

[Title of the Invention]

Silicon nitride etching liquid composition

[Technical Field]

[0001]

The present invention relates to a silicon nitride etching liquid composition for producing a 3D non-volatile memory cell, and a method for producing a 3D non-volatile memory cell using said etching liquid composition.

[Background Art]

[0002]

In recent years, technological innovation of NAND flash memories has been progressing in the area of non-volatile memory, which is a memory that retains memory without supplying power. NAND flash memories are used as a storage device for SmartMedia and SSD, and the like.

[0003]

Conventionally, the structure of NAND flash memory is a planar type (Fig. 1), and the line width becomes narrower as the miniaturization progresses, which adversely affects the life and performance. Recently, development of 3D type (Fig. 2) is progressing, and by stacking vertically, NAND flash memories can be manufactured with a sufficient line width, realizing longer life, higher speed, and larger capacity compared to the conventional type.

[0004]

As an example of a method for producing 3D NAND flash memories, the following steps are performed: (1) on a substrate on which silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) are alternately laminated, (2) holes are formed by dry etching, (3) a gate electrode (p-Si electrode) covered with an insulating film (SiO_2) is embedded in said holes, (4) grooves (intervals) are formed on the laminated film by

dry etching, (5) ions are injected to the substrate surface to form an impurity region, (6) Si_3N_4 is etched by wet etching, (7) on the exposed substrate and SiO_2 surface, a TiN film is formed as a barrier metal and a W film is formed as an electrode, and (8) TiN and W are collectively etched with mixed acid.

[0005]

As an etching liquid composition for etching Si_3N_4 in the above step (6) (Fig. 3), an etching liquid composition comprising phosphoric acid, ammonium ions and a silicon compound is disclosed (Patent Documents 1 to 3).

When phosphoric acid and silicon compounds are contained in the etching liquid composition, they react to generate $\text{Si}(\text{OH})_x$. In the presence of $\text{Si}(\text{OH})_x$, the etching rates of SiO_2 and Si_3N_4 decrease, respectively; however, since the rate of decrease in the etching rate of SiO_2 is larger, as a result the etch selectivity of Si_3N_4 relative to SiO_2 is improved. On the other hand, when $\text{Si}(\text{OH})_x$ is excessively present, $\text{Si}(\text{OH})_x$ adheres to the surface of SiO_2 with a solubility exceeding the saturation solubility, causing regrowth of SiO_2 (hereinafter referred to as "regrowth of SiO_2 ") (Fig. 4). Patent Documents 1 to 3 describe that ammonium ions in the etching liquid composition bind to $\text{Si}(\text{OH})_x$ to form a water-soluble compound, thereby suppressing the regrowth of SiO_2 .

[0006]

In addition, as the etching liquid composition of silicon nitride, the followings are also disclosed: an etching liquid composition comprising an inorganic acid, a siloxane compound, an ammonium compound, and a solvent (Patent Document 4); an etching liquid composition comprising a composite silane consisting of phosphoric acid and two or more kinds of silane compounds, and water (Patent

Document 5); as well as an etching liquid composition comprising phosphoric acid and an organic compound comprising silicon, and an organic solvent (Patent Document 6).

[Citation List]

[Patent Documents]

[0007]

[Patent Document 1] U.S. Patent No. 8940182

[Patent Document 2] U.S. Patent No. 9136120

[Patent Document 3] U.S. Patent No. 9368647

[Patent Document 4] JP A No. 2018-085513

[Patent Document 5] JP A No. 2018-182312

[Patent Document 6] JP A No. 2000-058500

[Summary of the Invention]

[Problems to Be Solved by the Invention]

[0008]

Under the circumstance in which the number of laminated 3D NAND memory cells increases, the present inventors have attempted to improve the etch selectivity of Si_3N_4 relative to SiO_2 , and have investigated to separately dissolve Si_3N_4 as a silicon compound in an etching liquid composition comprising phosphoric acid. However, said dissolution required high-temperature and long-term treatment, and the inventors have also faced the problem of high cost of silicon compound. Furthermore, in cases that as the number of laminated memory cells increases, the SiO_2 film becomes thinner than the conventional SiO_2 film, i.e., the aspect ratio in the unit cell of the laminated structure increases, there has been a concern that the pattern of the SiO_2 film would collapse due to the surface tension of the liquid during drying of the substrate, after completion of etching Si_3N_4 (Fig. 5).

Therefore, in the production of 3D non-volatile memory cells, the present inventors have proceeded with a study having a task of providing a silicon nitride etching liquid composition that can selectively etch Si_3N_4 with a practical etch selectivity for SiO_2 , suppress the regrowth of SiO_2 , and also suppress the pattern collapse of the SiO_2 film.

[Means of Solving the Problems]

[0009]

In earnest research to solve the above problems, the present inventors have found that a silicon nitride etching liquid composition comprising phosphoric acid, one or more kinds of silane coupling agents and water, and not comprising ammonium ions, is capable of, in the production of 3D non-volatile memory cells, selectively etching Si_3N_4 with a practical etch selectivity for SiO_2 while suppressing the regrowth of SiO_2 and suppressing the pattern collapse of the SiO_2 film; and moreover, the present inventors have found that when said etching liquid composition further comprises an inorganic silicate, the etch selectivity of Si_3N_4 relative to SiO_2 can be further improved; as a result of further research, the present inventors have completed the present invention.

[0010]

The present inventors presume that the reason why the etching liquid composition comprising phosphoric acid, one or more kinds of silane coupling agents and water, and not comprising ammonium ions, is capable of, in the production of 3D non-volatile memory cells, selectively etching Si_3N_4 with a practical etch selectivity for SiO_2 while suppressing the regrowth of SiO_2 and suppressing the pattern collapse of the SiO_2 film, is as follows.

That is, when the etching liquid composition comprises phosphoric acid and a silane coupling agent, these react and

are adsorbed on the surface of SiO₂, and as a result, the etch selectivity of Si₃N₄ relative to SiO₂ is improved. In addition, since the etching liquid composition comprises a silane coupling agent, adhesion of Si(OH)_x to the surface of SiO₂ can be prevented, and regrowth of SiO₂ can be suppressed (Fig. 6). Furthermore, it is presumed that the inclusion of a hydrophobic group in the silane coupling agent can make the surface of the SiO₂ film hydrophobic, increase the contact angle, and prevent the pattern collapse of the SiO₂ film (Fig. 7).

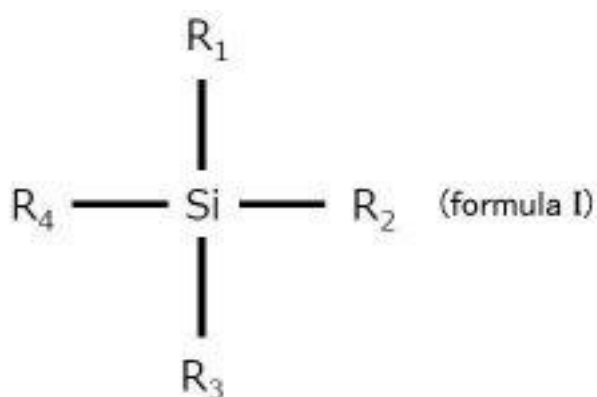
[0011]

Namely, the present invention relates to the following:

[1] A silicon nitride etching liquid composition for producing a 3D non-volatile memory cell, comprising phosphoric acid, one or more kinds of silane coupling agents and water, and not comprising ammonium ions.

[2] The etching liquid composition according to [1], wherein the silane coupling agent is a compound represented by the formula 1:

[Chemical formula 1]



wherein

R₁ is an alkyl group or an alkoxy group,

R₂ is an alkyl group or an alkoxy group,

R₃ is an alkyl group or an alkoxy group,

R₄ is a group comprising one or more selected from the group consisting of N atoms, O atoms, S atoms, P atoms, Cl atoms and F atoms.

[0012]

[3] The etching liquid composition according to [2], wherein the silane coupling agent is the one in which at least two of R₁, R₂, and R₃ in the formula 1 are alkoxy groups.

[4] The etching liquid composition according to [2] or [3], wherein the silane coupling agent comprises an amino group or a mercapto group in R₄ of the formula 1.

[5] The etching liquid composition according to any one of [2] to [4], wherein the silane coupling agent further comprises a phenyl group or an octyl group in R₄ of the formula 1.

[0013]

[6] The etching liquid composition according to any one of [2] to [5], wherein the silane coupling agent is selected from the group consisting of 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-(2-aminoethylamino)propyltrimethoxysilane, 3-(2-aminoethylamino)propyltriethoxysilane, trimethoxy[3-(methylamino)propyl]silane, [3-(N,N-dimethylamino)propyl]trimethoxysilane, trimethoxy[3-(phenylamino)propyl]silane, N-[2-(N-vinylbenzylamino)ethyl]-3-aminopropyltrimethoxysilane, N-[8-(trimethoxysilyl)octyl]ethane-1,2-diamine, N-[3-(trimethoxysilyl)propyl]-1-butaneamine, [3-(diethylamino)propyl]trimethoxysilane, 3-[(1,3-dimethylbutylidene)amino]propyltriethoxysilane, (3-mercaptopropyl)trimethoxysilane, (3-mercaptopropyl)triethoxysilane and N,N-bis[(diphenylphosphino)methyl]-3-

(triethoxysilyl)propylamine.

[0014]

[7] The etching liquid composition according to any one of [1] to [6], comprising 60 to 95 wt% of phosphoric acid and 0.01 to 10 wt% of a silane coupling agent.

[8] The etching liquid composition according to any one of [1] to [7], further comprising one or more kinds of water-soluble polar organic solvents.

[9] The etching liquid composition according to [8], wherein the water-soluble polar organic solvent is selected from the group consisting of methanol, ethanol and acetone.

[10] The etching liquid composition according to any one of [1] to [9], further comprising an inorganic silicate.

[11] The etching liquid composition according to [10], wherein the inorganic silicate is sodium silicate or potassium silicate.

[0015]

[12] A method of producing a 3D non-volatile memory cell, which comprises etching silicon nitride using the etching liquid composition according to any one of [1] to [11].

[13] A 3D non-volatile memory cell obtained by etching silicon nitride using the etching liquid composition according to any one of [1] to [11].

[Advantageous Effects of the Invention]

[0016]

The etching liquid composition of the present invention can selectively etch Si_3N_4 with a practical etch selectivity for SiO_2 in the production of 3D non-volatile memory cells, and can suppress regrowth of SiO_2 and also suppress pattern collapse of a SiO_2 film. In other words, Si_3N_4 can be selectively etched safely in a short time and economically, without a need to separately dissolve Si_3N_4 in the etching liquid composition. Furthermore, since the

regrowth of SiO_2 can be suppressed even when the etching liquid composition does not comprise ammonium ions, production cost of the etching liquid composition can be suppressed. In addition, even in the production of a highly laminated 3D non-volatile memory cell, the memory cell having a stable pattern can be produced without collapsing the pattern of a SiO_2 film.

Moreover, when the etching liquid composition of the present invention further comprises an inorganic silicate, the etch selectivity of Si_3N_4 relative to SiO_2 can be further improved.

[Brief Description of Drawings]

[0017]

[Fig. 1] Figure 1 is a diagram showing a structure of planar NAND flash memory.

[Fig. 2] Figure 2 is a diagram showing a structure of 3D NAND flash memory.

[Fig. 3] Figure 3 is a diagram showing before and after etching Si_3N_4 .

[Fig. 4] Figure 4 is a diagram showing principle of regrowth of SiO_2 .

[Fig. 5] Figure 5 is a diagram showing principle of pattern collapse of SiO_2 film.

[Fig. 6] Figure 6 is a diagram showing principle of suppressing regrowth of SiO_2 .

[Fig. 7] Figure 7 is a diagram showing suppression of pattern collapse of SiO_2 film.

[Embodiments for Carrying out the Invention]

[0018]

Hereinafter, the present invention will be described in detail based on preferred embodiments of the present invention.

The present invention relates to a silicon nitride

etching liquid composition for producing a 3D non-volatile memory cell, comprising phosphoric acid, one or more kinds of silane coupling agents and water and not comprising ammonium ions.

[0019]

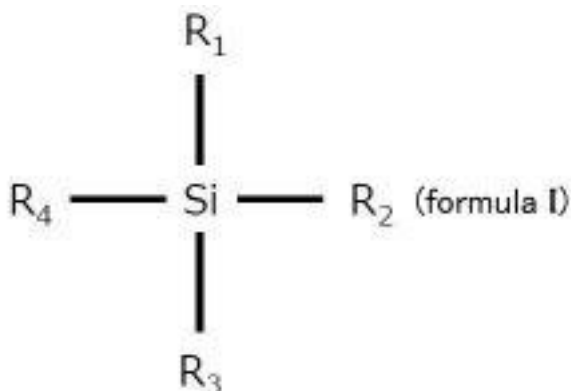
The etching liquid composition of the present invention is a silicon nitride etching liquid composition for producing a 3D non-volatile memory cell.

As long as the 3D non-volatile memory is a non-volatile memory of 3D type, the type and operation format of the memory are not particularly limited, and examples thereof include 3D NAND flash memories, etc. The etching liquid composition of the present invention is particularly suitable for producing a 3D non-volatile memory having a high lamination or a high aspect ratio of a unit cell, and examples of such memory include those with a SiO₂ film having a film thickness of 10 nm to 50 nm.

[0020]

The silane coupling agent used in the present invention is not particularly limited, and it is preferably a compound represented by the formula 1:

[Chemical formula 2]



wherein

R₁ is an alkyl group or an alkoxy group,

R₂ is an alkyl group or an alkoxy group,
R₃ is an alkyl group or an alkoxy group,
R₄ is a group comprising one or more selected from the
group consisting of N atoms, O atoms, F atoms, P atoms, S
atoms and Cl atoms.

[0021]

The alkyl groups of R₁ to R₃ in the formula 1 are linear, branched and cyclic alkyl groups which may have a substituent.

The linear alkyl group is not particularly limited, and examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, and a decyl group, etc.

The branched alkyl group is not particularly limited, and examples thereof include an isopropyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, and an isopentyl group, etc.

The cyclic alkyl group is not particularly limited, and examples thereof include cyclobutyl, cyclopentyl, a cyclohexyl group, and a cyclooctyl group, etc.

[0022]

The alkoxy groups of R₁ to R₃ in the formula 1 are linear, branched and cyclic alkoxy groups which may have a substituent.

Examples of the linear, branched, and cyclic alkoxy groups include alkoxy groups in which an oxygen atom is located at the 1-position of the above linear, branched, and cyclic alkyl groups.

[0023]

R₄ which is a group comprising one or more selected from the group consisting of N atoms, O atoms, F atoms, P atoms, S atoms and Cl atoms is not particularly limited, and examples thereof include an amino group, an alkoxy group, a

fluoro group, a phosphine group, a mercapto group, and a chloro group, etc. R₄ may further comprise an alkyl group, a phenyl group, and an ether, etc.

[0024]

As the silane coupling agent, more preferably, at least two of R₁ to R₃ of the formula 1 are alkoxy groups, or R₄ of the formula 1 comprises an amino group or a mercapto group, or R₄ of the formula 1 further comprises a phenyl group or an octyl group that is a bulky alkyl group. Furthermore preferably, R₁ to R₃ of the formula 1 are methoxy groups or ethoxy groups, respectively, and also R₄ of the formula 1 comprises an amino group or a mercapto group; and such examples include 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-(2-aminoethylamino)propyltrimethoxysilane, 3-(2-aminoethylamino)propyltriethoxysilane, trimethoxy[3-(methylamino)propyl]silane, [3-(N,N-dimethylamino)propyl]trimethoxysilane, N-[3-(trimethoxysilyl)propyl]-1-butaneamine, [3-(diethylamino)propyl]trimethoxysilane, 3-[(1,3-dimethylbutylidene)amino]propyltriethoxysilane, (3-mercaptopropyl)trimethoxysilane, and (3-mercaptopropyl)triethoxysilane, etc.

[0025]

Similarly, more preferable examples are those wherein R₁ to R₃ of the formula 1 are methoxy groups or ethoxy groups, respectively, and R₄ of the formula 1 further comprises a phenyl group or an octyl group, and those wherein R₁ to R₃ of the formula 1 are methoxy groups or ethoxy groups, respectively, and R₄ of the formula 1 comprises an amino group or a mercapto group, and R₄ further comprises a phenyl group or an octyl group; and such examples include trimethoxy[3-(phenylamino)propyl]silane, N-[2-(N-

vinylbenzylamino)ethyl]-3-aminopropyltrimethoxysilane, and
 N,N-bis[(diphenylphosphino)methyl]-3-
 (triethoxysilyl)propylamine, N-[8-
 (trimethoxysilyl)octyl]ethane-1,2-diamine, etc.
 [0026]

As the silane coupling agent, in terms of easily
 available raw materials, most preferable examples are 3-
 aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane,
 3-(2-aminoethylamino)propyltrimethoxysilane, and 3-(2-
 aminoethylamino)propyltriethoxysilane. On the other hand,
 from the viewpoint of etch selectivity of Si_3N_4 relative to
 SiO_2 , most preferable examples are 3-
 aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane,
 [3-(N,N-dimethylamino)propyl]trimethoxysilane, N-[2-(N-
 vinylbenzylamino)ethyl]-3-aminopropyltrimethoxysilane, N-
 [3-(trimethoxysilyl)propyl]-1-butaneamine, [3-
 (diethylamino)propyl]trimethoxysilane, (3-
 mercaptopropyl)trimethoxysilane, (3-
 mercaptopropyl)triethoxysilane, N-[8-
 (trimethoxysilyl)octyl]ethane-1,2-diamine, trimethoxy[3-
 (phenylamino)propyl]silane, and N,N-
 bis[(diphenylphosphino)methyl]-3-
 (triethoxysilyl)propylamine. In addition, from the
 viewpoint of suppressing pattern collapse of SiO_2 film, most
 preferable examples are trimethoxy[3-
 (phenylamino)propyl]silane and N-[8-
 (trimethoxysilyl)octyl]ethane-1,2-diamine.
 [0027]

The silane coupling agent may be used alone or in
 combination.

The concentration of the silane coupling agent in the
 etching liquid composition is not particularly limited, and
 it is preferably 0.01 to 10 wt%, more preferably 0.05 to 5

wt%, and still more preferably 0.1 to 3 wt%.

[0028]

The etching liquid composition of the present invention comprises phosphoric acid. The concentration of phosphoric acid in the etching liquid composition is not particularly limited, and is preferably 60 to 95 wt%, more preferably 80 to 95 wt%.

[0029]

The etching liquid composition of the present invention preferably comprises 0.01 to 10 wt% of a silane coupling agent and 60 to 95 wt% of phosphoric acid, and more preferably comprises 0.05 to 5 wt% of a silane coupling agent and 80 to 95 wt% of phosphoric acid, and furthermore preferably comprises 0.1 to 3 wt% of a silane coupling agent and 80 to 95 wt% of phosphoric acid.

[0030]

The etching liquid composition of the present invention comprises the above-mentioned silane coupling agent and phosphoric acid, and these react and adsorb to the surface of SiO_2 ; as a result, Si_3N_4 can be selectively etched relative to SiO_2 . Furthermore, by having a group comprising one or more selected from the group consisting of N atoms, O atoms, F atoms, P atoms, S atoms and Cl atoms or by further comprising a phenyl group or a bulky alkyl group in R_4 of the formula 1 of the silane coupling agent, regrowth of SiO_2 can be suppressed. In addition, by comprising a hydrophobic group, for example, a bulky alkyl group, a halogen group, a phenyl group or the like in R_4 of the silane coupling agent, the surface of the SiO_2 film can be made hydrophobic and pattern collapse of the SiO_2 film can be suppressed.

[0031]

The etching liquid composition of the present invention comprises water. Water constitutes the balance

of phosphoric acid, one or more silane coupling agents, and any additional components mentioned below that may be contained.

[0032]

It is preferable that the etching liquid composition of the present invention further comprises a water-soluble polar organic solvent, because solubility of the silane coupling agent in the etching liquid composition is improved.

The water-soluble polar organic solvent is not particularly limited, and preferable examples are methanol, ethanol and acetone, and more preferable examples are methanol and ethanol. The water-soluble polar organic solvent may be used alone or in combination.

[0033]

It is preferable that the etching liquid composition of the present invention further comprises an inorganic silicate, because selectivity of SiO_2 film relative to Si_3O_4 film is improved. The inorganic silicate forms $\text{Si}(\text{OH})_x$ in the etching liquid composition.

The inorganic silicate is not particularly limited, and preferable examples are sodium silicate or potassium silicate.

[0034]

The etching liquid composition of the present invention may comprise additional components other than the water-soluble polar organic solvent and the inorganic silicate, as long as they do not interfere with the etching of silicon nitride, and examples thereof include fluorine compounds. It is preferable that the etching liquid composition of the present invention further comprises a fluorine compound, because etching rate of Si_3N_4 becomes high. As the fluorine compound, hydrofluoric acid, ammonium fluoride and hexafluorosilicic acid are preferable, and

hexafluorosilicic acid is more preferable.

[0035]

The etching liquid composition of the present invention does not comprise ammonium ions. The etching liquid composition of the present invention can suppress regrowth of SiO_2 even when it does not comprise ammonium ions.

[0036]

The present invention also relates to a method for producing a 3D non-volatile memory cell, which comprises etching silicon nitride using the etching liquid composition according to the present invention. Furthermore, the present invention also relates to a 3D non-volatile memory cell obtained by said method.

[Examples]

[0037]

Next, the etching liquid composition of the present invention will be explained in more detail with reference to examples and comparative examples described below; however, the present invention is not limited thereto.

[0038]

<Evaluation 1: Etch selectivity of Si_3N_4 film/ SiO_2 film>
(Preparation of wafer (before immersion))

Using a substrate in which a Si_3N_4 film was formed on a Si substrate, a Si_3N_4 wafer (before immersion) was obtained by cutting into a size of 15 mm × 15 mm. Similarly, a SiO_2 wafer (before immersion) was obtained using a substrate on which a SiO_2 film was formed.

[0039]

(Pretreatment of Si_3N_4 wafer)

The Si_3N_4 wafer (before immersion) was immersed in a 0.6 wt% hydrofluoric acid aqueous solution and allowed to stand at 25°C for 40 seconds. Then, the wafer was taken out

and rinsed with ultrapure water (DIW) for 1 minute to obtain a Si_3N_4 wafer (after pretreatment).

[0040]

(Immersion of wafer in etching liquid composition)

The above Si_3N_4 wafer (after pretreatment) was immersed in 100 mL of an etching liquid composition having the composition shown in Table 1, and stirred and immersed at 165°C for 2 to 4 minutes. Then, the wafer was taken out and rinsed with ultrapure water (DIW) for 1 minute to obtain a Si_3N_4 wafer (after immersion).

In addition, the SiO_2 wafer (before immersion) was immersed in 100 mL of an etching liquid composition having the composition shown in Table 1, and stirred and immersed at 165°C for 30 to 60 minutes. Then, the wafer was taken out and rinsed with ultrapure water (DIW) for 1 minute to obtain a SiO_2 wafer (after immersion).

[0041]

[Table 1]

Sample	Phosphoric acid (wt%)	Silane coupling agent	(wt%)	Inorganic silicate	(wt%)	Water-soluble polar organic solvent	(wt%)	Water (wt%)
Comp. Ex.1	85.5	-	-	-	-	-	-	14.5
Comp. Ex.2	85.22	-	-	Potassium silicate	0.02	-	-	14.76
Ex.1	85.07	3-aminopropyltriethoxysilane	0.5	-	-	-	-	14.43
Ex.2	84.43	3-aminopropyltriethoxysilane	0.5	-	-	Ethanol	0.75	14.32
Ex.3	84.43	3-(2-aminoethylamino)propyltrimethoxysilane	0.5	-	-	Ethanol	0.75	14.32
Ex.4	84.43	3-aminopropyltriethoxysilane	0.25	-	-	Ethanol	0.75	14.32
		3-(2-aminoethylamino)propyltrimethoxysilane	0.25					
Ex.5	84.15	3-aminopropyltriethoxysilane	0.25	Sodium metasilicate	0.03	Ethanol	0.75	14.57
		3-(2-aminoethylamino)propyltrimethoxysilane	0.25					
Ex.6	84.15	3-aminopropyltriethoxysilane	0.25	Potassium silicate	0.02	Ethanol	0.75	14.58
		3-(2-aminoethylamino)propyltrimethoxysilane	0.25					
Ex.7	84.21	[3-(N,N-dimethylamino)propyl]trimethoxysilane	0.47	Potassium silicate	0.02	Ethanol	0.7	14.59
Ex.8	83.99	trimethoxy[3-(phenylamino)propyl]silane	0.58	Potassium silicate	0.02	Ethanol	0.86	14.55
Ex.9	83.07	N-[2-(N-vinylbenzylamino)ethyl]-3-aminopropyltrimethoxysilane	0.84	Potassium silicate	0.02	Ethanol	1.67	14.39
Ex.10	83.51	N-[3-(trimethoxysilyl)propyl]-1-butylamine	0.8	Potassium silicate	0.02	Ethanol	1.2	14.47
Ex.11	84.09	[3-(diethylamino)propyl]trimethoxysilane	0.53	Potassium silicate	0.02	Ethanol	0.79	14.57
Ex.12	84.07	(3-mercaptopropyl)triethoxysilane	0.44	Potassium silicate	0.02	Ethanol	0.81	14.66
Ex.13	84.03	N,N-bis[(diphenylphosphino)methyl]-3-(triethoxysilyl)propylamine	1.39	Potassium silicate	0.02	-	-	14.56
Ex.14	83.8	N-[8-(trimethoxysilyl)octyl]ethane-1,2-amine	0.66	Potassium silicate	0.02	Ethanol	0.99	14.53

[0042]

(Measurement of etching rate of etching liquid composition)

The film thickness of the Si₃N₄ wafer (after pretreatment) or SiO₂ wafer (before immersion) was measured with a reflection spectroscopic film thickness measurement system (manufactured by Otsuka Electronics Co., Ltd., model number: FE-3000), and the film thickness of the Si₃N₄ wafer

or SiO₂ wafer (after immersion) was measured with a reflection spectroscopic film thickness measurement system (manufactured by Otsuka Electronics Co., Ltd., model number: FE-3000). The etching rate (E.R.) of the etching liquid composition for Si₃N₄ or SiO₂ is calculated from the film thickness difference before and after immersion, and the etching rate of Si₃N₄ is divided by the etching rate of SiO₂ to obtain the etch selectivity of Si₃N₄ film/SiO₂ film. The results are shown in Table 2.

[0043]

<Evaluation 2: Presence or absence of oxide film growth>
(Preparation of wafer (before immersion))

A substrate on which a Si₃N₄ film and a SiO₂ film were alternately laminated, and grooves (intervals) were formed on the laminated film by dry etching, was cut into a size of 15 mm × 15 mm to obtain a wafer for evaluation.

[0044]

(Pretreatment of evaluation wafer)

The above evaluation wafer (before immersion) was immersed in a 0.6 wt% hydrofluoric acid aqueous solution and allowed to stand at 25°C for 40 seconds. Then, the wafer was taken out and rinsed with ultrapure water (DIW) for 1 minute to obtain an evaluation wafer (after pretreatment).

[0045]

(Immersion of wafer in etching liquid composition)

The above evaluation wafer (after pretreatment) was immersed in 100 mL of an etching liquid composition having the composition shown in Table 1, and stirred and immersed at 165°C for 60 minutes. Then, the wafer was taken out and rinsed with ultrapure water (DIW) for 1 minute to obtain the above evaluation wafer (after immersion).

[0046]

(Confirmation of oxide film growth of etching liquid

composition)

The above evaluation wafer (after immersion) was observed with an FE-SEM (manufactured by Hitachi High-Technologies Corporation, model number: SU8220) to confirm the presence or absence of oxide film growth. The results are shown in Table 2.

[0047]

<Evaluation 3: Contact angle of water on SiO₂ film>

(Preparation of wafer (before immersion))

A substrate on which a SiO₂ film was formed was cut into a size of 15 mm × 15 mm to obtain a SiO₂ wafer (before immersion).

[0048]

(Immersion of wafer in etching liquid composition)

The above SiO₂ wafer (before immersion) was immersed in 100 mL of an etching liquid composition having the composition shown in Table 1, and stirred and immersed at 165°C for 10 minutes. Then, the wafer was taken out and rinsed with ultrapure water (DIW) for 1 minute to obtain the above evaluation wafer (after immersion).

[0049]

(Measurement of contact angle of water on SiO₂ film after treatment with etching liquid composition)

The contact angle of the above SiO₂ wafer (after immersion) was measured with a solid-liquid interface analyzer (manufactured by Kyowa Interface Science Co., Ltd., model number: DropMaster 500). The results are shown in Table 2.

[0050]

[Table 2]

Sample	Si ₃ N ₄ /SiO ₂ etch selectivity	Presence/absence of oxide film growth	Water contact angle on SiO ₂ film
Comp. Ex. 1	73	None	Less than 5°
Comp. Ex. 1	1000 or more	Present	Less than 5°
Example 1	184	None	5.5°
Example 2	158	None	8.1°
Example 3	160	None	5.4°
Example 4	244	None	11.5°
Example 5	1000 or more	None	5.9°
Example 6	1000 or more	None	8.3°
Example 7	1000 or more	None	5.2°
Example 8	1000 or more	None	36.7°
Example 9	1000 or more	None	72.5°
Example 10	1000 or more	None	32.0°
Example 11	1000 or more	None	15.3°
Example 12	1000 or more	None	5.7°
Example 13	1000 or more	None	29.1°
Example 14	1000 or more	None	38.7°

[Claims]

1. A method of producing a 3D non-volatile memory cell, which comprises etching silicon nitride using a silicon nitride etching liquid composition, wherein the etching liquid composition comprises phosphoric acid, one or more kinds of silane coupling agents and water, and not comprising ammonium ions, and wherein the silane coupling agent is selected from the group consisting of 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-(2-aminoethylamino)propyltrimethoxysilane, 3-(2-aminoethylamino)propyltriethoxysilane, trimethoxy[3-(methylamino)propyl]silane, [3-(N,N-dimethylamino)propyl]trimethoxysilane, trimethoxy[3-(phenylamino)propyl]silane, N-[2-(N-vinylbenzylamino)ethyl]-3-aminopropyltrimethoxysilane, N-[8-(trimethoxysilyl)octyl]ethane-1,2-diamine, N-[3-(trimethoxysilyl)propyl]-1-butaneamine, [3-(diethylamino)propyl]trimethoxysilane, 3-[(1,3-dimethylbutylidene)amino]propyltriethoxysilane, (3-mercaptopropyl)trimethoxysilane, (3-mercaptopropyl)triethoxysilane and N,N-bis[(diphenylphosphino)methyl]-3-(triethoxysilyl)propylamine.
2. The method according to claim 1, wherein the etching liquid composition comprises 60 to 95 wt% of phosphoric acid and 0.01 to 10 wt% of a silane coupling agent.
3. The method according to any one of claim 1 or 2, wherein the etching liquid composition further comprises one or more kinds of water soluble polar organic solvents.
4. The method according to claim 3, wherein the water-soluble polar organic solvent is selected from the group

consisting of methanol, ethanol and acetone.

5. The method according to any one of claims 1 to 4, wherein the etching liquid composition further comprises an inorganic silicate.
6. The method according to claim 5, wherein the inorganic silicate is sodium silicate or potassium silicate.