

DESCRIPTION

TITLE OF INVENTION: ETCHING METHOD, METHOD FOR
MANUFACTURING SEMICONDUCTOR DEVICE, ETCHING DEVICE, SURFACE
5 TREATMENT GAS COMPOSITION, AND ETCHING GAS COMPOSITION
CONTAINING SURFACE TREATMENT MATERIAL

TECHNICAL FIELD

[0001]

10 The present disclosure relates to an etching method, a method for
manufacturing a semiconductor device, an etching device, a surface treatment gas
composition, and a surface treatment material-containing etching gas composition.

BACKGROUND ART

15 [0002]

A manufacturing process of a semiconductor device includes etching a silicon
oxide film present as a CVD oxide film, a thermal oxide film, or a natural oxide film on
a surface of a semiconductor wafer. Wet etching with a chemical liquid or plasma
etching using reactive gas plasma has been performed to etch such a silicon oxide film.

20 [0003]

However, wet etching has a drawback in that the chemical liquid used is likely
to adversely affect parts other than the etching target, while plasma etching has a
drawback in that wafers can be electrically damaged by plasma.

[0004]

25 To overcome these drawbacks, a method of dry etching without plasma has
been tried. For example, Patent Literature 1 discloses a method of performing dry
etching by reacting a silicon oxide with gaseous hydrogen fluoride and a gaseous
organic amine compound without plasma.

30

CITATION LIST

- Patent Literature

[0005]

Patent Literature 1: WO 2020/054476

SUMMARY OF INVENTION

- Technical Problem

[0006]

5 According to the method of Patent Literature 1, dry etching of a silicon oxide can be performed without plasma, but extensive studies of the present disclosers have revealed that the method still has room for improvement in terms of selectively etching films containing Si and O and not containing N.

[0007]

10 The present disclosure aims to solve the problem newly found by the present disclosers and provide an etching method enabling selective etching of a film containing Si and O and not containing N, a method for manufacturing a semiconductor device using the etching method, an etching device, a surface treatment gas composition, and a surface treatment material-containing etching gas composition.

15 - Solution to Problem

[0008]

As a result of extensive studies, the present disclosers have found that, when (I) an etching gas composition containing HF gas and (II) a surface treatment gas composition containing a surface treatment material are brought into contact with a
20 substrate having a film at least containing Si and O and not containing N and a film at least containing Si and N, the film containing Si and O and not containing N can be selectively etched. The present disclosure has been completed based on this finding.

[0009]

Specifically, Embodiment (1) of the present disclosure relates to an etching
25 method, including bringing (I) an etching gas composition containing HF gas and (II) a surface treatment gas composition containing a surface treatment material into contact with a substrate having a film at least containing Si and O and not containing N and a film at least containing Si and N to selectively etch the film containing Si and O and not containing N.

30 [0010]

Embodiment (2) of the present disclosure relates to the etching method described in Embodiment (1) of the present disclosure,

wherein the surface treatment material chemically modifies a surface of the film containing Si and N.

[0011]

Embodiment (3) of the present disclosure relates to the etching method described in Embodiment (1) of the present disclosure,

wherein the surface treatment material chemically modifies a surface of the film containing Si and N and a surface of the film containing Si and O and not containing N.

[0012]

Embodiment (4) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (3) of the present disclosure,

wherein the surface treatment material is a compound represented by Formula

[A]:

R-X [A]

wherein R represents a monovalent group, and X represents Br, Cl, I, F, -C(O)Cl, -C(O)F, -C(O)H, or -NCO.

[0013]

Embodiment (5) of the present disclosure relates to the etching method described in Embodiment (4) of the present disclosure,

wherein R in the Formula [A] represents a group unreactive with HF.

[0014]

Embodiment (6) of the present disclosure relates to the etching method described in Embodiment (5) of the present disclosure,

wherein R in the Formula [A] represents a group free from at least one of an amino group or a hydroxy group.

[0015]

Embodiment (7) of the present disclosure relates to the etching method described in Embodiment (4) of the present disclosure,

wherein R in the Formula [A] represents an electron-withdrawing group.

[0016]

Embodiment (8) of the present disclosure relates to the etching method described in Embodiment (7) of the present disclosure,

wherein R in the Formula [A] represents: XSO_2^- where X represents a halogen atom; XCO^- where X represents a halogen atom; or $\text{C}_n\text{R}^1_{2n+1}\text{SO}_2^-$ where R^1 s are the same as or different from each other and each represent a hydrogen atom or a halogen atom, and n represents an integer of not more than 6.

5 [0017]

Embodiment (9) of the present disclosure relates to the etching method described in Embodiment (7) of the present disclosure,

wherein R in the Formula [A] represents FSO_2^- , FCO^- , CF_3SO_2^- , or CH_3SO_2^- .

[0018]

10 Embodiment (10) of the present disclosure relates to the etching method described in Embodiment (4) of the present disclosure,

wherein R in the Formula [A] represents: $\text{C}_n\text{R}^2_{2n+1}-$ where R^2 s are the same as or different from each other and each represent a hydrogen atom or a halogen atom, and n represents an integer of not more than 6; or $(\text{C}_n\text{R}^3_{2n+1})_3\text{Si}-$ where R^3 s are the same as or different from each other and each represent a hydrogen atom or a halogen atom, and

15 [0019]

Embodiment (11) of the present disclosure relates to the etching method described in Embodiment (4) of the present disclosure,

20 wherein R in the Formula [A] represents an alkyl group with 6 or less carbon atoms, or $(\text{CH}_3)_3\text{Si}-$.

[0020]

Embodiment (12) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (11) of the present disclosure,

25 wherein the etching gas composition further contains at least one selected from the group consisting of an inert gas, NH_3 , an organic amine compound, and an alcohol.

[0021]

Embodiment (13) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (12) of the present disclosure,

30 wherein the film containing Si and O and not containing N is selectively etched without plasma.

[0022]

Embodiment (14) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (13) of the present disclosure,

wherein (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material are simultaneously brought into contact with the substrate.

[0023]

Embodiment (15) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (13) of the present disclosure,

wherein the method includes a surface treatment step including bringing (II) the surface treatment gas composition containing a surface treatment material into contact with the substrate, and an etching step including bringing (I) the etching gas composition containing HF gas into contact with the substrate after the surface treatment step.

[0024]

Embodiment (16) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (15) of the present disclosure, wherein a temperature of the substrate during the etching is 20°C to 300°C.

[0025]

Embodiment (17) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (16) of the present disclosure, wherein a pressure during the etching is 1 Pa to 10 kPa.

[0026]

Embodiment (18) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (17) of the present disclosure, wherein a pressure during the etching is 1 Pa or higher and lower than 1 kPa.

[0027]

Embodiment (19) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (18) of the present disclosure, wherein the film containing Si and O and not containing N is a silicon oxide (SiO) film.

[0028]

Embodiment (20) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (19) of the present disclosure, wherein the film containing Si and N is a silicon nitride (SiN) film.

[0029]

5 Embodiment (21) of the present disclosure relates to the etching method described in any one of Embodiments (1) to (20) of the present disclosure, wherein in the substrate, the film containing Si and O and not containing N is a silicon oxide (SiO) film, the film containing Si and N is a silicon nitride (SiN) film, the silicon nitride film is adjacent to the silicon oxide film, and the silicon oxide film and
10 the silicon nitride film are exposed.

[0030]

Embodiment (22) of the present disclosure relates to a method for manufacturing a semiconductor device, including

applying the etching method described in any one of Embodiments (1) to (21)
15 of the present disclosure to a substrate having a film at least containing Si and O and not containing N and a film at least containing Si and N to selectively etch the film containing Si and O and not containing N.

[0031]

Embodiment (23) of the present disclosure relates to a method for
20 manufacturing a semiconductor device, including

applying the etching method described in any one of Embodiments (1) to (21) of the present disclosure to a substrate having a silicon nitride film and a silicon oxide film to selectively etch the silicon oxide film.

[0032]

25 Embodiment (24) of the present disclosure relates to an etching device, including

a stage for placing a substrate thereon,

(I) an HF gas supply unit for supplying HF gas to the substrate, and

(II) a surface treatment gas supply unit for supplying a surface treatment gas
30 composition containing a surface treatment material to the substrate.

[0033]

Embodiment (25) of the present disclosure relates to a surface treatment gas composition containing a surface treatment material.

[0034]

Embodiment (26) of the present disclosure relates to a surface treatment material-containing etching gas composition, containing HF gas and a surface treatment material.

5

- Advantageous Effects of Invention

[0035]

An etching method according to the present disclosure includes bringing (I) an etching gas composition containing HF gas and (II) a surface treatment gas composition
10 containing a surface treatment material into contact with a substrate having a film at least containing Si and O and not containing N and a film at least containing Si and N to selectively etch the film containing Si and O and not containing N. The use of (I) the etching gas composition containing HF gas together with (II) the surface treatment gas composition containing a surface treatment material enables selective etching of the
15 film containing Si and O and not containing N.

[0036]

A method for manufacturing a semiconductor device according to the present disclosure includes applying the etching method according to the present disclosure to a substrate having a film at least containing Si and O and not containing N and a film at
20 least containing Si and N to selectively etch the film containing Si and O and not containing N, or includes applying the etching method according to the present disclosure to a substrate having a silicon nitride film and a silicon oxide film to selectively etch the silicon oxide film. The method for manufacturing a semiconductor device according to the present disclosure includes applying the etching method
25 according to the present disclosure for etching, and therefore enables selective etching of a film containing Si and O and not containing N (e.g., a silicon oxide film) on a semiconductor substrate to manufacture a high-quality semiconductor device.

[0037]

An etching device according to the present disclosure includes
30 a stage for placing a substrate thereon,
(I) an HF gas supply unit for supplying HF gas to the substrate, and
(II) a surface treatment gas supply unit for supplying a surface treatment gas composition containing a surface treatment material to the substrate. The use of (I) HF gas together with (II) the surface treatment gas composition containing a surface

treatment material enables selective etching of a film containing Si and O and not containing N.

[0038]

A surface treatment gas composition according to the present disclosure
5 contains a surface treatment material and therefore enables selective etching of a film containing Si and O and not containing N.

[0039]

A surface treatment material-containing etching gas composition according to
the present disclosure contains HF gas and a surface treatment material and therefore
10 enables selective etching of a film containing Si and O and not containing N.

BRIEF DESCRIPTION OF DRAWINGS

[0040]

FIG. 1 shows a schematic diagram illustrating an exemplary test results when
15 the surface treatment material $\text{CF}_3\text{SO}_2\text{F}$ (TfF) is brought into contact with an SiN film.

FIG. 2 shows a schematic diagram illustrating an exemplary test results when
the surface treatment material $\text{CF}_3\text{SO}_2\text{F}$ (TfF) is brought into contact with an SiO_2 film.

FIG. 3 shows a schematic diagram schematically illustrating an etching device
according to an embodiment of the present disclosure.

20

DESCRIPTION OF EMBODIMENTS

[0041]

Hereinafter, the present disclosure is described in detail, but the description of
constituent elements described below illustrates embodiments of the present disclosure,
25 and the present disclosure is not limited to these specific contents. Various
modifications can be made within the scope of the gist of the present disclosure.

[0042]

Herein, the expression “X to Y” in the description of a numerical range means
“X or more and Y or less”, unless otherwise stated. For example, “1 to 5% by mass”
30 means “1% by mass or more and 5% by mass or less”.

[0043]

<Etching method>

An etching method according to the present disclosure includes bringing (I) an
etching gas composition containing HF gas and (II) a surface treatment gas composition

containing a surface treatment material into contact with a substrate having a film at least containing Si and O and not containing N and a film at least containing Si and N to selectively etch the film containing Si and O and not containing N.

[0044]

5 Examples of the film at least containing Si and O and not containing N (also simply referred to as film containing Si and O) include silicon oxide (SiO) films (Here, SiO refers to films containing silicon and oxygen atoms without specifying the stoichiometric ratio of the elements; e.g., SiO_x (x is 1 or more and 2 or less) such as SiO_2).

10 Herein, the term “film at least containing Si and O and not containing N” means that the amount of N is 1% by mass or less, preferably 0.1% by mass or less, more preferably 0.01% by mass or less, still more preferably 0.00% by mass based on 100% by mass of the film.

[0045]

15 Examples of the film at least containing Si and N (also simply referred to as film containing Si and N) include silicon nitride (SiN) films (Here, SiN refers to films containing silicon and nitrogen atoms without specifying the stoichiometric ratio of the elements; e.g., SiO_x (x is 0.3 or more and 9 or less) or Si_3N_4), silicon oxycarbonitride (SiOCN) films (Here, SiOCN refers to films containing silicon, oxygen, carbon, and
20 nitrogen atoms without specifying the stoichiometric ratio of the elements), silicon oxynitride (SiON) films (Here, SiON refers to films containing silicon, oxygen, and nitrogen atoms without specifying the stoichiometric ratio of the elements; e.g., $\text{Si}_4\text{O}_x\text{N}_y$ (x is 3 or more and 6 or less, and y is 2 or more and 4 or less) or $\text{Si}_4\text{O}_5\text{N}_3$), and silicon carbonitride (SiCN) films (Here, SiCN refers to films containing silicon, carbon, and
25 nitrogen atoms without specifying the stoichiometric ratio of the elements; e.g., materials containing 20 to 50 at% of silicon, 5 to 30 at% of carbon, and 10 to 30 at% of nitrogen). Silicon nitride films are preferred among these.

[0046]

30 The temperature of the process of bringing (I) the etching gas composition containing HF gas into contact with the film formed on the substrate (substrate temperature) is preferably 20°C to 300°C, more preferably 20°C to 250°C, still more preferably 20°C to 200°C. In order to more suitably provide selective etching of the film containing Si and O, the temperature is preferably 130°C to 250°C, more preferably 160°C to 230°C. In order to suppress damage to the film formed on the substrate, the
35 temperature may be 20°C to 200°C, 30°C to 150°C, or 50°C to 120°C. The above

temperature range is also preferable for the temperature of the process of bringing (II) the surface treatment gas composition containing a surface treatment material into contact with the film formed on the substrate, or the temperature of the process of simultaneously bringing (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material into contact with the film formed on the substrate.

[0047]

The etching method according to the present disclosure preferably includes selectively etching the film containing Si and O without plasma. This is because, in the case where the substrate is a semiconductor device substrate, the substrate, when brought into contact with plasma gas, may be electrically damaged by the plasma gas.

[0048]

The etching method according to the present disclosure is suitable for selectively etching the film containing Si and O. In the etching method according to the present disclosure, preferably, the film containing Si and O is selectively etched, and the film containing Si and N is etched at a rate of 1.0 nm/min or lower, more preferably 0.5 nm/min or lower.

Herein, the phrase “selectively etching the film containing Si and O” means that the ratio of the etching rate of the film containing Si and O to the etching rate of the film containing Si and N (film containing Si and O/film containing Si and N) is 2 or higher. The etching rate ratio is preferably 5 or higher, more preferably 10 or higher, still more preferably 15 or higher, particularly preferably 30 or higher, most preferably 100 or higher, further most preferably 350 or higher, even most preferably 400 or higher. Although the upper limit is not limited, it is, for example, 10000 or lower.

Herein, the etching rate is calculated from the film thicknesses measured before and after the etching process using a spectroscopic ellipsometer, relative to the flow time of the etching gas.

[0049]

In the etching method according to the present disclosure, the film containing Si and O is preferably etched at a rate of 1.5 nm/min or higher, more preferably 10 nm/min or higher, still more preferably 30 nm/min or higher, particularly preferably 50 nm/min or higher. The upper limit is not limited and is, for example, 10 $\mu\text{m}/\text{min}$ or lower. At the above rate, selective etching of the film containing Si and O tends to be more suitably achieved.

[0050]

In the etching method according to the present disclosure, the substrate is preferably a semiconductor device substrate, such as a silicon substrate, a compound semiconductor substrate, a quartz substrate, or a glass substrate. In addition to the film at least containing Si and O and the film at least containing Si and N, a polycrystalline silicon film, a film containing a metal nitride, a silicon film, a metal wiring film, or other films may be formed on the surface of the substrate. An embodiment in which a silicon nitride film is adjacent to a silicon oxide film, and the silicon oxide film and the silicon nitride film are exposed is suitable for the etching method according to the present disclosure. An embodiment in which a silicon nitride film is adjacent to a silicon oxide film and a polycrystalline silicon film, and the silicon oxide film, the polycrystalline silicon film, and the silicon nitride film are exposed is suitable for the etching method according to the present disclosure.

For example, the substrate may be placed on a stage in an etching device, which will be described later, and the substrate as well as the film containing Si and O and the film containing Si and N formed on the surface of the substrate may be heated by heating the stage.

[0051]

The film may be formed on the surface of the substrate by any method. Examples include chemical vapor deposition (CVD) and sputtering. Moreover, the film containing Si and O and the film containing Si and N may have any thickness. For example, the thickness may be 0.1 nm to 1 μm .

[0052]

In the etching method according to the present disclosure, the etching is preferably performed with the substrate provided in a chamber. The etching method according to the present disclosure preferably includes subjecting the interior of a chamber to a reduced pressure condition. The etching method according to the present disclosure more preferably includes bringing (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material into contact with the substrate having the film at least containing Si and O and the film at least containing Si and N in a chamber, followed by subjecting the interior of the chamber to a reduced pressure condition. This is because by-products generated during etching can be removed.

The term “reduced pressure condition” means a condition where the pressure in the chamber is lower than the pressure during etching (processing pressure) and is approximately 0.133 kPa or lower.

[0053]

The etching method according to the present disclosure preferably includes purging the interior of the chamber with an inert gas. The etching method according to the present disclosure more preferably includes bringing (I) the etching gas composition
 5 containing HF gas into contact with (II) the surface treatment gas composition containing a surface treatment material, followed by purging the interior of the chamber with an inert gas. This is because by-products generated during etching can be removed.

10 The etching method according to the present disclosure may include subjecting the interior of the chamber to a reduced pressure condition, followed by purging the interior of the chamber with an inert gas.

For example, oxide, oxynitride, or other films are usually formed on the surface of SiN, which is an example of the film containing Si and N. Therefore, the etching method according to the present disclosure may include removing these films before
 15 bringing (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material into contact with the substrate.

[0054]

<<(I) Etching gas composition containing HF gas>>

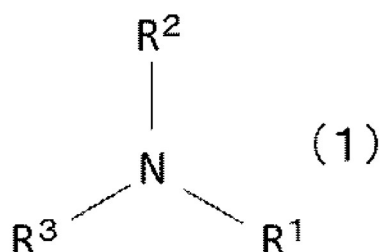
20 The etching gas composition (I) may be any composition that contains HF gas and may contain HF gas in an amount of 100% by volume based on 100% by volume of the etching gas composition (I). The etching gas composition (I) preferably further contains at least one selected from the group consisting of an inert gas, NH₃, an organic amine compound, and an alcohol, more preferably at least one selected from the group
 25 consisting of NH₃, an organic amine compound, and an alcohol, still more preferably at least one selected from the group consisting of an organic amine compound and an alcohol, particularly preferably an organic amine compound. In this case, selective etching of the film containing Si and O tends to be more suitably achieved. Each of these may be used alone, or two or more of these may be used in combination.

30 [0055]

Examples of the inert gas include Ar, N₂, He, Ne, and Kr. Each of these may be used alone, or two or more of these may be used in combination. Ar is preferred among these because it is stable and inexpensive.

[0056]

Examples of usable organic amine compounds include compounds represented by the following Formula (1). Each of these may be used alone, or two or more of these may be used in combination.



- 5 In the Formula (1), N represents a nitrogen atom; R¹ represents a C1-C10 hydrocarbon group optionally having a ring, a heteroatom, or a halogen atom; and R² and R³ each represent a hydrogen atom or a C1-C10 hydrocarbon group optionally having a ring, a heteroatom, or a halogen atom, provided that the hydrocarbon group, when having a carbon number of 3 or more, may have a branched chain structure or a
- 10 ring structure, and the heteroatom of the hydrocarbon group is a nitrogen atom, an oxygen atom, a sulfur atom, or a phosphorus atom, and that: when both R¹ and R² are hydrocarbon groups having a carbon number of 1 or more, R¹ and R² may be directly bonded to form a ring structure; when R¹ or R² is directly bonded by a double bond to form a ring structure, they may form an aromatic ring in the absence of R³; and R¹, R²,
- 15 and R³ may be the same hydrocarbon group or different hydrocarbon groups.

[0057]

- Examples of R¹ include a methyl group, an ethyl group, a propyl group, and a butyl group. The hydrogen atoms of these organic groups may be partially replaced by halogen atoms such as fluorine or chlorine. Examples of R² and R³ include a hydrogen
- 20 atom, a methyl group, an ethyl group, a propyl group, and a butyl group. The hydrogen atoms of these organic groups may be partially or fully replaced by halogen atoms such as fluorine or chlorine. The organic amine compounds represented by the Formula (1) may be heterocyclic amines having a five-membered ring structure or a six-membered ring structure.

25 [0058]

Specific examples of organic amine compounds include monomethylamine, dimethylamine, trimethylamine, dimethylethylamine, diethylmethylamine, monoethylamine, diethylamine, triethylamine, mono-normal propylamine, di-normal propylamine, monoisopropylamine, diisopropylamine, monobutylamine, dibutylamine,

monotertiary butylamine, ditertiary butylamine, pyrrolidine, piperidine, piperazine, pyridine, and pyrazine. Other specific examples include the above-listed compounds in which part or all of C-H bonds are replaced by C-F bonds, such as trifluoromethylamine, 1,1,1-trifluorodimethylamine, perfluorodimethylamine, 2,2,2-trifluoroethylamine, perfluoroethylamine, bis(2,2,2-trifluoroethyl)amine, perfluorodiethylamine, and 3-fluoropyridine. These organic amine compounds are preferred because their conjugated acids have a pKa of not less than 3.2, which is the pKa of HF, and they can form a salt with hydrogen fluoride, have a constant vapor pressure in a temperature range of 20°C to 100°C, and can be supplied as gas without decomposition in the temperature range.

[0059]

Particularly from easy availability and other standpoints, preferred examples of the organic amine compounds include monomethylamine, dimethylamine, trimethylamine, monoethylamine, monopropylamine, isopropylamine, 1,1,1-trifluorodimethylamine, 2,2,2-trifluoroethylamine, and bis(2,2,2-trifluoroethyl)amine.

[0060]

Secondary amines and tertiary amines are also preferred among the organic amine compounds because they provide a high etching rate for the film containing Si and O (such as a silicon oxide). Specific examples of the secondary amines include dimethylamine, diethylamine, di-normal propylamine, diisopropylamine, dibutylamine, and ditertiary butylamine. Specific examples of the tertiary amines include trimethylamine, dimethylethylamine, diethylmethylamine, and triethylamine.

[0061]

Examples of the alcohol include methanol, ethanol, 1-propanol, and isopropyl alcohol. Each of these may be used alone, or two or more of these may be used in combination.

[0062]

The amount of HF gas based on 100% by volume of the etching gas composition (I) may be 100% by volume, preferably 10 to 90% by volume, more preferably 20 to 80% by volume, still more preferably 30 to 70% by volume, particularly preferably 40 to 60% by volume.

The amount of inert gases, NH₃, organic amine compounds, or alcohols (when two or more of these are used in combination, the combined amount of inert gases, NH₃, organic amine compounds, and alcohols) based on 100% by volume of the etching gas composition (I) is preferably 10 to 90% by volume, more preferably 20 to 80% by

volume, still more preferably 30 to 70% by volume, particularly preferably 40 to 60% by volume.

When the gas formulation of the etching gas composition (I) is within the above range, selective etching of the film containing Si and O tends to be more suitably achieved.

The combined amount of HF gas, inert gases, NH_3 , organic amine compounds, and alcohols based on 100% by volume of the etching gas composition (I) is preferably 80% by volume or more, more preferably 90% by volume or more, still more preferably 95% by volume or more, particularly preferably 98% by volume or more, and may be 100% by volume.

Herein, the amounts of gas components in the gas composition can be measured by infrared spectroscopy.

[0063]

<<(II) Surface treatment gas composition containing surface treatment material>>

(II) The surface treatment material may be any compound that can treat a surface of a substrate, and it is preferably a compound that can chemically modify a surface of the film containing Si and N, more preferably a compound that can chemically modify a surface of the film containing Si and N and a surface of the film containing Si and O. Each of these surface treatment materials may be used alone, or two or more of these may be used in combination.

Herein, the phrase “chemically modify” means chemically binding.

[0064]

Preferably, the surface treatment material chemically modifies a surface of the film containing Si and N, and more preferably it chemically modifies a surface of the film containing Si and N and a surface of the film containing Si and O.

FIG. 1 shows a schematic diagram illustrating exemplary test results when the surface treatment material $\text{CF}_3\text{SO}_2\text{F}$ (TfF) is brought into contact with an SiN film. As understood from FIG. 1, when the surface treatment material $\text{CF}_3\text{SO}_2\text{F}$ (TfF) is brought into contact with the SiN film, the surface of the SiN film is chemically modified.

Moreover, FIG. 2 shows a schematic diagram illustrating exemplary test results when the surface treatment material $\text{CF}_3\text{SO}_2\text{F}$ (TfF) is brought into contact with an SiO_2 film. As understood from FIG. 2, when the surface treatment material $\text{CF}_3\text{SO}_2\text{F}$ (TfF) is brought into contact with the SiO_2 film, the surface of the SiO_2 film is chemically modified.

As a result of the studies of the present disclosers, it is assumed that the surface of the film containing Si and N, when chemically modified, becomes less reactive to HF, inhibiting etching, while the surface of the film containing Si and O, when chemically modified, becomes more reactive to HF, promoting etching.

Here, even when the surface of the film containing Si and N is chemically modified to a greater extent by the surface treatment material than the surface of the film containing Si and O, the film containing Si and O is believed to be etched more than the film containing Si and N because of the etching-inhibiting effect and the etching-promoting effect.

[0065]

Specific examples of the compound that can chemically modify a surface of the film containing Si and N and a surface of the film containing Si and O include compounds represented by the following Formula [A]. Each of these may be used alone, or two or more of these may be used in combination.

R-X [A]

In the Formula [A], R represents a monovalent group, and X represents Br, Cl, I, F, -C(O)Cl, -C(O)F, -C(O)H, or -NCO.

[0066]

R in the Formula [A] may be any monovalent group and is preferably a group unreactive with HF, more preferably a group free from an amino group and/or a hydroxy group. In this case, chemical modification of the surface of the film containing Si and N and the surface of the film containing Si and O tends to be achieved without inhibiting the etching of the film containing Si and O by HF gas.

[0067]

In order to more suitably achieve selective etching of the film containing Si and O, R in the Formula [A] is preferably an electron-withdrawing group. Specific examples of the electron-withdrawing group include XSO₂- (where X represents a halogen atom), XCO- (where X represents a halogen atom), and C_nR¹_{2n+1}SO₂- (where R¹s are the same as or different from each other and each represent a hydrogen atom or a halogen atom, and n represents an integer of not more than 6).

Examples of the halogen atom as X or R¹ include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. A fluorine atom is preferred among these.

R¹ is preferably a hydrogen atom or a fluorine atom.

n is preferably 1 to 5, more preferably 1 to 3, still more preferably 1.

Preferred specific examples of the electron-withdrawing group include FSO₂-, FCO-, CF₃SO₂-, and CH₃SO₂-. FSO₂- or CF₃SO₂- is preferred among these.

[0068]

In order to more suitably achieve selective etching of the film containing Si and O, R in the Formula [A] is also preferably C_nR²_{2n+1}- (where R²s are the same as or different from each other and each represent a hydrogen atom or a halogen atom, and n represents an integer of not more than 6) or (C_nR³_{2n+1})₃Si- (where R³s are the same as or different from each other and each represent a hydrogen atom or a halogen atom, and n represents an integer of not more than 6). Preferred specific examples of the group include alkyl groups with 6 or less carbon atoms and (CH₃)₃Si-.

The halogen atom as R² or R³, including preferred embodiments thereof, is as described for the halogen atom as X or R¹.

R² and R³ are each preferably a hydrogen atom or a fluorine atom, more preferably a hydrogen atom.

n is preferably 1 to 5, more preferably 1 to 3, still more preferably 1.

[0069]

X in the Formula [A] is Br, Cl, I, F, -C(O)Cl, -C(O)F, -C(O)H, or -NCO. Such X can cause chemical reactions with a surface of the film containing Si and N and a surface of the film containing Si and O for chemical modification. X is preferably Cl, I, F, -C(O)Cl, or -NCO, more preferably -C(O)Cl or -NCO, still more preferably -NCO, among these.

[0070]

Examples of the compounds represented by Formula [A] include CH₃I, CH₃Br, CH₃Cl, CH₃F, tBu-NCO, CH₃NCO, FSO₂NCO, CF₃SO₂NCO, CH₃COCl, CH₃COF, CH₃COH, CF₃SO₂F, CF₃SO₂Cl, CF₃SO₂Br, CF₃SO₂I, CH₃SO₂F, CH₃SO₂Cl, CH₃SO₂Br, CH₃SO₂I, FCOF, FCOCl, FCOBr, and FCOI. Each of these may be used alone, or two or more of these may be used in combination. CH₃I, tBu-NCO, FSO₂NCO, CH₃COCl, CF₃SO₂F, and CF₃SO₂Cl are preferred among these, with FSO₂NCO being more preferred.

[0071]

The surface treatment gas composition (II) may be any composition that contains a surface treatment material and may contain the surface treatment material in an amount of 100% by volume based on 100% by volume of the surface treatment gas composition (II). The surface treatment gas composition (II) may further contain at least one selected from the group consisting of an inert gas, NH₃, an organic amine

compound, and an alcohol, preferably an inert gas. Each of these may be used alone, or two or more of these may be used in combination. The inert gas, the organic amine compound, and the alcohol are as described in the above <<(I) Etching gas composition containing HF gas>>.

5 [0072]

The amount of surface treatment materials based on 100% by volume of the surface treatment gas composition (II) is preferably 60% by volume or more, more preferably 80% by volume or more, still more preferably 90% by volume or more, particularly preferably 95% by volume or more, and may be 100% by volume. When
10 the gas formulation of the surface treatment gas composition (II) is within the above range, selective etching of the film containing Si and O tends to be more suitably achieved.

[0073]

[First etching method]

15 First, a first etching method will be described as the etching method according to the present disclosure. The first etching method includes simultaneously bringing (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material into contact with the substrate. In the following, the etching gas used in the first etching method is referred to as surface
20 treatment material-containing etching gas composition, and the surface treatment material-containing etching gas composition is a mixture of (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material and at least contains HF gas and the surface treatment material.

25 [0074]

In the following description, the film at least containing Si and O and the film at least containing Si and N are also referred to as films to be etched.

When (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material are simultaneously
30 brought into contact with the heated films to be etched, it is believed that the surface treatment material in the composition (II) may chemically modify a surface of the film containing Si and N and a surface of the film containing Si and O, so that the chemically modified surface of the film containing Si and N becomes less reactive to HF, inhibiting etching, while the chemically modified surface of the film containing Si

and O becomes more reactive to HF, promoting etching, as a result of which the film containing Si and O, among the films to be etched, can be selectively etched.

[0075]

(I) The etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material, including preferred embodiments thereof, are as described above.

[0076]

The volume ratio between (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material is preferably such that “(I) etching gas composition containing HF gas:(II) surface treatment gas composition containing surface treatment material” is 10:0.01 to 10, more preferably 10:0.05 to 6, still more preferably 10:0.3 to 3. Too low a proportion of HF gas tends to result in a decrease in etching rate, while too high a proportion of HF gas leads to an excessively high cost. Also, too high a proportion of (II) the surface treatment gas composition containing a surface treatment material tends to decrease the progress of etching.

Even a trace amount of (II) the surface treatment gas composition containing a surface treatment material can exert the effect. Thus, 1 ppm by volume or more of (II) the surface treatment gas composition containing a surface treatment material is sufficient based on 100% by volume of the surface treatment material-containing etching gas composition.

[0077]

The surface treatment material-containing etching gas composition is a mixture of (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material and at least contains HF gas and the surface treatment material.

[0078]

The amount of HF gas based on 100% by volume of the surface treatment material-containing etching gas composition is preferably 10 to 80% by volume, more preferably 20 to 70% by volume, still more preferably 30 to 60% by volume, particularly preferably 40 to 50% by volume.

The amount of surface treatment materials based on 100% by volume of the surface treatment material-containing etching gas composition is preferably 1 to 35% by volume, more preferably 2 to 25% by volume, still more preferably 3 to 20% by volume, particularly preferably 5 to 15% by volume.

The amount of inert gases, NH_3 , organic amine compounds, or alcohols (when two or more of these are used in combination, the combined amount of inert gases, NH_3 , organic amine compounds, and alcohols) based on 100% by volume of the surface treatment material-containing etching gas composition is preferably 10 to 80% by volume, more preferably 20 to 70% by volume, still more preferably 30 to 60% by volume, particularly preferably 40 to 50% by volume.

The combined amount of HF gas, surface treatment materials, inert gases, NH_3 , organic amine compounds, and alcohols based on 100% by volume of the surface treatment material-containing etching gas composition is preferably 80% by volume or more, more preferably 90% by volume or more, still more preferably 95% by volume or more, particularly preferably 98% by volume or more, and may be 100% by volume.

When the gas formulation of the surface treatment material-containing etching gas composition is within the above range, selective etching of the film containing Si and O tends to be more suitably achieved.

[0079]

The first etching method preferably includes simultaneously bringing (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material into contact with the substrate in a chamber; and subjecting the interior of the chamber to a reduced pressure condition, and etching is performed by repeating these steps. The step of subjecting the interior of the chamber to a reduced pressure condition may be replaced by purging the interior of the chamber with an inert gas. Alternatively, the step of subjecting the interior of the chamber to a reduced pressure condition may be followed by purging the interior of the chamber with an inert gas. A preferred embodiment of the first etching method includes simultaneously bringing (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material into contact with the substrate in a chamber, followed by subjecting the interior of the chamber to a reduced pressure condition and/or purging the interior of the chamber with an inert gas.

[0080]

[Second etching method]

Next, a second etching method will be described as the etching method according to the present disclosure. The second etching method includes a surface treatment step including bringing (II) the surface treatment gas composition containing a surface treatment material into contact with the substrate; and an etching step

including bringing (I) the etching gas composition containing HF gas into contact with the substrate after the surface treatment step.

[0081]

When (II) the surface treatment gas composition containing a surface treatment material is brought into contact with the heated films to be etched (which corresponds to the surface treatment step), the surface treatment material in the composition (II) may chemically modify a surface of the film containing Si and N and a surface of the film containing Si and O, so that the chemically modified surface of the film containing Si and N becomes less reactive to HF, inhibiting etching, while the chemically modified surface of the film containing Si and O becomes more reactive to HF, promoting etching. When (I) the etching gas composition containing HF gas is then brought into contact with the substrate for an etching step, it is believed that the film containing Si and O, among the films to be etched, can be selectively etched.

In the second etching method of the present disclosure, the above steps may be repeated multiple times to repeatedly etch the films to be etched. One etching cycle can etch a certain thickness, and therefore a desired thickness of a layer can be precisely etched by specifying the number of cycles.

[0082]

(I) The etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material, including preferred embodiments thereof, are as described above.

[0083]

Preferably, the second etching method includes performing the surface treatment step and the etching step each in a chamber and further includes subjecting the interior of the chamber to a reduced pressure condition. Etching is preferably performed by repeating these steps. The step of subjecting the interior of the chamber to a reduced pressure condition may be replaced by purging the interior of the chamber with an inert gas. Alternatively, the step of subjecting the interior of the chamber to a reduced pressure condition may be followed by purging the interior of the chamber with an inert gas. A preferred embodiment of the second etching method includes performing the surface treatment step, followed by the step of subjecting the interior of the chamber to a reduced pressure condition and/or purging the interior of the chamber with an inert gas; and then performing the etching step, followed by the step of subjecting the interior of the chamber to a reduced pressure condition and/or purging the interior of the chamber with an inert gas.

[0084]

[Etching device]

The etching method of the present disclosure can be achieved using, for example, an etching device as described below. Such an etching device is another embodiment of the present disclosure.

An etching device according to the present disclosure includes a stage for placing a substrate thereon, an HF gas supply unit for supplying (I) HF gas to the substrate, and a surface treatment gas supply unit for supplying a surface treatment gas composition containing (II) a surface treatment material to the substrate. The etching device according to the present disclosure may further include an inert gas supply unit for supplying an inert gas into the chamber. Moreover, the etching device according to the present disclosure may further include an additional gas supply unit for supplying NH_3 , an organic amine compound, or an alcohol into the chamber.

[0085]

FIG. 3 shows a schematic diagram schematically illustrating an etching device according to an embodiment of the present disclosure.

An etching device 100 shown in FIG. 3 includes a chamber 110 for placing a substrate 113 thereon, that is connected to an HF gas supply unit 140 for supplying HF gas, a surface treatment gas supply unit 150 for supplying a surface treatment gas composition containing a surface treatment material, an inert gas supply unit 130 for supplying an inert gas, and an additional gas supply unit 160 for supplying NH_3 , an organic amine compound, or an alcohol, and a heating means 111 for heating the chamber 110. Note that the etching device 100 may not include the inert gas supply unit 130 or the additional gas supply unit 160.

[0086]

The etching device 100 further includes a control unit that is not shown in the figure. For example, the control unit includes a computer and is provided with a program, a memory, and a CPU. The program incorporates a group of steps to implement a series of operations in the first etching method or the second etching method. In accordance with the program, operations may be performed such as adjusting the temperature of the substrate 113, opening or closing the valves of the supply units, adjusting the flow rates of the gases, and adjusting the pressure in the chamber 110. This program is stored on a computer storage medium, such as a compact disk, a hard disk, a magneto-optical disk, or a memory card, and installed in the control unit.

[0087]

The chamber 110 is provided with a stage 112 for placing the substrate 113 thereon. The chamber 110 is not limited as long as it is resistant to the HF gas used and is depressurizable to a predetermined pressure. Usually, a general chamber or the like
5 included in a semiconductor etching device may be used. The supply pipes for supplying the etching gas and other pipes, for example, are also not limited as long as they are resistant to HF gas, and any general pipes can be used.

[0088]

10 The HF gas supply unit 140 supplies HF gas through pipes 141 and 145 to a pipe 121 while controlling the amount of supply using valves 143 and 144 and a flow rate controlling means 142.

[0089]

15 The surface treatment gas supply unit 150 supplies a surface treatment gas composition through pipes 151 and 155 to the pipe 121 while controlling the amount of supply using valves 153 and 154 and a flow rate controlling means 152.

[0090]

The inert gas supply unit 130 supplies an inert gas through pipes 131 and 135 to the pipe 121 while controlling the amount of supply using valves 133 and 134 and a flow rate controlling means 132.

20 [0091]

The additional gas supply unit 160 supplies NH_3 , an organic amine compound, or an alcohol through pipes 161 and 165 to the pipe 161 while controlling the amount of supply using valves 163 and 164 and a flow rate controlling means 162. The additional gas supply unit 160 may supply a mixture of NH_3 , an organic amine compound, and/or
25 an alcohol. The etching device 100 may include a plurality of additional gas supply units 160.

[0092]

30 The heating means 111 for heating the chamber 110 is disposed outside the chamber 110. A heater (not shown) may also be provided as a second heating means inside the stage 112. Here, when a plurality of stages are placed in the chamber 110, each stage may be provided with a heater so that the temperature of the substrate on each stage can be individually set to a predetermined temperature.

[0093]

35 A gas discharge means for discharging the reacted gas is disposed on one side of the chamber 110. The reacted gas can be discharged from the chamber 110 through a

pipe 122 by a vacuum pump 127 of the gas discharge means. The reacted gas may be collected by a liquid nitrogen trap (not shown) disposed between the pipe 122 and the vacuum pump 127. Valves 125 and 126 may be disposed in the pipes 121 and 122, respectively, to control the pressure. Moreover, in FIG. 3, the reference signs PI (123 and 124) each represent a pressure gauge. According to its readings, the control unit

[0094]

Etching methods are specifically described using the etching device 100 as an example.

10 [First etching method using the etching device]

In a first etching method according to the present disclosure, (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material are simultaneously brought into contact with the substrate. In other words, the surface treatment material-containing etching gas

15 composition containing HF gas and a surface treatment material is brought into contact with the films to be etched.

[0095]

In the first etching method, first, the substrate 113 provided with the films to be etched, including the film at least containing Si and O and the film at least containing Si and N, is placed in the chamber 110. Next, the interiors of the chamber 110, the pipes 121 and 122, the pipes 131 and 135, the pipes 141 and 145, and the pipes 151 and 155 are each subjected to vacuum evacuation to a predetermined pressure using the vacuum pump 127, and then the substrate 113 is heated with the heating means 111.

When the temperature of the substrate 113 reaches a predetermined

25 temperature, HF gas and a surface treatment gas composition are supplied at respective predetermined flow rates from the HF gas supply unit 140 and the surface treatment gas supply unit 150, respectively, to the pipe 121. Here, an inert gas may be supplied at a predetermined flow rate from the inert gas supply unit 130 to the pipe 121. Moreover, NH₃, an organic amine compound, or an alcohol may be supplied at a predetermined

30 flow rate from the additional gas supply unit 160 to the pipe 121.

[0096]

The HF gas and the surface treatment gas composition are mixed according to a specific formulation and then supplied to the chamber 110. The mixed surface treatment material-containing etching gas composition is introduced into the chamber

35 110 while controlling the pressure in the chamber 110 to a predetermined pressure.

Etching is performed by reacting the surface treatment material-containing etching gas composition with the films to be etched for a predetermined period of time. This etching method allows for plasmaless etching without plasma and eliminates the need to excite the surface treatment material-containing etching gas composition using plasma or the like during the etching. The flow rate of the surface treatment material-containing etching gas composition can be appropriately set according to the volume of the chamber, the pressure in the chamber, or other conditions.

[0097]

Here, etching associated with plasma means that gas or the like at about 0.01 to 1.33 kPa, for example, is introduced into a reactor, and a high-frequency power is applied to an outer coil or a counter electrode to generate low-temperature gas plasma in the reactor, thereby performing etching with the active chemical species such as ions or radicals formed in the plasma.

The etching method according to the present disclosure can provide contact with the gas without plasma to perform dry etching without generating the gas plasma described above.

[0098]

After completion of the etching step, the heating with the heating means 111 is stopped to lower the temperature. At the same time, the vacuum pump 127 is stopped, followed by purging with the inert gas to release the vacuum. As described above, the first etching method using the etching device can selectively etch the film containing Si and O, among the films to be etched.

[0099]

(Etching conditions in first etching method)

In the first etching method according to the present disclosure, the temperature of the films to be etched when the surface treatment material-containing etching gas composition is brought into contact with the films to be etched may be any temperature at which the surface treatment material-containing etching gas composition can react with the film containing Si and O. In particular, the temperature of the film to be etched as a target of removal is preferably equal to the process temperature (substrate temperature) described above. The substrate temperature is substantially equal to the temperature of the films to be etched, but the substrate temperature or the temperature of the films to be etched may be increased by the reaction heat during the etching reaction. In the present disclosure, at least the process temperature (substrate

temperature), specifically, the temperature in the chamber or the temperature of the stage on which the substrate is placed, is preferably within the above temperature range.
[0100]

Moreover, upon bringing the surface treatment material-containing etching gas composition into contact with the films to be etched, the pressure in the chamber (pressure during etching) in which the substrate with the films to be etched is placed is not limited, and it is usually within a range of 0.1 Pa to 101.3 kPa.
[0101]

The pressure in the chamber in the etching step is preferably 1 Pa to 100 kPa, more preferably 1 Pa to 10 kPa, still more preferably 10 Pa or higher and lower than 1 kPa, most preferably 100 Pa or higher and lower than 1 kPa, because, at such a pressure, selective etching of the film containing Si and O tends to be more suitably achieved.
[0102]

The processing time of the etching step is not limited. In view of the efficiency of the semiconductor device manufacturing process, the processing time is preferably within 60 minutes. Here, the processing time of the etching step refers to the period of time from when the surface treatment material-containing etching gas composition is introduced into the chamber in which the substrate is placed to when the surface treatment material-containing etching gas composition is discharged from the chamber using a vacuum pump or other devices to terminate the etching process.
[0103]

[Second etching method using the etching device]

A second etching method according to the present disclosure includes a surface treatment step including bringing (II) the surface treatment gas composition containing a surface treatment material into contact with the substrate, and an etching step including bringing (I) the etching gas composition containing HF gas into contact with the substrate after the surface treatment step.
[0104]

In the second etching method, first, the substrate 113 provided with the film at least containing Si and O and the film at least containing Si and N is placed in the chamber 110. Next, the interiors of the chamber 110, the pipes 121 and 122, the pipes 131 and 135, the pipes 141 and 145, and the pipes 151 and 155 are each subjected to vacuum evacuation to a predetermined pressure using the vacuum pump 127, and then the substrate 113 is heated with the heating means 111.

[0105]

When the temperature of the substrate 113 reaches a predetermined temperature, first, a surface treatment gas composition is supplied at a predetermined flow rate from the surface treatment gas supply unit 150 to the pipe 121. Here, an inert gas may be supplied at a predetermined flow rate from the inert gas supply unit 130 to the pipe 121. The pressure in the chamber 110 is controlled to a predetermined pressure while introducing the surface treatment gas composition or both the surface treatment gas composition and the inert gas into the chamber 110. The surface treatment gas composition is introduced into the chamber 110 for a predetermined period of time to allow the surface treatment gas composition to adsorb onto (react with) the films to be etched.

After vacuum evacuation of the gas containing the surface treatment gas composition, HF gas is supplied at a predetermined flow rate from the HF gas supply unit 140 to the pipe 121. Here, the inert gas may be supplied at a predetermined flow rate from the inert gas supply unit 130 to the pipe 121. Moreover, NH_3 , an organic amine compound, or an alcohol may be supplied at a predetermined flow rate from the additional gas supply unit 160 to the pipe 121. The pressure in the chamber 110 is controlled to a predetermined pressure while introducing HF gas or both HF gas and another gas into the chamber 110. HF gas is introduced into the chamber 110 for a predetermined period of time, whereby the film containing Si and O, among the films to be etched, can be selectively etched.

[0106]

The second etching method according to the present disclosure may include repeated cycles, each of which includes the surface treatment step, including introducing the surface treatment gas composition into the chamber 110, and the etching step, including introducing HF gas into the chamber 110.

In the second etching method according to the present disclosure, the etching conditions in one cycle may be set to predetermined conditions to control the thickness of the film to be etched that can be etched in one cycle. Thus, the thickness of the film to be etched that can be etched in one cycle may be set to be small to precisely control the etching thickness.

The second etching method according to the present disclosure preferably includes performing the surface treatment step, followed by the step of subjecting the interior of the chamber to a reduced pressure condition, and then performing the etching step. Also preferably, every cycle includes the step of subjecting the interior of the chamber to a reduced pressure condition.

[0107]

Note that the second etching method also allows for plasmaless etching without plasma and eliminates the need to excite the etching gas using plasma or the like during the etching. The flow rates of the HF gas and the surface treatment gas composition
5 may be appropriately set according to the volume of the chamber, the pressure in the chamber, or other conditions.

[0108]

As described above, the second etching method of the present disclosure using the etching device can provide contact with the gas without plasma to perform dry
10 etching without generating the gas plasma described above.

[0109]

After completion of the etching step, the heating with the heating means 111 is stopped to lower the temperature. At the same time, the vacuum pump 127 is stopped, followed by purging with the inert gas to release the vacuum. The second etching
15 method using the etching device can selectively etch the film containing Si and O, among the films to be etched.

[0110]

(Etching conditions in second etching method)

In the second etching method according to the present disclosure, the
20 temperature of the films to be etched may be any temperature at which (II) the surface treatment gas composition containing a surface treatment material can react with the film containing Si and N and the film containing Si and O, and also at which (I) the etching gas composition containing HF gas can react with the film containing Si and O. In particular, the temperature of the film to be etched as a target of removal is preferably
25 equal to the process temperature (substrate temperature) described above. Desirably, the temperature of the films to be etched in the surface treatment step is equal to the temperature of the films to be etched in the etching step. The substrate temperature is substantially equal to the temperature of the films to be etched, but the substrate temperature or the temperature of the films to be etched may be increased by the
30 reaction heat during the etching reaction. In the present disclosure, at least the process temperature (substrate temperature), specifically, the temperature in the chamber or the temperature of the stage on which the substrate is placed, is preferably within the above temperature range.

[0111]

Moreover, the pressure in the chamber in the etching step is as described for the etching conditions in the first etching method.

Meanwhile, the pressure in the chamber in the surface treatment step is preferably 1 Pa to 100 kPa, more preferably 10 Pa to 10 kPa, still more preferably 10 Pa to 2 kPa, and may be 1 kPa to 20 kPa. At such a pressure, selective etching of the film containing Si and O tends to be more suitably achieved.

[0112]

The processing time in the surface treatment step and the etching step is not limited, but the processing time in one cycle of the surface treatment step is preferably within 60 minutes, while the processing time in one cycle of the etching step is preferably within 60 minutes. Here, the processing time of the etching step refers to the period of time from when the etching gas is introduced into the chamber in which the substrate is placed to when the etching gas is discharged from the chamber using a vacuum pump or other devices to terminate the etching process.

[0113]

[Method of manufacturing semiconductor device]

The etching method of the present disclosure described above may be used as a method that includes applying the above-described etching method to the substrate having the film at least containing Si and O and the film at least containing Si and N, preferably a substrate having a silicon nitride film and a silicon oxide film, to selectively etch the film containing Si and O, preferably the silicon oxide film. When the etching method of the present disclosure is used to selectively etch the film containing Si and O, preferably the silicon oxide film, on the substrate, a semiconductor device can be manufactured at a low cost.

A method for manufacturing a semiconductor device according to the present disclosure is characterized by including applying the above-described etching method to the substrate having the film at least containing Si and O and the film at least containing Si and N, preferably a substrate having a silicon nitride film and a silicon oxide film, to selectively etch the film containing Si and O, preferably the silicon oxide film. The step of reacting the substrate having the film at least containing Si and O and the film at least containing Si and N, preferably a substrate having a silicon nitride film and a silicon oxide film, with HF gas and the surface treatment material in the composition (II) to selectively etch the film containing Si and O, preferably the silicon oxide film, without plasma can be carried out by the etching method of the present disclosure described

above. The substrate may further have a polycrystalline silicon film. The substrate is preferably a silicon substrate.

EXAMPLES

5 [0114]

The present disclosure is described in detail below with reference to examples, but the present disclosure is not limited to the examples.

First, a silicon wafer provided with an SiN film and a silicon wafer provided with an SiO₂ film were prepared as substrates to be processed. The film thicknesses of
10 each substrate to be processed before and after the etching process were measured with a spectroscopic ellipsometer (product name: SE-2000, Semilab Japan KK) to determine the etching amount and the SiO₂/SiN selection ratio.

[0115]

(Simultaneous flow method)

15 [Example 1-1]

An etching device 100 as shown in FIG. 3 was used. First, the substrates to be processed were placed on a stage in a chamber. After sufficiently vacuuming the interior of the chamber, the temperature of the stage was adjusted to 120°C. The temperature of each substrate was the same as the temperature of the stage and was
20 substantially equal to the temperature of each film to be etched. Next, N₂ gas was allowed to flow through the chamber to sufficiently dry the interior. Subsequently, HF gas, trimethylamine gas, and CH₃COCl gas were allowed to flow through the chamber for one minute. The flow rate of each gas and the pressure in the chamber at that point are as shown in Table 1. Finally, after vacuuming the interior of the chamber and
25 purging with N₂ gas, the substrates to be processed were taken out. Table 1 shows the results. The silicon wafer provided with an SiN film and the silicon wafer provided with an SiO₂ film as the substrates to be processed were all placed in the same chamber and simultaneously subjected to the etching process. Note that HF gas and trimethylamine gas constitute an etching gas composition (I); CH₃COCl gas constitutes
30 a surface treatment gas composition (II); and HF gas, trimethylamine gas, and CH₃COCl gas constitute a surface treatment material-containing etching gas composition.

[0116]

[Example 1-2] to [Example 1-4], [Comparative Example 1-1]

A test was performed under the same conditions as in Example 1-1, except that the conditions were changed as indicated in Table 1. Table 1 shows the results.

[0117]

(Alternating flow method)

5 [Example 2-1]

First, the substrates to be processed were placed on a stage in a chamber. After sufficiently vacuuming the interior of the chamber, the temperature of the stage was adjusted to 120°C. Next, N₂ gas was allowed to flow through the chamber to sufficiently dry the interior.

10 (A) Thereafter, CH₃I gas was allowed to flow through the chamber under the conditions indicated in Table 2, followed by sufficient vacuuming and purging with N₂ gas.

(B) Next, HF gas and trimethylamine gas were allowed to flow through the chamber under the conditions indicated in Table 2, followed by sufficient vacuuming and purging with N₂ gas.

15 Finally, the substrates to be processed were taken out from the chamber. Table 2 shows the results. Note that the etching rate was determined relative to the flow time of the etching gas. The silicon wafer with an SiN film and the silicon wafer with an SiO₂ film as the substrates to be processed were all placed in the same chamber and simultaneously processed. Moreover, any condition that is not specified here is as described in Example 1-1.

[0118]

[Example 2-2] to [Example 2-24], [Comparative Example 2-1] to [Comparative Example 2-3]

25 A test was performed as in Example 2-1, except that the conditions were changed as indicated in Table 2. Table 2 shows the results.

[0119]

[Table 1]

		Processing conditions							Post-etch evaluation result				
		Etching gas	Additive gas ①	Additive gas ②	Etching gas flow rate	Additive gas ① flow rate	Additive gas ② flow rate	Pressure	Temperature	Time	SiO ₂ etching amount	SiN etching amount	SiO ₂ /SiN selection ratio
					sccm			Pa	deg.C	min	nm	nm	-
Example 1-1	HF	Trimethylamine		CH ₃ COCl	50	50	10	100	120	1	55	<0.1	> 550
Example 1-2				CF ₃ SO ₂ F							98	0.2	490
Example 1-3				CF ₃ SO ₂ Cl							76	0.2	380
Example 1-4				FSO ₂ NCO							68	0.2	340
Comparative Example 1-1				Ar							95	8	12

[0120]

[Table 2]

	Pre-treatment conditions						Etching conditions						Post-etch evaluation result			
	Pre-treatment gas	Flow rate sccm	Pressure Pa	Temperature deg.C	Time min	Etching additive gas	Flow rate sccm	Etching gas	Flow rate sccm	Pressure Pa	Temperature deg.C	Time min	SiO ₂ etching amount nm	SiN etching amount nm	SiO ₂ /SiN selection ratio	
Example 2-1	CH ₃ I	50	2000	120	5	Trimethylamine	50	HF	50	100	120	1	98	0.1	980	
Example 2-2		50	100	120	5	Trimethylamine	50	HF	50	100	120	1	98	0.2	490	
Example 2-3		50	10,000	120	5	Trimethylamine	50	HF	50	100	120	1	98	0.1	980	
Example 2-4		50	2000	200	5	Trimethylamine	50	HF	50	100	200	1	258	0.2	1290	
Example 2-5		50	2000	60	5	Trimethylamine	50	HF	50	100	60	1	43	<0.1	>430	
Example 2-6		50	2000	120	5	Trimethylamine	50	HF	50	800	120	1	384	0.2	1920	
Example 2-7		50	2000	120	5	Ethanol	50	HF	50	800	120	1	251	0.3	837	
Example 2-8	tBu-NCO	50	2000	120	5	Trimethylamine	50	HF	50	100	120	1	103	0.1	1030	
Example 2-9	FSO ₂ NCO	50	2000	120	5	Trimethylamine	50	HF	50	100	120	1	123	<0.1	>1230	
Example 2-10	CH ₃ COC1	50	2000	120	5	Trimethylamine	50	HF	50	100	120	1	72	<0.1	>720	
Example 2-11	CF ₃ SO ₂ F	50	2000	120	5	Trimethylamine	50	HF	50	100	120	1	101	0.2	505	
Example 2-12	CF ₃ SO ₂ Cl	50	2000	120	5	Trimethylamine	50	HF	50	100	120	1	89	0.2	445	
Example 2-13	CH ₃ I	50	2000	120	5	Ammonia	50	HF	50	100	120	1	21	0.1	210	
Example 2-14	tBu-NCO	50	2000	120	5	Ammonia	50	HF	50	100	120	1	24	0.1	240	
Example 2-15	FSO ₂ NCO	50	2000	120	5	Ammonia	50	HF	50	100	120	1	31	<0.1	>310	
Example 2-16	CH ₃ COC1	50	2000	120	5	Ammonia	50	HF	50	100	120	1	18	<0.1	>180	
Example 2-17	CF ₃ SO ₂ F	50	2000	120	5	Ammonia	50	HF	50	100	120	1	25	0.2	125	
Example 2-18	CF ₃ SO ₂ Cl	50	2000	120	5	Ammonia	50	HF	50	100	120	1	29	0.2	145	
Example 2-19	CH ₃ I	50	2000	120	5	Ar	50	HF	50	100	120	1	5	<0.1	>50	
Example 2-20	tBu-NCO	50	2000	120	5	Ar	50	HF	50	100	120	1	6	<0.1	>60	
Example 2-21	FSO ₂ NCO	50	2000	120	5	Ar	50	HF	50	100	120	1	7	<0.1	>70	
Example 2-22	CH ₃ COC1	50	2000	120	5	Ar	50	HF	50	100	120	1	2	<0.1	>20	
Example 2-23	CF ₃ SO ₂ F	50	2000	120	5	Ar	50	HF	50	100	120	1	6	<0.1	>60	
Example 2-24	CF ₃ SO ₂ Cl	50	2000	120	5	Ar	50	HF	50	100	120	1	8	<0.1	>80	
Comparative Example 2-1	Ar	50	2000	120	5	Trimethylamine	50	HF	50	100	120	1	96	9	10.7	
Comparative Example 2-2	Ar	50	2000	120	5	Ammonia	50	HF	50	100	120	1	23	19	1.2	
Comparative Example 2-3	Ar	50	2000	120	5	Ar	50	HF	50	100	120	1	9	7	1.3	

[0121]

As shown in Tables 1 and 2, in the examples in which (I) an etching gas composition containing HF gas and (II) a surface treatment gas composition containing a surface treatment material were brought into contact with a substrate having a film at least containing Si and O and a film at least containing Si and N, selective etching of the film containing Si and O was achieved. The results demonstrate that the use of (I) the etching gas composition containing HF gas together with (II) the surface treatment gas composition containing a surface treatment material enables selective etching of the film containing Si and O.

REFERENCE SIGNS LIST

[0122]

100 etching device

110 chamber

111 heating means

112 stage

113 substrate

121, 122 pipe

123, 124 PI (pressure gauge)

125, 126 valve

127 vacuum pump

130 inert gas supply unit

131, 135 pipe

132 flow rate controlling means

133, 134 valve

140 HF gas supply unit

141, 145 pipe

142 flow rate controlling means

143, 144 valve

150 surface treatment gas supply unit

151, 155 pipe

152 flow rate controlling means

153, 154 valve

160 additional gas supply unit

161, 165 pipe

162 flow rate controlling means

163, 164 valve

CLAIMS

[Claim 1] An etching method, comprising

bringing (I) an etching gas composition containing HF gas and (II) a surface
 5 treatment gas composition containing a surface treatment material into contact with a
 substrate having a film at least containing Si and O and not containing N and a film at
 least containing Si and N to selectively etch the film containing Si and O and not
 containing N.

10 [Claim 2] The etching method according to claim 1,
 wherein the surface treatment material chemically modifies a surface of the
 film containing Si and N.

[Claim 3] The etching method according to claim 1,
 15 wherein the surface treatment material chemically modifies a surface of the
 film containing Si and N and a surface of the film containing Si and O and not
 containing N.

[Claim 4] The etching method according to claim 1,
 20 wherein the surface treatment material is a compound represented by Formula
 [A]:

R-X [A]

wherein R represents a monovalent group, and X represents Br, Cl, I, F, -C(O)Cl, -
 C(O)F, -C(O)H, or -NCO.

25 [Claim 5] The etching method according to claim 4,
 wherein R in the Formula [A] represents a group unreactive with HF.

[Claim 6] The etching method according to claim 5,
 30 wherein R in the Formula [A] represents a group free from at least one of an
 amino group or a hydroxy group.

[Claim 7] The etching method according to claim 4,
 wherein R in the Formula [A] represents an electron-withdrawing group.

35

[Claim 8] The etching method according to claim 7,

wherein R in the Formula [A] represents: XSO_2^- where X represents a halogen atom; XCO^- where X represents a halogen atom; or $\text{C}_n\text{R}^1_{2n+1}\text{SO}_2^-$ where R^1 's are the same as or different from each other and each represent a hydrogen atom or a halogen atom, and n represents an integer of not more than 6.

[Claim 9] The etching method according to claim 7,

wherein R in the Formula [A] represents FSO_2^- , FCO^- , CF_3SO_2^- , or CH_3SO_2^- .

[Claim 10] The etching method according to claim 4,

wherein R in the Formula [A] represents: $\text{C}_n\text{R}^2_{2n+1}-$ where R^2 's are the same as or different from each other and each represent a hydrogen atom or a halogen atom, and n represents an integer of not more than 6; or $(\text{C}_n\text{R}^3_{2n+1})_3\text{Si}-$ where R^3 's are the same as or different from each other and each represent a hydrogen atom or a halogen atom, and n represents an integer of not more than 6.

[Claim 11] The etching method according to claim 4,

wherein R in the Formula [A] represents an alkyl group with 6 or less carbon atoms, or $(\text{CH}_3)_3\text{Si}-$.

[Claim 12] The etching method according to claim 1,

wherein the etching gas composition further contains at least one selected from the group consisting of an inert gas, NH_3 , an organic amine compound, and an alcohol.

[Claim 13] The etching method according to claim 1,

wherein the film containing Si and O and not containing N is selectively etched without plasma.

[Claim 14] The etching method according to claim 1,

wherein (I) the etching gas composition containing HF gas and (II) the surface treatment gas composition containing a surface treatment material are simultaneously brought into contact with the substrate.

[Claim 15] The etching method according to claim 1,

wherein the method comprises a surface treatment step including bringing (II) the surface treatment gas composition containing a surface treatment material into contact with the substrate, and an etching step including bringing (I) the etching gas composition containing HF gas into contact with the substrate after the surface treatment step.

[Claim 16] The etching method according to claim 1,
wherein a temperature of the substrate during the etching is 20°C to 300°C.

[Claim 17] The etching method according to claim 1,
wherein a pressure during the etching is 1 Pa to 10 kPa.

[Claim 18] The etching method according to claim 1,
wherein a pressure during the etching is 1 Pa or higher and lower than 1 kPa.

[Claim 19] The etching method according to claim 1,
wherein the film containing Si and O and not containing N is a silicon oxide (SiO) film.

[Claim 20] The etching method according to claim 1,
wherein the film containing Si and N is a silicon nitride (SiN) film.

[Claim 21] The etching method according to claim 1,
wherein in the substrate, the film containing Si and O and not containing N is a silicon oxide (SiO) film, the film containing Si and N is a silicon nitride (SiN) film, the silicon nitride film is adjacent to the silicon oxide film, and the silicon oxide film and the silicon nitride film are exposed.

[Claim 22] A method for manufacturing a semiconductor device, comprising applying the etching method according to any one of claims 1 to 21 to a substrate having a film at least containing Si and O and not containing N and a film at least containing Si and N to selectively etch the film containing Si and O and not containing N.

[Claim 23] A method for manufacturing a semiconductor device, comprising

applying the etching method according to any one of claims 1 to 21 to a substrate having a silicon nitride film and a silicon oxide film to selectively etch the silicon oxide film.

- 5 [Claim 24] An etching device, comprising
a stage for placing a substrate thereon,
(I) an HF gas supply unit for supplying HF gas to the substrate, and
(II) a surface treatment gas supply unit for supplying a surface treatment gas
composition containing a surface treatment material to the substrate.

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[Claim 25] A surface treatment gas composition, comprising a surface treatment material.

- [Claim 26] A surface treatment material-containing etching gas composition,
15 comprising HF gas and a surface treatment material.