of sample 1.5 mL
25 : Laser He-Ne, 3.0 mW, and 633 nm
: Scattered light detection angle 173 degrees

[0105] (3) Crystallinity of silica

Measurement was made using a powder X-ray diffraction measuring device (Mini Flex600 manufactured by Rigaku Corporation), and the size of crystallites was
30 obtained using the following Scherrer equation, the full width at half maximum and a diffraction angle of the peak appearing near 20 to 23 degrees. The crystallinity was obtained from the following equation, using the size of crystallites obtained using the

Scherrer equation.

Scherrer equation: Size of crystallites ($\text{\AA}$) = $K \times \lambda / (\beta \times \cos\theta)$

Crystallinity = (size of crystallites of obtained powder) / (size of crystallites of

5 crystalline silica; 47.8 nm) $\times 100$

[0106] (4) pKa

The pKa values of maleic acid, oxalic acid, toluic acid, and cresol were obtained from the titration curves through full titration using "MCU-710" manufactured by KYOTO ELECTRONICS MANUFACTURING CO., LTD. Measurement was made
10 using hydrochloric acid as a titrant.

Known documents (Chemicalbook etc.) were referenced to for the pKa values of *p*-toluenesulfonic acid and benzenesulfonic acid.

[0107] 5. Evaluation of etching liquids

Etch rate and selection rate ratio

15 A 1 cm $\times$ 1 cm silicon nitride film wafer in which the thickness of the silicon nitride film (SiN film) was measured in advance was immersed in the etching liquids (Examples 1 to 46 and Comparative Examples 1 to 7) that were prepared to have the corresponding compositions so as to be etched at 160°C to 170°C for 90 minutes. Then, the wafer was cooled and washed with water, and the thickness of the silicon nitride
20 film was measured again, and the difference therebetween was regarded as the etch amount. An optical interference film thickness measuring device ("Random ACE VM-100" available from SCREEN Semiconductor Solutions Co., Ltd.) was used to measure the film thickness.

Also, 1.5 cm $\times$ 1 cm LP-TEOS was used as the silicon oxide film (SiO₂ film),
25 and the etch amount of the silicon oxide film was obtained by performing measurement under the same conditions as those for the silicon nitride film.

Then, the etch rate of the silicon nitride film, the etch rate of the silicon oxide film, and the selection rate ratio were calculated using the following equation. The results of calculation are shown in Tables 1 to 5.

30 Etch rate ($\text{\AA}/\text{min}$) of silicon nitride film (SiN film) = Etch amount ($\text{\AA}$) of silicon nitride film / 90 (min)

Etch rate ($\text{\AA}/\text{min}$) of silicon oxide film (SiO₂ film) = Etch amount ($\text{\AA}$) of silicon oxide film

/ 90 (min)

Selection rate ratio = etch rate of silicon nitride film / etch rate of silicon oxide film

[0108] Precipitation and adhesion of silica to SiO₂ film

600 ppm of silicon nitride powder (having an average particle size of 30 nm
 5 and manufactured by FUJIFILM Wako Pure Chemical Corporation) was added to the
 etching liquids (Examples 1, 11 to 15, and 32 to 46, and Comparative Example 2) that
 were prepared to have the corresponding compositions, and was dispersed through
 ultrasonic waves, and then a 2 cm × 1 cm thermal oxide film wafer in which the
 thickness of the SiO₂ oxide film was measured in advance was immersed therein.
 10 Then, a 1 cm × 1 cm silicon nitride film wafer was immersed in an aqueous solution of
 0.5% hydrofluoric acid for 30 seconds and was washed with water, and the resulting
 wafer was etched at 160°C to 170°C for 90 minutes. Then, the etched wafer was
 cooled and washed with water, and the thickness of the SiO₂ oxide film was measured
 again. An optical interference film thickness measuring device (“Random ACE
 15 VM-100” available from SCREEN Semiconductor Solutions Co., Ltd.) was used to
 measure the film thickness.

Then, the amounts of silica that precipitated and adhered to the SiO₂ film
 were calculated using the following equation. The results of calculation are shown in
 Tables 2, 4, and 5.

20

Amount of silica that precipitated and adhered to silicon oxide film (Å) = (thickness of
 silicon oxide film after immersion in etching liquid) – (thickness of silicon oxide film
 before immersion in etching liquid)

[0109] Evaluation of circulation stability

25 The circulation stability of the etching liquids of Examples 1, 16 to 31, and
 Comparative Examples 6 and 7 was evaluated.

First, the etching agents that were prepared to have the corresponding
 compositions were heated at 160°C to 170°C for 120 minutes, and were cooled to at
 room temperature. Then, a 0.2 μm-filter [“DISMIC” manufactured by ADVANTEC,
 30 syringe filter, material was hydrophilic polytetrafluoroethylene (PTFE)] was used to
 measure the flow rate for 3 minutes under a pressure of 0.25 MPa. The results of
 measurement are shown in Table 3.

[0110] [Table 1]

Table 1	Composition									Etch rate		Selection rate ratio (SiN/SiO ₂)
	phosphoric acid	silica solution						organic phosphonic acid compound	high-temperature stabilizing agent			
		silica source		crystallinity of silica	amount of silica dissolved in etching liquid	alkali	amount of alkali blended into etching liquid	PVPA	PTS	SiN film	SiO ₂ film	
		mass%	type	%	mass%	type	mass%	mass%	mass%	Å/min	Å/min	
Ex. 1	83	A1	fumed silica	0	0.02	TMAH	0.13	—	—	64	0.21	307
Ex. 2	83	A2	colloidal silica (sol-gel method)	0	0.02	TMAH	0.13	—	—	64	0.17	381
Ex. 3	83	A3	colloidal silica (water glass method)	0	0.02	TMAH	0.13	—	—	64	0.19	328
Ex. 4	83	A1	fumed silica	0	0.02	TMAH	0.13	0.05	0.01	65	0.19	336
Ex. 5	83	A1	fumed silica	0	0.02	TMAH	0.13	0.5	0.01	64	0.13	497
Ex. 6	83	A1	fumed silica	0	0.02	ETMAH	0.13	—	—	63	0.22	286
Ex. 7	83	A1	fumed silica	0	0.02	NaOH	0.13	—	—	64	0.21	305
Ex. 8	83	A1	fumed silica	0	0.02	KOH	0.13	—	—	63	0.21	300
Ex. 9	83	A6	silica obtained by drying and calcining colloidal silica A3 (600°C for 2h)	2.7	0.02	TMAH	0.13	—	—	64	0.20	320
Ex. 10	83	A7	silica obtained by drying and calcining colloidal silica A3 (700°C for 2 h)	3.8	0.02	TMAH	0.13	—	—	65	0.22	295
Comp. Ex. 1	83	A4	TEOS	—	—	TMAH	0.13	—	—	64	4.65	14
Comp. Ex. 2	83	—	—	—	—	—	—	—	—	70	16.00	4
Comp. Ex. 3	83	—	—	—	—	tetramethylammonium chloride	0.13	—	—	70	13.99	5
Comp. Ex. 4	83	A5	silane inorganic acid salt	—	—	—	—	—	—	61	0.51	121
Comp. Ex. 5	83	A5	silane inorganic acid salt	—	—	tetramethylammonium chloride	0.13	—	—	63	0.55	115

[0111] [Table 2]

Table 2	Composition										Etch rate		Selection rate ratio(SiN/SiO ₂)	Precipitation and adhesion of silica to SiO ₂ film (Å)
	phosphoric acid	silica solution					nonionic surfactant							
		silica source	amount of silica dissolved in etching liquid	alkali	amount of alkali blended into etching liquid	type	HLB	blending amount	SiN film	SiO ₂ film				
								mass%	type	mass%	type	mass%		
Ex. 1	83	A1	fumed silica	0.02	TMAH	0.13	—	—	—	—	64	0.21	307	35
Ex. 11	83	A1	fumed silica	0.02	TMAH	0.13	B1	polyoxyethylene lauryl ether	8.1	0.05	65	0.27	237	17
Ex. 12	83	A1	fumed silica	0.02	TMAH	0.13	B2	polyoxyethylene lauryl ether	12.1	0.05	65	0.26	253	20
Ex. 13	83	A1	fumed silica	0.02	TMAH	0.13	B3	polyoxyethylene lauryl ether	18.4	0.05	65	0.25	260	22
Ex. 14	83	A1	fumed silica	0.02	TMAH	0.13	B4	polyoxyethylene oleyl ether	12	0.05	64	0.29	223	19
Ex. 15	83	A1	fumed silica	0.02	TMAH	0.13	B5	polyoxyethylene polyoxypropylene lauryl myristyl ether	12.5	0.05	65	0.24	272	24

[0112] As shown in Table 1, the etching liquids of Examples 1 to 10 into which the silica solution was blended had improved SiN/SiO₂ selection rate ratios, compared to Comparative Examples 1 to 5 into which no silica solution was blended.

Also, as shown in Table 2, the amounts of silica that precipitated and adhered
5 to the SiO₂ film in the etching liquids of Examples 11 to 15 into which the silica solution, phosphoric acid, and a nonionic surfactant were blended were reduced, compared to that of Example 1 into which no nonionic surfactant was blended.

[0113] [Table 3]

Table 3	Composition									Phosphoric acid /high-temperature stabilizing agent		Etch rate		Selection rate ratio (SiN/SiO ₂)	Circulatio n stability		
	phosphori c acid	solution containing silicon compound / silica solution					high-temperature stabilizing agent										
		silica source			amount of silica dissolved in etching liquid	alkali	amoun t of alkali blende d into etching liquid	type	concentratio n	pK a	mass ratio M2/M1	mole ratio m2/m1	SiN film			SiO ₂ film	
																	mass%
Ex. 16	83	A1	fumed silica			0.02	TMAH	0.13	<i>p</i> toluenesulfonic acid	0.01	-2. 8	8300	14392	64	0.21	305	27
Ex. 17	83	A1	fumed silica			0.02	TMAH	0.13	<i>p</i> toluenesulfonic acid	0.03	-2. 8	2767	4797	65	0.20	325	25
Ex. 18	83	A1	fumed silica			0.02	TMAH	0.13	<i>p</i> toluenesulfonic acid	0.05	-2. 8	1660	2878	64	0.21	305	23
Ex. 19	83	A1	fumed silica			0.02	TMAH	0.13	<i>p</i> toluenesulfonic acid	0.1	-2. 8	830	1439	65	0.21	310	14
Ex. 20	83	A1	fumed silica			0.02	TMAH	0.13	benzenesulfonic acid	0.01	0.7	8300	13220	66	0.22	300	26
Ex. 21	83	A1	fumed silica			0.02	TMAH	0.13	maleic acid	0.01	1.8 7	8300	9706	65	0.21	310	12
Ex. 22	83	A1	fumed silica			0.02	TMAH	0.13	oxalic acid	0.01	1.2 7	8300	7531	66	0.21	314	18
Ex. 23	83	A1	fumed silica			0.02	ETMA H	0.13	<i>p</i> toluenesulfonic acid	0.01	-2. 8	8300	14392	64	0.22	291	25
Ex. 24	83	A1	fumed silica			0.02	ETMA H	0.13	<i>p</i> toluenesulfonic acid	0.05	-2. 8	1660	2878	64	0.21	305	24
Ex. 25	83	A1	fumed silica			0.02	NaOH	0.13	<i>p</i> toluenesulfonic acid	0.01	-2. 8	8300	14392	66	0.22	300	25
Ex. 26	83	A1	fumed silica			0.02	KOH	0.13	<i>p</i> toluenesulfonic acid	0.01	-2. 8	8300	14392	65	0.19	342	25
Ex. 27	83	A2	colloidal silica (sol-gel method)			0.02	TMAH	0.13	<i>p</i> toluenesulfonic acid	0.01	-2. 8	8300	14392	65	0.18	361	26
Ex. 28	83	A8	methyl silicate oligomer			silicon compoun d 0.02	—	—	<i>p</i> toluenesulfonic acid	0.01	-2. 8	8300	14392	64	0.35	183	14

Table 3	Composition									Phosphoric acid /high-temperature stabilizing agent		Etch rate		Selection rate ratio (SiN/SiO ₂)	Circulation stability
	phosphoric acid	solution containing silicon compound / silica solution					high-temperature stabilizing agent								
		silica source		amount of silica dissolved in etching liquid	alkali	amount of alkali blended into etching liquid	type	concentration	pK _a	mass ratio M2/M1	mole ratio m2/m1	SiN film	SiO ₂ film		
															mass%
Ex. 29	83	A9	3-[[3-aminopropyl(dimethyl)silyl]oxy-dimethylsilyl]propane-1-amine	silicon compound 0.02	—	—	<i>p</i> -toluenesulfonic acid	0.01	−2.8	8300	14392	64	8.50	8	11
Ex. 1	83	A1	fumed silica	0.02	TMAH	0.13	—	—	—	—		64	0.21	307	2
Ex. 30	83	A1	fumed silica	0.02	TMAH	0.13	toluic acid	0.01	4.4	8300	8534.69	64	0.2	320	6
Ex. 31	83	A1	fumed silica	0.02	TMAH	0.13	cresol	0.01	10.6	8300	9036.73	64	0.21	305	4
Comp. Ex. 6	83	A8	methyl silicate oligomer	silicon compound 0.02	—	—	—	—	—	—	—	64	0.35	183	1
Comp. Ex. 7	83	A9	3-[[3-aminopropyl(dimethyl)silyl]oxy-dimethylsilyl]propane-1-amine	silicon compound 0.02	—	—	—	—	—	—	—	64	8.50	8	1

[0114] As shown in Table 3, Examples 16 to 27 into which specific high-temperature stabilizing agents and phosphoric acid were blended had good SiN/SiO₂ selection rate ratios. Also, it is conceivable that it is possible to inhibit the clogging of a filter used in circulation because the 0.2 μm-filter flow rates of Examples 16 to 27 were higher, compared to Example 1 and Examples 30 and 31 into which no specific high-temperature stabilizing agent was blended. It is conceivable that it is possible to inhibit the clogging of a filter used in circulation because the 0.2 μm-filter flow rates of Examples 28 and 29 into which specific high-temperature stabilizing agents and phosphoric acid were blended were higher, compared to Comparative Examples 6 and 7 into which no specific high-temperature stabilizing agent was blended.

[0115] [Table 4]

Table 4	Composition		Etch rate		Selection rate ratio (SiN/SiO ₂)	Precipitation and adhesion of silica to SiO ₂ film (Å)
	phosphoric acid	organic phosphonic acid compound				
		PVPA	SiN film	SiO ₂ film		
	mass%	mass%	Å/min	Å/min		
Ex. 32	83	0.05	65	14.2	5	71
Ex. 33	83	0.5	65	13.5	5	52
Comp. Ex. 2	83	—	70	16.00	4	80

[0116] As shown in Table 4, with Examples 32 and 33 into which organic phosphonic acid compounds and phosphoric acid were blended, precipitation and adhesion of silica to the SiO₂ film were suppressed, compared to Comparative Example 2 into which no organic phosphonic acid was blended.

[0117] [Table 5]

Table 5	Composition									Etch rate		Selection rate ratio (SiN/SiO ₂)	Precipitation and adhesion of silica to SiO ₂ film (Å)
	phosphoric acid	silica solution					organic phosphonic acid compound						
		silica source	amount of silica dissolved in etching liquid	alkali	amount of alkali blended into etching liquid	type	weight average molecular weight	blending amount	SiN film	SiO ₂ film			
											mass%		
Ex. 1	83	A1	fumed silica	0.02	TMAH	0.13	—	—	—	64	0.21	307	35
Ex. 34	83	A1	fumed silica	0.02	TMAH	0.13	PVPA	10000	0.05	65	0.19	333	20
Ex. 35	83	A1	fumed silica	0.02	TMAH	0.13	PVPA	10000	0.10	62	0.16	395	11
Ex. 36	83	A1	fumed silica	0.02	TMAH	0.13	PVPA	10000	0.50	59	0.13	452	9
Ex. 37	83	A1	fumed silica	0.02	TMAH	0.13	PVPA	10000	1.00	56	0.12	475	3
Ex. 38	83	A1	fumed silica	0.02	TMAH	0.13	PVPA	10000	5.00	52	0.10	498	2
Ex. 39	83	A1	fumed silica	0.02	ETMAH	0.13	PVPA	10000	0.05	64	0.18	356	19
Ex. 40	83	A1	fumed silica	0.02	ETMAH	0.13	PVPA	10000	0.50	59	0.14	420	8
Ex. 41	83	A1	fumed silica	0.02	NaOH	0.13	PVPA	10000	0.05	66	0.18	360	20
Ex. 42	83	A1	fumed silica	0.02	KOH	0.13	PVPA	10000	0.05	64	0.19	347	21
Ex. 43	83	A2	colloidal silica (sol-gel method)	0.02	TMAH	0.13	PVPA	10000	0.05	66	0.19	346	19
Ex. 44	83	A1	fumed silica	0.02	TMAH	0.13	octylphosphonic acid CH ₃ -(CH ₂) ₇ -PO ₃ H ₂	molecular weight: 190	0.05	65	0.19	341	24
Ex. 45	83	A1	fumed silica	0.02	TMAH	0.13	dodecylphosphonic acid CH ₃ -(CH ₂) ₁₁ -PO ₃ H ₂	molecular weight: 250	0.05	65	0.19	342	21
Ex. 46	83	A1	fumed silica	0.02	TMAH	0.13	polyoxyethylene alkyl(12-15) ether phosphonic acid	molecular weight: 372	0.05	64	0.21	305	20
Comp. Ex. 2	83	—	—	—	—	—	—	—	—	70	16.00	4	80

[0118] As shown in Table 5, with Examples 34 to 46 into which organic phosphonic acid compounds, phosphoric acid, and silica solutions were blended, precipitation and adhesion of silica to the SiO₂ film were further suppressed and the SiN/SiO₂ selection rate ratios were further improved, compared to Comparative Example 2 into which no
5 organic phosphonic acid compound or silica solution were blended, and Example 1 into which no organic phosphonic acid compound was blended.

Industrial Applicability

[0119] The etching liquid of this disclosure is useful in a method for producing a
10 semiconductor substrate for high density or high integration.

CLAIMS

- [1] An etching liquid for use in a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film,
wherein the etching liquid is obtained by blending a solution containing silica and an alkali, phosphoric acid, and water together,
the solution is a silica solution in which at least a part of the silica is dissolved in the alkali,
the amount of phosphoric acid blended into the etching liquid is 70 mass% or more, and
the alkali is at least one selected from tetramethylammonium hydroxide, tetraethylammonium hydroxide, trimethylethylammonium hydroxide, benzyltrimethylammonium hydroxide, ethyltrimethylammonium hydroxide, methylbenzyltrimethylammonium hydroxide, tetraethylammonium hydroxide, sodium hydroxide, and potassium hydroxide.
- [2] The etching liquid according to claim 1,
wherein silica before being dissolved in the alkali is at least one selected from fumed silica and colloidal silica.
- [3] The etching liquid according to claim 1 or 2,
wherein the content of silica dissolved in the etching liquid is 0.0005 mass% to 1 mass% inclusive.
- [4] The etching liquid according to any of claims 1 to 3,
wherein the etching liquid has a pH of 2 or less at 25°C.
- [5] The etching liquid according to any of claims 1 to 4,
wherein the etching liquid has an etching temperature of 110°C to 180°C inclusive.
- [6] An etching method comprising:

a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid according to any of claims 1 to 5.

[7] A method for producing a semiconductor substrate, comprising:

a step of removing a silicon nitride film from a substrate having the silicon nitride film and a silicon oxide film, using the etching liquid according to any of claims 1 to 5.