



US012387940B2

(12) **United States Patent**
Suzuki et al.

(10) **Patent No.:** **US 12,387,940 B2**

(45) **Date of Patent:** ***Aug. 12, 2025**

(54) **DRY ETCHING METHOD**

(71) Applicant: **Central Glass Company, Limited**, Ube (JP)

(72) Inventors: **Shoi Suzuki**, Ube (JP); **Akifumi Yao**, Ube (JP)

(73) Assignee: **CENTRAL GLASS COMPANY, LIMITED**, Ube (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 533 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **17/677,367**

(22) Filed: **Feb. 22, 2022**

(65) **Prior Publication Data**

US 2022/0172956 A1 Jun. 2, 2022

Related U.S. Application Data

(62) Division of application No. 16/762,790, filed as application No. PCT/JP2018/039406 on Oct. 24, 2018, now Pat. No. 11,289,340.

(30) **Foreign Application Priority Data**

Nov. 14, 2017 (JP) 2017-218692

(51) **Int. Cl.**

H01L 21/311 (2006.01)

C09K 13/08 (2006.01)

(Continued)

(52) **U.S. Cl.**

CPC **H01L 21/31116** (2013.01); **C09K 13/08** (2013.01); **C23F 1/12** (2013.01); **H01L 21/3065** (2013.01)

(58) **Field of Classification Search**

CPC H01L 21/31116; H01L 21/3065; H01L 21/0217; H01L 21/02532; H01L 21/02595;

(Continued)

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,626,775 A 5/1997 Robert et al.
5,922,624 A 7/1999 Verhaverbeke et al.

(Continued)

FOREIGN PATENT DOCUMENTS

JP 8-59215 A 3/1996
JP 9-181054 A 7/1997

(Continued)

OTHER PUBLICATIONS

International Search Report (PCT/ISA/210) issued in PCT Application No. PCT/JP2018/039406 dated Dec. 11, 2018 with English translation (five (5) pages).

(Continued)

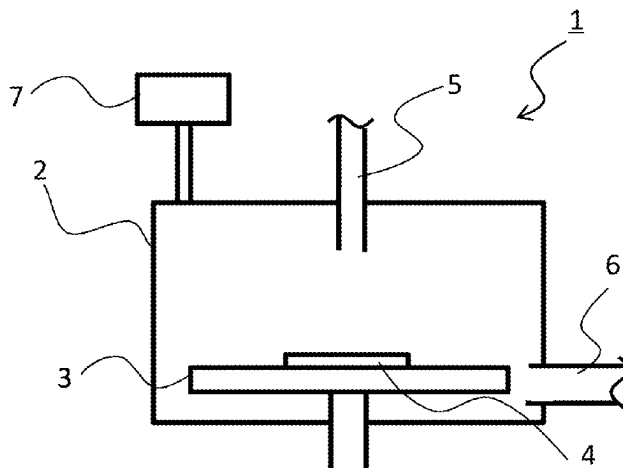
Primary Examiner — Anita K Alanko

(74) *Attorney, Agent, or Firm* — Crowell & Moring LLP

(57) **ABSTRACT**

A dry etching method according to the present invention includes etching silicon nitride by bringing a mixed gas containing hydrogen fluoride and a fluorine-containing carboxylic acid into contact with the silicon nitride in a plasma-less process at a temperature lower than 100° C. Preferably, the amount of the fluorine-containing carboxylic acid contained is 0.01 vol % or more based on the total amount of the hydrogen fluoride and the fluorine-containing carboxylic acid. Examples of the fluorine-containing carboxylic acid are monofluoroacetic acid, difluoroacetic acid, trifluoroacetic acid, difluoropropionic acid, pentafluoropropionic acid, pentafluorobutyric acid and the like. This dry etching method enables etching of the silicon nitride at a high

(Continued)



etching rate and shows a high selectivity ratio of the silicon nitride to silicon oxide and polycrystalline silicon while preventing damage to the silicon oxide.

2010/0197143 A1 8/2010 Nishimura et al.
2012/0231630 A1 9/2012 Takada et al.
2018/0337253 A1 11/2018 Bilodeau et al.

10 Claims, 1 Drawing Sheet

(51) Int. Cl.

C23F 1/12 (2006.01)

H01L 21/3065 (2006.01)

(58) Field of Classification Search

CPC ... H01L 21/67069; C09K 13/00; C09K 13/08;
C23F 1/12

See application file for complete search history.

FOREIGN PATENT DOCUMENTS

JP 9-509531 A 9/1997
JP 2000-58505 A 2/2000
JP 2002-158181 A 5/2002
JP 2008-187105 A 8/2008
JP 2009-43973 A 2/2009
JP 2009043973 A * 2/2009
JP 2009-129980 A 6/2009
JP 2010-509777 A 3/2010
JP 2010-182730 A 8/2010
JP 2011-119310 A 6/2011
JP 2014-197603 A 10/2014
WO WO 2017/091572 A1 6/2017

(56)

References Cited

U.S. PATENT DOCUMENTS

6,140,203 A 10/2000 Schuegraf
6,159,859 A 12/2000 Robertson, III et al.
6,221,680 B1 4/2001 Hakey et al.
2003/0001134 A1 1/2003 Sekiya et al.
2005/0189575 A1 9/2005 Torek
2008/0125342 A1 5/2008 Visintin et al.
2008/0179292 A1 7/2008 Nishimura et al.

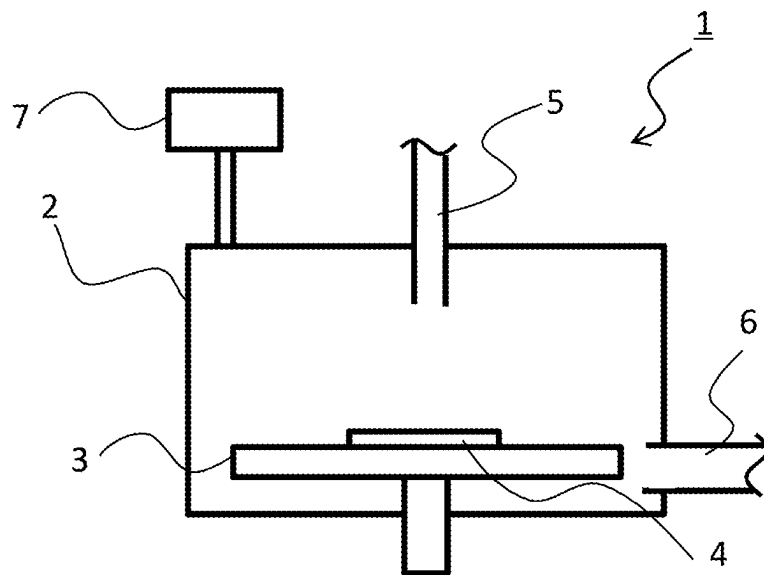
OTHER PUBLICATIONS

Japanese-language Written Opinion (PCT/ISA/237) issued in PCT Application No. PCT/JP2018/039406 dated Dec. 11, 2018 (five (5) pages).

Taiwanese-language Office Action issued in Taiwanese Application No. 107139099 dated Apr. 29, 2018 (six (6) pages).

Taiwanese-language Office Action issued in Taiwanese Application No. 107139099 dated Oct. 9, 2018 (four (4) pages).

* cited by examiner



DRY ETCHING METHOD

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. patent application Ser. No. 16/762,790, filed May 8, 2020, which is a 371 of International Application No. PCT/JP2018/039406, filed Oct. 24, 2018, which claims priority to Japanese Patent Application No. 2017-218692, filed Nov. 14, 2017, the disclosures of all of which are expressly incorporated by reference herein.

FIELD OF THE INVENTION

The present disclosure relates to a dry etching method for etching, with a HF-containing gas, silicon nitride (SiN) as an etching target.

BACKGROUND ART

In the case of a semiconductor device having a structure in which silicon nitride (hereinafter sometimes abbreviated as "SiN") is located adjacent to silicon oxide (hereinafter sometimes abbreviated as "SiO₂") and/or polycrystalline silicon (hereinafter sometimes abbreviated as "p-Si") on a single crystal silicon substrate, the manufacturing of the semiconductor device includes selective etching of SiN.

Wet etching using hot phosphoric acid and dry etching using a plasma generated from a compound gas such as CF₄ are known as methods of etching SiN.

For example, Patent Document 1 discloses a dry etching method using an etching gas containing a gas of a compound represented by the formula: CH_xF_{4-x} (where x is 2 or 3), an oxygen gas etc. for selective etching of SiN in the presence of SiO₂, metal silicide or silicon. It is specifically described in Patent Document 1 that the dry etching method is adapted for selectively etching a SiN film through an opening of a SiO₂ film while using a p-Si film under the SiN film as an etch stop layer.

In the wet etching using hot phosphoric acid and in the dry etching using a plasma, however, not only SiN but also SiO₂ are etched. These etching techniques thus face the problem that it is difficult to ensure the selectivity ratio of SiN to SiO₂.

Then, Patent Document 2 discloses a method of etching a SiN film formed on a SiO₂ film by feeding a HF gas in a plasma-less heating environment.

As a solution to the problem of a low etching rate of the SiN film on the SiO₂ film in the etching method of Patent Document 2, Patent Document 3 discloses the addition of a F₂ gas to the HF gas.

When the SiN film is etched with the HF gas as disclosed in Patent Document 2, the SiO₂ film is also etched with HF and NH₃ generated as a reaction product so that it is not possible to attain a high selectivity ratio SiN/SiO₂. When the F₂ gas is added as disclosed in Patent Document 3, p-Si is etched with F₂ and the like so that it is not possible to attain a high selectivity ratio SiN/Si.

Patent Document 4 then discloses a method of etching a SiN film with a mixed gas of HF and NO at a high selectivity ratio relative to a SiO₂ film and/or p-Si film. It is specifically described in this patent document that the addition of NO as an etching gas (assist gas) allows prevention of damage to the SiO₂ film.

PRIOR ART DOCUMENTS

Patent Documents

- 5 Patent Document 1: Japanese Laid-Open Patent Publication No. H8-59215
- Patent Document 2: Japanese Laid-Open Patent Publication No. 2008-187105 (also published as Japanese Patent No. 4833878)
- 10 Patent Document 3: Japanese Laid-Open Patent Publication No. 2010-182730 (also published as Japanese Patent No. 5210191)
- Patent Document 4: Japanese Laid-Open Patent Publication No. 2014-197603 (also published as Japanese Patent No. 6073172)

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

- 20 The etching method of Patent Document 4 provides an improvement in the selectivity ratio of SiN, but cannot sufficiently prevent damage to the SiO₂ film because of the generation of NH₃ as a by-product during etching of SiN. With the recent progress of fine processing, a surface roughness caused by such damage is becoming a non-negligible problem. There has been a demand for improvements to avoid this damage problem.

For prevention of damage to SiO₂, it is conceivable to dilute the mixed etching gas of HF and NO with the addition of an inert gas such as N₂, Ar or He. However, this technique presents a new problem that the originally intended etching rate of SiN becomes significantly lowered. In order to complement such a low etching rate, it is conceivable to lengthen the processing time of the etching step and thereby secure the etching amount. The time of exposure of the SiO₂ to the etching gas however increases with increase in processing time, which results in the development of damage to the SiO₂ surface. Consequently, the addition of the inert gas does not arrive at a solution to the damage problem.

In view of the foregoing, it is an object of the present disclosure to provide a dry etching method capable of etching SiN at a high etching rate and, in the case of manufacturing a semiconductor device on a silicon substrate, achieving a high selectivity ratio of SiN to SiO₂ or p-Si and preventing damage to SiO₂.

Means for Solving the Problems

As a result of extensive researches, the present inventors have found that: a fluorine-containing carboxylic acid has the capabilities of trapping NH₃ generated as a by-product during etching of SiN with HF, causing no etching of SiO₂ and p-Si, and not interfering etching of SiN with HF; and it is possible to solve the above-mentioned problems by etching SiN with a gas containing HF and the fluorine-containing carboxylic acid. The present disclosure has been accomplished based on this finding.

Accordingly, the present disclosure provides a dry etching method of etching silicon nitride, comprising: bringing a mixed gas containing hydrogen fluoride and a fluorine-containing carboxylic acid into contact with the silicon nitride in a plasma-less process at a temperature lower than 100° C.

Effects of the Invention

The present disclosure provides the effect of etching SiN at a high etching rate and, in the case of manufacturing a

semiconductor device on a silicon substrate, achieving a high selectivity ratio of SiN to SiO₂ and p-Si and preventing damage to SiO₂.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of a reaction device used in Examples and Comparative Examples.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Hereinafter, the present disclosure will be described in detail below. It should be understood that: the following description of features of the present disclosure is merely embodiments of the present disclosure and is not intended to limit the present disclosure to these embodiments; and various changes and modifications can be made to the embodiments within the spirit and scope of the present disclosure.

A dry etching method according to the present disclosure is for etching silicon nitride by using a mixed gas containing hydrogen fluoride and a fluorine-containing carboxylic acid as a dry etching gas composition and bringing this dry etching gas composition into contact with the silicon nitride in a plasma-less process at a temperature lower than 100° C.

The content amount of the fluorine-containing carboxylic acid in the mixed gas is preferably 0.01 vol % or more based on the total amount of the hydrogen fluoride and the fluorine-containing carboxylic acid.

The upper limit of the content amount of the fluorine-containing carboxylic acid is naturally determined depending on the vapor pressures of the respective compounds and the process pressure. When the process pressure is lower than the vapor pressure of the fluorine-containing carboxylic acid, the concentration of the HF decreases as the content amount of the fluorine-containing carboxylic acid becomes large. This leads to an insufficiency of the HF, which makes it impossible to ensure the sufficient etching rate of SiN. It is thus preferable to control the maximum content amount of the fluorine-containing carboxylic acid such that the concentration ratio of the HF to the fluorine-containing carboxylic acid (HF/fluorine-containing carboxylic acid) is 1 or higher.

The content amount of the fluorine-containing carboxylic acid in the mixed gas is more preferably 0.01 vol % to 50 vol %, still more preferably 0.1 vol % to 30 vol %, yet more preferably 3 vol % to 15 vol %, based on the total amount of the hydrogen fluoride and the fluorine-containing carboxylic acid.

Examples of the fluorine-containing carboxylic acid usable in the dry etching method according to the present disclosure are monofluoroacetic acid (CH₂FCOOH), difluoroacetic acid (CHF₂COOH), trifluoroacetic acid (CF₃COOH), difluoropropionic acid (CH₃CF₂COOH), pentafluoropropionic acid (C₂F₅COOH), heptafluorobutyric acid (C₃F₇COOH) and the like. These carboxylic acid gases are preferred because each can be supplied as a gas that exhibits an acid dissociation constant pK_a lower than or equal to 3.2, which is an acid dissociation constant of the HF, so as to allow preferential trapping of NH₃, has a certain vapor pressure in the temperature range of 20 to 100° C. and does not get decomposed in this temperature range. It is feasible to vaporize the fluorine-containing carboxylic acid by heating, depressurization, bubbling etc. and supply the fluorine-containing carboxylic acid in vaporized form.

Although the fluorine-containing carboxylic acid is not necessarily an anhydride, the content of water in the fluorine-containing carboxylic acid is preferably lower than 1 mass %. It is because, when the water content of the fluorine-containing carboxylic acid is high, the fluorine-containing carboxylic acid generates H₂O by vaporization thereof so that there may occur etching of SiO₂ by combination of the HF and H₂O.

The mixed gas may contain, as a dilute gas, an inert gas that does not react with the HF or fluorine-containing carboxylic acid. It is feasible to adjust the etching rate of the SiN according to the content amount of the inert gas in the mixed gas. Examples of the inert gas are N₂, He, Ne, Ar, Kr and the like. The content amount of the inert gas in the mixed gas is generally in the range of 0 vol % to 90 vol %.

The process temperature at which the silicon nitride and the dry etching gas composition are brought into contact with each other is preferably higher than or equal to 20° C. and lower than 100° C., more preferably higher than or equal to 40° C. and lower than or equal to 80° C., still more preferably higher than or equal to 50° C. and lower than or equal to 75° C.

The process pressure is preferably in the range of 0.1 kPa to 101.3 kPa, more preferably 1 kPa to 50 kPa.

The silicon nitride as the etching target of the present disclosure refers to a compound represented by SiN_x (where x is greater than 0 and smaller than or equal to 2) such as Si₃N₄.

It is preferable that, in the case where the dry etching gas composition according to the present disclosure is brought into contact with silicon nitride, silicon oxide and polycrystalline silicon, the SiN-to-SiO₂ etching selectivity ratio (SiN/SiO₂) and the SiN-to-p-Si etching selectivity ratio (SiN/Si) are each 100 or higher. Further, it is preferable that the etching rate of SiN is at a high level of 100 nm/min or higher.

The dry etching method according to the present disclosure enables high-rate, high-selectivity etching of the SiN without causing damage to the SiO₂ and p-Si. Moreover, the dry etching method according to the present disclosure can be implemented in a plasma-less process at a low temperature of lower 100° C.

When NH₃ is generated as a by-product during the etching of the SiN, there occurs a side reaction in which the NH₃ reacts with the HF to form NH₄F. This leads to a decrease in the concentration of the HF at the SiN surface and thus becomes a cause of lowering the etching rate of the SiN. In the dry etching method according to the present disclosure, however, it is expected that the occurrence of the above side reaction is prevented by the addition of the fluorine-containing carboxylic acid whereby the lowering of the etching rate is suppressed.

In the case where a trace amount of water is contained in the HF or in the case where absorbed water is present on the SiO₂ surface, the etching of the SiO₂ may proceed by the combined action of the trace water and HF. In the dry etching method according to the present disclosure, it is expected that the trace water is removed by the addition of the fluorine-containing carboxylic acid whereby the etching of the SiO₂ is further prevented.

In the case of manufacturing a semiconductor device on a silicon substrate, the dry etching method according to the present disclosure is applicable to the selective etching of SiN from the structure in which SiN is adjacent to SiO₂ and/or p-Si or in which SiO₂ and/or p-Si and SiN are exposed. Examples of such a structure are those in which a SiO₂ and/or p-Si film is covered by a SiN film and in which

5

a SiO₂ film, a SiN film and a p-Si film are laminated to one another. For example, the dry etching method according to the present disclosure can be applied to the manufacturing of a three-dimensional memory by forming a through hole in a laminated film of SiO₂ and SiN, supplying the etching gas composition through the through hole and thereby, while leaving the SiO₂, selectively etching the SiN such that the three-dimensional memory has a configuration in which a plurality of SiO₂ layers are arranged in parallel to each other with a clearance held therebetween.

EXAMPLES

The present disclosure will be described in more detail below by way of the following examples and comparative examples. It should be understood that the present disclosure is not limited to the following examples.

FIG. 1 is a schematic view of a reaction device 1 used in each of the examples and comparative examples. In the reaction device, a stage 3 with a heater function was

6

After the etching, the etching rate was respectively determined from changes in thicknesses of the p-Si film of the silicon wafer A, the SiO₂ film of the silicon wafer B and the SiN film of the silicon wafer C before and after the etching. The SiN-to-p-Si etching rate ratio SiN/p-Si and the SiN-to-SiO₂ etching rate ratio SiN/SiO₂ were also determined.

Furthermore, the surface roughness Ra of the SiO₂ film was evaluated by measurement with an atomic force microscope (AFM). The term "surface roughness Ra" as used herein refers to an arithmetic average roughness according to JIS B 0601:1994.

Examples 2 to 5 and Comparative Examples 1 to 3

The etching test and evaluation were carried out in the same manner as in Example 1, except that the kind and concentration of the additive gas were changed.

The etching conditions and evaluation results of Examples 1 to 5 and Comparative Examples 1 to 3 are shown in TABLE 1.

TABLE 1

	Process pressure	Process temp.	Kind of additive gas	Conc. [vol %] of additive gas	Conc. [vol %] of HF	SiN etching rate [nm/min]	SiN/p-Si	SiN/SiO ₂	Surface roughness Ra [μm] of SiO ₂ film
Example 1	10 kPa	70° C.	CF ₃ COOH	0.1	99.9	839	>1000	156	<1
Example 2	10 kPa	70° C.	CF ₃ COOH	1	99	794	>1000	181	<1
Example 3	10 kPa	70° C.	CF ₃ COOH	5	95	729	>1000	281	<1
Example 4	10 kPa	70° C.	CF ₃ COOH	10	90	554	>1000	241	<1
Example 5	10 kPa	70° C.	C ₂ F ₅ COOH	5	95	712	>1000	264	<1
Comparative Example 1	10 kPa	70° C.	none	0	100	845	>1000	82	2.2
Comparative Example 2	10 kPa	70° C.	F ₂	1	99	1004	2	1674	<1
Comparative Example 3	10 kPa	70° C.	NO	10	90	699	>1000	233	3.6

arranged in a chamber 2. A heater was also disposed around the chamber 2 so as to heat a wall of the chamber. A gas supply unit was arranged to supply a dry etching gas composition into the chamber 2 although not specifically shown in the drawing. A gas introduction hole 5 was provided on an upper part of the chamber 2 such that the dry etching gas composition was introduced into the chamber through the gas introduction hole 5 and brought into contact with a sample 4 placed on the stage 3. The gas inside the chamber 2 was discharged through a gas discharge line 6. Although not specifically shown in the drawing, a vacuum exhaust pump (as a vacuum exhaust unit) is connected to the gas discharge line so as to depressurize the inside of the chamber 2. Further, a pressure gauge 7 is disposed on the chamber 7.

Example 1

As the sample 4, a silicon wafer A with a p-Si film, a silicon wafer B with a SiO₂ film and a silicon wafer C with a SiN film were placed on the stage 3. Herein, each of the SiN film and the p-Si film was formed by a CVD method; and the SiO₂ film was formed by performing thermal oxidation treatment on a surface of the silicon wafer. The temperature of the stage 3 was set to 70° C. A mixed gas of HF and CF₃COOH (as prepared by mixing 99.9 vol % of HF with 0.1 vol % of CF₃COOH) was fed in a total amount of 1000 scm to the sample. The pressure inside the chamber 2 was set to 10 kPa. The sample was then subjected to etching.

In Examples 1 to 5, the SiN film was selectively etched as compared to the p-Si and SiO₂ films. Since there was almost no damage to the surface of the SiO₂ film, the surface of the SiO₂ film was smaller than 1 μm in roughness Ra and was very smooth.

On the other hand, in Comparative Example 1 where the etching was done only with the HF gas as in Patent Document 2, not only the SiN film but also the SiO₂ film were etched so that the etching rate ratio SiN/SiO₂ was low. In Comparative Example 2 where the etching was done with the mixed gas of HF and F₂ as in Patent Document 3, the p-Si film was etched with the F₂ gas so that the etching rate ratio SiN/p-Si was low. In Comparative Example 3 where the etching was done with mixed gas of HF and NO as in Patent Document 4, there occurred damage to the SiO₂ film so that the surface of the SiO₂ film after the etching was rough.

DESCRIPTION OF REFERENCE NUMERALS

- 1: Reaction device
- 2: Chamber
- 3: Stage
- 4: Sample
- 5: Gas introduction port
- 6: Gas discharge line
- 7: Pressure gauge

7

The invention claimed is:

1. A dry etching method, comprising:

bringing, into contact with a structure comprising silicon nitride and silicon oxide, a mixed gas comprising hydrogen fluoride and a fluorine-containing carboxylic acid in a plasma-less process at a temperature lower than 100° C., thereby selectively etching the silicon nitride,

wherein an etching selectivity ratio of the silicon nitride to the silicon oxide (SiN/SiO₂) is 100 or higher.

2. The dry etching method according to claim 1, wherein an amount of the fluorine-containing carboxylic acid in the mixed gas is 0.01 vol % or more based on a total amount of the hydrogen fluoride and the fluorine-containing carboxylic acid.

3. The dry etching method according to claim 2, wherein the amount of the fluorine-containing carboxylic acid in the mixed gas is 0.1 vol % to 30 vol % based on the total amount of the hydrogen fluoride and the fluorine-containing carboxylic acid.

4. The dry etching method according to claim 3, wherein the amount of the fluorine-containing carboxylic acid in the mixed gas is 0.1 vol % to 10 vol % based on the total amount of the hydrogen fluoride and the fluorine-containing carboxylic acid.

5. The dry etching method according to claim 1, wherein an etching rate of the silicon nitride is 100 nm/min or higher.

8

6. The dry etching method according to claim 1, wherein the mixed gas further comprises an inert gas.

7. The dry etching method according to claim 1, wherein the fluorine-containing carboxylic acid is at least one kind selected from the group consisting of mono-fluoroacetic acid, difluoroacetic acid, trifluoroacetic acid, difluoropropionic acid, pentafluoropropionic acid, and heptafluorobutyric acid.

8. The dry etching method according to claim 1, wherein the structure further comprises polycrystalline silicon so that the polycrystalline silicon is etched by contact with the mixed gas, and

wherein an etching selectivity ratio of the silicon nitride to the polycrystalline silicon (SiN/Si) is 100 or higher.

9. The dry etching method according to claim 1, wherein the fluorine-containing carboxylic acid is trifluoroacetic acid or pentafluoropropionic acid, and wherein an amount of the fluorine-containing carboxylic acid in the mixed gas is 0.1 vol % to 30 vol % based on a total amount of the hydrogen fluoride and the fluorine-containing carboxylic acid.

10. A manufacturing method of a semiconductor device, comprising:

applying the dry etching method according to claim 1 to a silicon substrate with a silicon oxide film, a polycrystalline silicon film, and a silicon nitride film, thereby selectively etching the silicon nitride film.

* * * * *