

Description

Title of Invention: ETCHING METHOD

Technical Field

[0001]

The present invention relates to an etching method, and particularly to a process technology for an isotropic dry etching method to be used in a step of removing a silicon nitride film from a three-dimensional memory, which is a semiconductor element, or the like.

Background Art

[0002]

In semiconductor devices, the demand for lower power consumption and increased storage capacity has led to further miniaturization and three-dimensional device structures. In manufacturing of a device with a three-dimensional structure, due to the three-dimensional and complex structure, in addition to "vertical (anisotropic) etching" which is performed in a direction perpendicular to a wafer surface, "isotropic etching" which can be performed also in a lateral direction is frequently used. As the isotropic etching, a wet process using a chemical has been performed but, with the advancement of miniaturization, problems such as pattern collapse due to surface tension of the chemical and etching residue in a minute gap have become apparent. Furthermore, the need for a large amount of chemical treatment also presents a problem in terms of environmental load and cost. Therefore, in the isotropic etching, it is necessary to replace the wet process using

the chemical with a dry process using no chemical.

[0003]

In semiconductor devices, silicon nitride films are used mainly, and therefore examples are known in which a dry etching process therefor uses a hydrogen fluoride (HF) gas, while using no plasma. For example, Patent Literature 1 describes a method in which a hydrogen fluoride gas is supplied at a wafer temperature of 60°C or more and 200°C or less to etch a silicon nitride film without damaging a thermal oxide film. Meanwhile, Patent Literature 2 describes a method in which a pressure in a chamber is controlled to 1333 Pa or more and a hydrogen fluoride gas is supplied at a temperature of 10 to 120°C to selectively etch a silicon nitride film with respect to a silicon oxide film.

[0004]

Patent Literature 3 describes, as a known example in which another component is added to a HF gas, a method in which a nitric oxide (NO) gas or/and an ozone gas and a HF gas are supplied to thereby selectively etch a silicon nitride film. Meanwhile, Patent Literature 4 describes a method in which a mixed gas containing a fluorine-containing carboxylic acid and a HF gas is brought into contact with a silicon nitride film at a temperature of less than 100°C without plasma to thereby etch the silicon nitride film.

[0005]

Patent Literature 5 discloses, as an example of etching using a fluorine-containing gas other than a HF gas, a method which selectively etches a silicon nitride film with respect to a silicon oxide film by using a chlorine trifluoride (ClF₃) gas. Meanwhile,

Patent Literature 6 discloses a method which selectively etches a silicon nitride film by using a fluorine-containing etching gas selected from the group consisting of nitrosyl fluoride (FNO), trifluoronitrogen oxide (F₃NO), nitryl fluoride (FNO₂), and combinations thereof. Patent Literature 7 further discloses etching of a silicon nitride film performed using an etching gas containing a halogen fluoride, which is a compound of bromine or iodine and fluoride, under a pressure of 1 Pa or more and 80 kPa or less without using plasma.

[0006]

Patent Literature 8 describes, as an example using radicals derived from any plasma, a method in which a fluorine-containing gas, an alcohol gas, an O₂ gas, and an inert gas each excited by an external plasma are supplied to thereby selectively etch a silicon nitride film with respect to silicon and/or a silicon oxide film. Meanwhile, Patent Literature 9 discloses a selective etching method for a silicon nitride film which includes a step of introducing a gas containing H and F and a step of selectively introducing radicals of an insert gas into a process space. Furthermore, Patent Literature 10 describes selective lateral etching of a silicon nitride film in a structure in which a silicon nitride film and a silicon oxide film are stacked, which is performed at -20°C or less and by using a precursor including oxygen and a precursor including fluorine, each generated from a plasma.

[0007]

Each of Patent Literature 6 and Patent Literature 10 describes that the silicon nitride films are selectively etched

laterally from a sidewall of a high-aspect-ratio opening that is formed in a structure in which the silicon nitride films and silicon oxide films of a 3D-NAND device serving as a three-dimensional memory are stacked in multiple layers.

[0008]

Meanwhile, Patent Literature 11 discloses that ammonium hexafluorosilicate[(NH₄)₂SiF₆], ammonium hydrogen fluoride[NH₄HF₂], or the like formed on a silicon nitride film is heated with a lamp or the like to be removed.

Citation List

Patent Literature

[0009]

Patent Literature 1: Japanese Unexamined Patent Application
Publication No. 2008-187105

Patent Literature 2: Japanese Unexamined Patent Application
Publication No. 2018-207088

Patent Literature 3: Japanese Unexamined Patent Application
Publication No. 2014-197603

Patent Literature 4: Japanese Unexamined Patent Application
Publication No. 2019-091890

Patent Literature 5: Japanese Unexamined Patent Application
Publication No. 2016-58544

Patent Literature 6: Japanese Unexamined Patent Application
Publication (Translation of PCT Application) No. 2021-509538

Patent Literature 7: International Publication WO 2021/079780

Patent Literature 8: Japanese Unexamined Patent Application
Publication No. 2015-228433

Patent Literature 9: Japanese Unexamined Patent Application
Publication No. 2019-012759

Patent Literature 10: US Patent No. 10319603

Patent Literature 11: Japanese Unexamined Patent Application
Publication No. 2005-161493

Summary of Invention

Technical Problem

[0010]

For example, in stacked layer processing of a 3D-NAND flash memory, which is a semiconductor element with a three-dimensional structure, and processing around a gate of a Fin FET, a technology of etching a silicon nitride film isotropically and highly selectively with respect to a polycrystalline silicon film or a silicon oxide film with atomic-layer-level controllability is in demand. Especially in a 3D-NAND structure, a large number of silicon oxide films (SiO_2 films) and silicon nitride films (SiN) are alternately stacked, and there is a step of selectively and isotropically etching small amounts of the silicon nitride films in a lateral direction from a structure obtained by forming a deep hole shape or a trench shape in the stacked layers.

[0011]

As described in the background art, in wet etching using an aqueous hydrofluoric acid solution or a buffered aqueous hydrofluoric acid solution, there is a problem of etching residue in a minute gap and a problem of poor etching controllability. Meanwhile, in dry etching using radicals, a rate at which highly reactive radicals serving as an active species are supplied is

limited, and accordingly, in a case of a deep hole shape or a trench shape, a problem is encountered in which an etching amount of a silicon nitride film in a top portion closer to a top surface thereof increases and an etching amount of the silicon nitride films in a bottom portion closer to a bottom decreases, resulting in a top-bottom difference in etching amount. In a case of gas etching using no plasma, a problem is encountered in which it is difficult to accurately etch a silicon nitride film with a high selectivity to a silicon oxide film, and a shape of a silicon oxide film portion intended to be left deteriorates. In a case of a deep hole shape or a trench shape, a problem is encountered in which, as a result of re-adhering of a reaction product to a top portion or the like, an etching amount of a top portion of the silicon nitride film is small to result in a top-bottom difference in etching amount.

[0012]

The present invention has been achieved in view of the problem described above, and provides a method that can etch a silicon nitride film with high accuracy and a high selectivity to a silicon oxide film without causing deterioration in a shape of the silicon oxide film intended to be left and further reduces a top-bottom difference in etching amount of the silicon nitride films.

Solution to Problem

[0013]

An etching method according to the present invention is a dry etching method that supplies a process gas into a process chamber to etch, without using a plasma, a film structure formed in advance

on a wafer placed in the process chamber to include stacked layers of silicon oxide films and a silicon nitride film vertically sandwiched between the silicon oxide films such that an end portion of each of the stacked layers forms a sidewall of a trench or a hole, and the etching method includes the steps of: (a) causing a hydrogen fluoride gas to react at a predetermined temperature to form a reacting layer on the silicon nitride film; (b) causing a polar solvent gas to flow to process the reacting layer formed in the step (a); and (c) performing heating at a temperature higher than that in the step (a) in a state where the hydrogen fluoride gas is not allowed to flow, to evaporate and remove the reacting layer formed in the step (a) and processed in the step (b). The step (a), the step (b), and the step (c) are repeatedly performed a plurality of times to laterally etch the silicon nitride film from the end portion.

[0014]

Further, an etching method of another embodiment of the present invention is a dry etching method that supplies a process gas into a process chamber to etch, without using a plasma, a film structure formed in advance on a wafer placed in the process chamber to include stacked layers of silicon oxide films and a silicon nitride film vertically sandwiched the silicon oxide films such that an end portion of each of the stacked layers forms a sidewall of a trench or a hole, and the etching method includes the steps of: (a) causing a hydrogen fluoride gas to react at a predetermined temperature to form a reacting layer on the silicon nitride film; and (d) performing heating at a temperature higher

than that in the step (a) in a state where a polar solvent gas is caused to flow while the hydrogen fluoride gas is not allowed to flow, to evaporate and remove the reacting layer formed in the step (a). The step (a) and the step (d) are repeatedly performed a plurality of times to laterally etch the silicon nitride film from the end portion.

Advantageous Effects of Invention

[0015]

According to the present invention, it is possible to provide a method that can etch a silicon nitride film with high accuracy and a high selectivity to a silicon oxide film without causing deterioration in a shape of the silicon oxide film intended to be left and further reduces a top-bottom difference in etching amount of the silicon nitride films. Objects, configurations, and effects other than the above will be apparent from the description of the following embodiments.

Brief Description of Drawings

[0016]

FIG. 1 is a graph illustrating respective etching thicknesses of a silicon nitride film and a silicon oxide film and a selectivity therebetween with respect to a methanol flow rate when a methanol gas flow is performed in a step according to a first embodiment of the present invention.

FIG. 2 is a graph illustrating respective etching thicknesses of a silicon nitride film and a silicon oxide film and a selectivity therebetween with respect to time when IR lamp irradiation is performed simultaneously with a methanol gas flow in

a step according to a third embodiment of the present invention.

FIG. 3 is a cross-sectional view illustrating an outline of an etching apparatus according to the first embodiment of the present invention.

FIG. 4 is a cross-sectional view illustrating an outline of an etching apparatus according to a fourth embodiment of the present invention.

FIG. 5-1 is a flow chart of an etching method for a silicon nitride film according to the embodiments of the present invention.

FIG. 5-2 is a flow chart of the etching method for the silicon nitride film according to the embodiment of the present invention.

FIG. 6-1 is a flow chart of an etching method for a silicon nitride film according to the embodiment of the present invention.

FIG. 6-2 is a flow chart of the etching method for the silicon nitride film according to the embodiment of the present invention.

FIG. 7-1 is a time chart schematically illustrating a flow of an operation with a lapse of time in an etching process according to Example 1 of the present invention.

FIG. 7-2 is a time chart schematically illustrating a flow of an operation with a lapse of time in an etching process according to Example 2 of the present invention.

FIG. 8 is a time chart schematically illustrating a flow of an operation with a lapse of time in an etching process according to Example 3 of the present invention.

FIG. 9-1 is a time chart schematically illustrating a flow of

an operation with a lapse of time in an etching process according to Example 4 of the present invention.

FIG. 9-2 is a time chart schematically illustrating a flow of an operation with a lapse of time in an etching process according to Example 5 of the present invention.

FIG. 10 is a partial cross-sectional view for illustrating the progress of an etching process performed on stacked layers including silicon nitride films and silicon oxide films according to an example of the present invention, which illustrates a pre-etching state.

FIG. 11 is a partial cross-sectional view for illustrating the progress of the etching process performed on the stacked layers including the silicon nitride films and the silicon oxide films according to the example of the present invention, which illustrates a case where ideal etching was performed.

FIG. 12 is a partial cross-sectional view for illustrating the progress of the etching process performed on the stacked layers including the silicon nitride films and the silicon oxide films according to the example of the present invention, which illustrates a case where selectivity is low.

FIG. 13 is a partial cross-sectional view for illustrating the progress of the etching process performed on the stacked layers including the silicon nitride films and the silicon oxide films according to the example of the present invention, which illustrates a case where a selectivity is relatively high, a corner of each of the silicon oxide film retains a rectangular shape, an etching amount is smaller in a top portion than in a bottom

portion, and a thickness of each of portions with the silicon oxide film is smaller in the bottom portion.

FIG. 14 is a partial cross-sectional view for illustrating the progress of the etching process performed on the stacked layers including the silicon nitride films and the silicon oxide films according to the example of the present invention, which illustrates a case where the selectivity is relatively high, and each of the silicon oxide films retains the rectangular shape in each of the top portion and the bottom portion.

Description of Embodiments

[0017]

An embodiment of the present invention will be described below with reference to the drawings. It should be noted that in the following description, the same components are indicated by the same reference numerals, and the repeated description thereof may be omitted. Note that, to clarify the illustration, the drawings may be schematic in comparison with the actual embodiment, but this is only exemplary, and is not intended to limit the interpretation of the present invention.

[0018]

The present invention relates to a process technology for an isotropic dry etching method to be used in a step of removing a silicon nitride film from a three-dimensional memory, which is a semiconductor element, or the like. The present inventors have conducted examination of dry etching using a hydrogen fluoride gas (HF) using no plasma for a sample in which a slit is formed in each of a single-layer silicon nitride film, a single-layer silicon

oxide film, and stacked layers thereof described later, which are formed by plasma CVD (Chemical Vapor Deposition). The following will describe, as a dry etching method according to the present invention, a dry etching method in which a process gas (hydrogen fluoride gas or polar solvent gas) is supplied into a process chamber to etch, without using a plasma, a film structure (see FIG. 10 and FIG. 11) formed in advance over a wafer disposed in the process chamber to include stacked layers of silicon oxide films and silicon nitride films vertically sandwiched therebetween such that end portions of the stacked layers form a sidewall of a trench or a hole.

Example 1

[0019]

[Configuration Example 1 of Etching Apparatus]

First, referring to FIG. 3, an outline of an etching apparatus 100 according to Example 1 of the present invention, including an entire configuration thereof, will be described. A process chamber 1 of the etching apparatus 100 is configured to include a base chamber (referred to also as a chamber) 11, and a wafer stage (referred to also as a stage or mounting table) 3 for mounting a wafer 2 as a sample is disposed therein. At an upper center portion of the process chamber 1, a shower plate 23 is disposed, and a process gas is supplied to the process chamber 1 via the shower plate 23.

[0020]

A flow rate of the process gas to be supplied is adjusted by a mass flow controller 52 disposed for each gas species in a mass

flow box 50. On a downstream side of the mass flow controller 52, a gas distributor 51 is disposed such that a gas to be supplied to the vicinity of a center of the process chamber 1 and a gas to be supplied to the vicinity of an outer periphery thereof when the process chamber 1 is viewed from above can be supplied by independently controlling respective flow rates and compositions thereof and that a spatial distribution of partial pressures of the process gas can be controlled in detail. In FIG. 3, argon (Ar), nitrogen (N₂), helium (He), hydrogen fluoride (HF), and methanol (CH₃OH) which is alcohol serving as a polar solvent gas are shown. Note that another process gas other than these can also be supplied. Particularly as the polar solvent, water, ethanol, isopropanol, or the like can also be used. However, in a case of using water, the water is frozen at 0°C or lower, so that it is necessary to use a temperature higher than 0°C as a stage temperature of a wafer stage 3.

[0021]

To a lower portion of the process chamber 1, in order to reduce a pressure in the process chamber 1, an exhaust means 15 is connected via a vacuum exhaust pipe 16. It is assumed that the exhaust means (exhaust device) 15 is formed of, e.g., a turbo molecular pump, a mechanical booster pump, or a dry pump. In addition, to adjust the pressure in the process chamber 1, a pressure adjustment means (pressure adjustment device) 14 is disposed on an upstream side of the exhaust means 15.

[0022]

Above the wafer stage 3, an IR lamp unit for heating the

wafer 2 is disposed. The IR lamp unit can be configured to mainly include an IR lamp 60, a reflecting plate 61, and an IR light transmission window 72. For the IR lamp 60, a circle-type (circular or annular) lamp is used. It is assumed that that light emitted from the IR lamp 60 is light (referred to as IR light herein) which is mainly in visible to infrared light regions. In the present example, as the IR lamp 60, lamps 60-1, 60-2, and 60-3 for three laps are disposed, but lamps for two laps, four laps, or the like may also be disposed. Over the IR lamp 60, the reflecting plate 61 for reflecting the IR light downward (in a direction in which the wafer is disposed) is disposed. Preferably, a material of the IR transmission window 72 does not include alkali metal ions or the like, transmits light in the infrared region, and has a heat resistance and, as a specific material, quartz is preferred.

[0023]

To the IR lamp 60, an IR lamp power source 73 is connected, and a high frequency cut filter 74 is disposed midway therebetween to prevent noise of high frequency power from flowing into the IR lamp power source 73. The IR lamp power source 73 also has a function of being able to independently control power to be supplied to the IR lamps 60-1, 60-2, and 60-3 to allow a radial distribution of an amount of heating of the wafer 2 to be adjusted (illustration of wiring is partly omitted). At a center of the IR lamp unit, a space for disposing the shower plate 23 for process gas introduction is formed.

[0024]

The wafer 3 has a flow path 39 for a refrigerant for cooling

the wafer stage 3 formed in the inside thereof, and the refrigerant is circulated and supplied by a chiller 38. In the present invention, as the chiller, a chiller capable of temperature control from, e.g., -50°C to 50°C is used. As a type of the wafer stage 3, a proximity cooling type is used herein.

[0025]

A surface of the wafer stage 3 is provided with projections 56, and the wafer 2 is mounted, while being supported by points formed of the projections 56. A height of each of the projections 56 is preferably about 0.1 mm to 1.0 mm, and the number of the supporting points is preferably 3 or more. Specifically, the 0.25 mm projections 56 the number of which is 6 were used herein. As a material of the wafer stage 3, a corrosion-resistant metal or metal compound with a high heat conductivity can be used herein.

[0026]

Due to a gap (clearance or space) resulting from the projections 56 and present between the wafer stage 3 and the wafer 2, by causing an inert gas such as He, Ar, or N_2 to flow throughout the entire chamber 11, the inert gas flows through the gap to cause heat conduction and cool the wafer 2. Note that, as a type of cooling of the wafer 2, an electrostatic adsorption type that will be described in Example 4 can also be used.

[0027]

Inside the wafer stage 3, a thermocouple 70 for measuring a temperature of the wafer stage 3 is disposed, and the thermocouple 70 is connected to a thermocouple thermometer 71. The temperature of the wafer stage 3 measured by the thermocouple thermometer 71

using thermocouple 70 was within $\pm 1^{\circ}\text{C}$ difference from the set temperature of the chiller 38.

[0028]

The proximity-cooled wafer stage 3 described above has an advantage of achieving lower cost due to a simple structure thereof. However, in a vacuum state where the chamber 11 is in an idling state, the wafer 2 is thermally insulated, and accordingly needs a given time after the inert gas is caused to flow until cooling begins. In addition, it has been proved that, since distances from the chiller 38 to the refrigerant and the wafer 2 are relatively long, a real wafer temperature tends to be higher than the set temperature of the chiller 38. As a result of measuring the temperature of the wafer with the thermocouple during cooling or during a process, it was found that the real wafer temperature was about 5°C higher than the set temperature of the chiller 38.

[0029]

Note that, as a mechanism for cooling the wafer stage 3 to be used in the etching apparatus 100 of the present invention, not only a mechanism that circulates the refrigerant, but also a Peltier element, which is a thermoelectric conversion device, or the like can also be used.

[0030]

The etching apparatus 100 used in the present invention can heat the inside of the chamber 11 except for the wafer stage 3 exposed to the hydrogen fluoride (HF) gas, such as the process chamber 1. For example, as the temperature, about 40°C to 120°C

can be used. Thus, it is possible to prevent the hydrogen fluoride (HF) gas or the like from adsorbing to the inside of the chamber 11 and minimize corrosion of the inside of the chamber 11.

[0031]

In the present invention, a HF gas under 50 Pa to 1000 Pa is used at a stage temperature of 40°C to -50°C. It is considered that, depending on the stage temperature of the wafer stage 3, the HF gas or the polar solvent in use may be aggregated on the silicon nitride film to be solidified or liquefied. As a result, in a case of using the electrostatic adsorption method, when the solidification or liquefaction occurs even at a back surface of the wafer 2, it is possible that a seal band for a back-side cooling gas may be broken to cause leakage of a cooling gas such as, e.g., He and result in an electrostatic chuck error. By contrast, the proximity-cooling stage 3 originally had the gap and therefore, even when the solidification or liquefaction of the HF or the polar solvent occurred, the wafer stage 3 is error-free, and stable processing was possible.

[0032]

In addition, in the electrostatic adsorption method, the space between the wafer 2 and the stage 3 is narrow and therefore, when the solidification or liquefaction of the HF or the polar solvent in use occurs, the wafer 2 is likely to stick to the wafer 3 under surface tension. Accordingly, a problem may occur in that, when the wafer 2 is raised with a pusher pin during dechucking of the wafer 2, the wafer 2 may be broken. As a solution to this also, the proximity cooling type having the 0.25 mm gap between the

wafer 2 and the stage 3 is used herein to be able to alleviate the problem of the sticking of the wafer 2 to the stage resulting from the liquefaction of the HF.

[0033]

As in the present invention, in the application of a process using a low temperature, there is a possibility that condensation may occur at a component inside the electrostatic chuck electrode serving as a cooling source which is in contact with an ambient atmosphere, and a short circuit may occur in an electric circuit such as that of a power supply unit. From this viewpoint also, a structure of the proximity-cooling stage 3 having simplified in-electrode components has an advantage.

[0034]

[Flow 1 of Etching Process]

Next, referring to FIG. 3, FIG. 5-1, and FIG. 7-1, a flow of an etching process (etching step) using a hydrogenfluoride gas and using no plasma and proposed in the present invention will be described. This flow is that of a dry etching method in which a process gas is supplied into a process chamber 1 to etch, without using a plasma, a film structure (see FIG. 10 and FIG. 11) formed in advance over a wafer 2 disposed in the process chamber 1 to include stacked layers of silicon oxide films and silicon nitride films vertically sandwiched between the silicon oxide films such that end portions of the stacked layers form a sidewall of a trench or a hole. First, after the wafer 2 is transported to the process chamber 1 via a transportation port (not shown) provided in the process chamber 1, the wafer 2 is left in place on the projections

56 provided at the wafer stage 3.

[0035]

Then, an Ar gas for wafer cooling is supplied to the wafer 2 via the mass flow controller 52, the gas distributor 51, and the shower plate 23 to perform the wafer cooling in S101 in FIG. 5-1. Since the Ar gas functions for heat transmission to the wafer 2 and as a dilution gas for diluting the HF gas, S101 and S102 in FIG. 5-1 are simultaneously performed herein. Note that a flow rate of the Ar gas can be changed when the wafer is to be cooled and when the Ar gas is to be used as the dilution gas. It is possible to allow the dilution Ar gas to flow continuously until the etching process is ended or alternatively prevent the dilution Ar gas from flowing. Instead of the Ar gas, an N₂ gas can also be used as the inert gas.

[0036]

Subsequently, in S103 in FIG. 5-1, the HF gas was supplied in a predetermined amount and for a predetermined time period to the process chamber 1, while heating was simultaneously performed, to form a reacting layer. As a heating type, heating using the IR (infrared) lamp 60 is used herein. A wafer temperature obtained as a result of the cooling using the stage 3 and the heating using the IR lamp 60 is preferably 30°C or more and 55°C or less, and is more preferably 35°C or more and 50°C or less. The film thickness of the reacting layer can be controlled by using a total pressure or a HF partial pressure and a heating temperature, and by using herein an output of the IR lamp, a time period, the number of repetitions, and the like. When the wafer temperature described previously is

lower than 30°C, the reacting layer is not satisfactorily formed, and consequently etching is less likely to occur. Conversely, when the wafer temperature is higher than 55°C, the reacting layer is excessively formed and therefore, when the reacting layer is to be decomposed and evaporated, the adjacent silicon oxide film is undesirably etched, and consequently a selectivity tends to decrease.

[0037]

In the present invention, a pressure to be used is preferably from about 10 Pa to 1000 Pa, preferably from 50 Pa to 1000 Pa, and is particularly preferably from 100 Pa to 1000 Pa. As the pressure is higher, the reacting layer on the silicon nitride film is more likely to be formed, and a temperature required for the formation decreases. Even when the pressure is increased, by controlling the output of the IR lamp 60, it is possible to form the reacting layer on the silicon nitride film without affecting the silicon oxide film.

[0038]

After the formation of the reacting layer is performed for a predetermined time, a step of stopping the supply of the HF gas and exhausting the HF gas remaining in a vapor phase is performed, though not shown in FIG. 5-1. In a case of performing vacuum exhaust, the pressure is preferably adjusted to 5 Pa or less. In other words, the step of exhausting the HF gas, while causing the inert gas to flow, is inserted between S103 and S104 subsequent thereto.

[0039]

Next, in S104 in FIG. 5-1, the polar solvent gas is caused to flow to modify the reacting layer, while partly removing the reacting layer. As the polar solvent gas, alcohol such as methanol, ethanol, or isopropanol or water can be used herein. An amount of the polar solvent gas caused to flow is preferably 0.1 to 3.0 L/min, and a time during which the polar solvent gas is caused to flow is preferably about 30 s to 300 s. A pressure at this time is preferably adjusted to about 10 to 1000 Pa. Note that, when the polar solvent gas is caused to flow, it is also possible to simultaneously cause an inert gas such as an Ar or nitrogen gas to flow as the dilution gas.

[0040]

After the formation of the reacting layer is performed for a predetermined time, the supply of the polar solvent gas is stopped, and the polar solvent gas remaining in the vapor phase is exhausted, though not shown in FIG. 5-1. In a case of performing vacuum exhaust, the pressure is preferably adjusted to 5 Pa or less. In other words, a step of exhausting the polar solvent gas, while causing the inert gas to flow, is inserted herein between S104 and S105 subsequent thereto.

[0041]

Next, in a state where the HF gas and the polar solvent gas are not allowed to flow, heating is performed to remove the reacting layer (S105 in FIG. 5-1). A temperature of the heating performed herein is preferably 70°C to 110°C (is 70°C or more and 110°C or less), and is more preferably 70°C to 100°C. When the heating temperature is lower than 70°C, the removal of the reacting

layer is insufficient, and accordingly the etching does not proceed. Meanwhile, in a case of using a temperature higher than 110°C as the heating temperature, the unintended etching of the adjacent silicon oxide film tends to occur during the decomposition and evaporation of the reacting layer, and there is a tendency that the selectivity decreases and the shape of the oxide film to be left deteriorates.

[0042]

During the removal, as a heating method, the IR lamp 60 is used. When the IR lamp 60 is used, an advantage that the heating can be performed within a short time is offered. Note that the heating method is not limited thereto, and it may also be possible to use, e.g., a method of heating the wafer stage 3 or a method of separately transporting the wafer 2 to an apparatus that performs only heating and performing a heating process. During irradiation with the IR lamp 60, an Ar gas or a nitrogen gas can be introduced. The heating process can also be performed a plurality of times as necessary. After the heating process, processing returns to S101 where wafer cooling is performed. Thereafter, on the assumption that steps from S101 to S105 are included in one cycle, the cycle is repeated N times. After the cycle is repeated a plurality of times until a required etching amount is obtained, the process is ended. The step S103 and the step S105 set herein the stage to a low temperature of -50°C or more and 0°C or less, perform lamp heating thereon to obtain a temperature of 30°C or more and 55°C or less for the stage in the step S103, and can further obtain a temperature of 70°C or more and 110°C or less as the stage

temperature in Step S105.

[0043]

FIG. 7-1 illustrates a time chart based on the flow shown in FIG. 5-1 when the etching apparatus 100 illustrated in FIG. 3 is used. One cycle includes a step of performing the IR lamp heating, while causing the HF gas to flow, a step of causing the polar solvent gas to flow, and the step of performing the IR lamp heating in a state where the HF gas and the polar solvent gas are not allowed to flow and, by repeating the cycle N times, the etching of the silicon nitride film is caused.

[0044]

[Etching Result 1]

A result of the etching using the hydrogen fluoride (HF) gas and using no plasma of the present invention will be shown. The temperature of the stage 3 was set to -30°C , and respective etching rates of a single-layer silicon nitride film (PE-SiN) and a single-layer silicon oxide film (PE-SiO₂), each formed by plasma CVD, were measured.

[0045]

As the base wafer 2, a high resistance substrate (31 Ωcm) having a diameter of 300 mm to which respective 2 cm square coupon samples of the silicon nitride film and the silicon oxide film had been bonded with a vacuum grease was used.

[0046]

After the foregoing wafer 2 was placed in the etching apparatus 100 illustrated in FIG. 3, the etching was performed according to the process flow shown in FIG. 5-1. To cool the

wafer, Ar was caused to flow at a flow rate of 1.4 L/min and under 900 Pa for 60 seconds. Then, in a state where the pressure was kept at 900 Pa, irradiation using the IR lamp 60 with an output of 60% was simultaneously performed for 60 seconds, while HF was introduced at 0.40 L/min and Ar serving as the dilution gas was introduced at 0.20 L/min. Thus, the reacting layer was formed on the silicon nitride film.

[0047]

Then, in a state where an exhaust valve (not shown) was 100% open, exhaust was performed for 120 seconds. By the exhaust operation, the fluorine gas and a reaction product are partially exhausted.

[0048]

Then, in a state where the stage 3 was kept at the set temperature, methanol serving as the polar solvent gas was caused to flow under a pressure of 300 Pa for 60 seconds. By causing the methanol gas to flow, the reacting layer was modified, while being partly removed. A flow rate of the methanol gas was set herein to 0.40, 0.80, and 1.2 L/min. By way of comparison, a flow not using the polar solvent gas was also performed herein.

[0049]

Then, in a state where the stage 3 was kept at the set temperature, Ar was caused to flow at 0.50 L/min, and the exhaust valve was 100% open, heating was performed with a lamp intensity of 70% for 40 seconds. By the process, the reacting layer modified by the polar solvent gas flow was removed. Then, back to the beginning, cooling was performed in a state where Ar was caused to

flow at 1.4 L/min and under a pressure of 900 Pa for 60 seconds. According to the flow in FIG. 5-1, the sequential process was performed herein in 10 cycles.

[0050]

Table 1-1 illustrates a result of actually measuring process temperatures during lamp irradiation by using a high resistance substrate with a thermocouple and using Ar in place of the HF gas. Reached temperatures are shown herein. The temperature measured when irradiation was performed for 60 seconds by using the IR lamp 60 used in the previous process with an output of 60% was 50°C. In addition, as a result of performing the temperature measurement for 40 seconds with an IR lamp output of 70% used as a heating process for removing the reacting layer, it was found that the reached temperature was 80°C.

[0051]

[Table 1-1]

Table 1-1: IR Lamp Output When Stage Temperature was -30°C and Temperature After 60 Seconds

IR output (%)	50	55	60	65
Temperature (°C)	30	38	50	57

FIG. 1 illustrates respective etching film thicknesses of a single-layer silicon nitride film (PE-SiN) and a single-layer silicon oxide film (PE-SiO₂, which is PE-SiO₂ in the table) each obtained after 10 cycles since the flow rate of the methanol gas flow was varied, and a selectivity of the silicon nitride film to

the silicon oxide film. FIG. 1 also shows a result when the methanol gas flow rate was set to 0 L/min and, and there was no methanol gas flow.

[0052]

By performing the methanol gas flow, the etching film thickness of the single-layer silicon nitride film was reduced, and the selectivity was consequently reduced. However, when the flow rate of the methanol gas flow was increased, the etching film thickness of the silicon nitride film increased and, when the flow rate was 1.2 L/min, an etching rate substantially equal to that when there was no methanol gas flow was observed. The selectivity was also slightly improved. It will be understood that an effect of the methanol gas flow is to contribute to any removal of the reacting layer.

[0053]

A film structure aimed at by the present invention is a structure required for a 3D-NAND in which a large number of silicon nitride films 103 and silicon oxide films 102 are alternately stacked on the substrate 101, and a deep hole or trench shape is formed therein as an opening portion 104, as illustrated in FIG. 10. The film thicknesses of the silicon nitride films 103 used herein are from several nanometers to 100 nm, while the film thicknesses of the silicon oxide films 102 used herein are from several nanometers to 100 nm. The number of these stacked layers is from several tens to several hundreds. A total thickness 105 of these stacked layers is from several micrometers to several tens of micrometers. A width 104W of the opening portion 104 is from

several tens of nanometers to several hundreds of nanometers. By the process of the present invention, the silicon nitride films 103 are laterally etched with a high selectivity to the silicon oxide films 102, as illustrated in an ideal cross-sectional view in FIG. 11. A dimension 106 of the lateral etching is from several nanometers to several tens of nanometers.

[0054]

In the lateral etching of the silicon nitride films 103, the selectivity to the silicon oxide films 102 is preferably 10 or more, and more preferably 20 or more. When the selectivity is low, etching of the silicon oxide films 102 that originally should not be etched simultaneously occurs, and consequently an end portion of each of the silicon oxide films 102 after the etching has a rounded shape as indicated by 111 in FIG. 12, not a rectangular shape, which adversely affects apparatus performance.

[0055]

Empirically, when the selectivity is 10 or more, or more preferably 20 or more, a shape closer to a rectangle as illustrated in FIG. 11 is obtained. When the selectivity is less than 5, the end portion of each of the silicon nitride films 103 unfavorably has a rounded shape, as indicated by 111 in FIG. 12.

[0056]

In an example of the present invention, by using a sample obtained by forming a slit-like space of 200 nm in a sample including a total of 40 layers of the silicon nitride films 103 (each having a film thickness of 30 nm) and the silicon oxide films 102 (each having a film thickness of 30 nm) which are alternately

stacked, etching characteristics were evaluated with a miniaturized pattern. By using conditions examined in FIG. 1 as experimental conditions, 10-cycle etching was performed. A result thereof is shown in Table 1-2.

[0057]

As a result, even when the etching proceeded with each of the silicon oxide films 102 to be left having a shape close to a rectangle, it was observed that, in the bottom portion, the film thickness of each of the portions with the silicon oxide films 102 was reduced as indicated by 112, though the etching of the silicon nitride film 103 efficiently occurred, as illustrated in FIG. 13. Meanwhile, in the top portion, as indicated by 111, there was no tendency that the film thickness of each of the portions with the silicon oxide films 102 was reduced, but there was a tendency that the etching amount 106 of the top was smaller than an etching amount 109 of the bottom.

[0058]

Table 1-2 shows an etching amount (obtained by subtracting an etching amount of each of the silicon oxide films 102 from an etching amount of each of the silicon nitride films 103), a selectivity (obtained by dividing the etching amount of the silicon nitride films 103 from an initial dimension thereof by the etching amount of the silicon oxide film 102) from a result of the slit pattern, and a thickness of the remaining SiO₂ (obtained by dividing a thickness 108 of a leading end 112 of the silicon oxide film 102 after the etching illustrated in FIG. 12 by an initial thickness 107 of the silicon oxide film 102). It is to be noted

herein that satisfactory etching conditions are a small top-bottom etching amount difference, a high selectivity, and the thickness of the remaining SiO₂ having a value close to 1.

[0059]

Note that, for easier understanding of an evaluation result, in Table 1-2, symbols such as ◎ (Excellent), ○ (Good), Δ (Satisfactory), and × (Unsatisfactory) are used. Table 103 shows a criteria therefor.

[0060]

[Table 1-2]

Table 1-2: Flow Rate of Methanol Gas Flow and Etching Result

Flow Rate of Methanol Gas Flow (L/min)	0	0.40	0.80	1.20
Etching Amount A of Top Nitride Film (nm)	37.2	34.0	36.7	43.9
Etching Amount B of Bottom Nitride Film (nm)	46.1	35.5	38.5	42.4
Etching Amount Difference A-B (nm)	Δ -8.9	◎ -1.5	◎ -1.8	◎ 1.5
Top Selectivity	◎ 48.9	○ 6.5	◎ 13.9	○ 7.1
Bottom Selectivity	○ 9.7	○ 6.0	◎ 13.7	◎ 17.8
Thickness Rate of Top Remaining SiO ₂	○ 0.90	○ 0.90	◎ 0.95	◎ 0.95
Thickness Rate of Bottom Remaining SiO ₂	× 0.70	○ 0.90	○ 0.90	○ 0.90

◎: (Excellent)

○: (Good)

Δ: (Satisfactory),

×: (Unsatisfactory)

[0061]

[Table 1-3]

Table 1-3: Symbols of and Criteria for Evaluation Result of Slit Sample

Symbol	×	Δ	○	◎
--------	---	---	---	---

Absolute Value of Top-Bottom Etching Amount Difference (nm)	10 <	5 - 10	< 5	< 2
Selectivity	< 5	-	5 - 10	10 <
Thickness Rate of Remaining SiO ₂	< 0.75	0.75 - 0.80	0.80 - 0.90	0.90 <

◎: (Excellent)

○: (Good)

△: (Satisfactory),

×: (Unsatisfactory)

As shown in Table 1-2, it was found that, even in terms of the etching amount of the silicon nitride films 103 in each of the slit samples, as the flow rate of the methanol gas flow was increased, the etching amount increased. It was found that, when the methanol gas flow was at 0 L/min, i.e., when a step of the methanol gas flow was not applied, the selectivity had a relatively satisfactory value, but the thickness of the remaining SiO₂ in the bottom was reduced to 0.70 and insufficient. It was also found that the top-bottom etching amount difference was as large as -8.9nm. In this case, the shape of the slit sample was the shape illustrated in FIG. 13.

[0062]

When the methanol gas flow is not used, the reaction product functions to increase the etching amount in the bottom portion, while functioning to conversely reduce the etching amount in the top. By contrast it was found that, in the slit sample to which the step of the methanol gas flow was applied, the thickness of the remaining SiO₂ in the bottom was improved to 0.90 or more, the top-bottom etching amount difference also decreased to 2.0 nm or less, and a satisfactory etching result as illustrated in FIG. 14 was

shown.

[0063]

Next, under experimental conditions under which the result in Table 1-2 was obtained, experiment was performed in which the methanol gas flow was fixed to 0.4 L/min and 300 Pa, while the time was varied to 60 s, 120 s, and 180 s. A result of the experiment with the slit samples at that time is shown in Table 1-4.

[0064]

[Table 1-4]

Table 1-4: Time of Methanol Gas Flow and Etching Result

Methanol Gas Flow Time (s)	60	120	180
Etching Amount A of Top Nitride Film (nm)	34.0	39.7	40.9
Etching Amount B of Bottom Nitride Film (nm)	35.5	40.9	41.9
Etching Amount Difference A-B (nm)	◎ -1.5	◎ -1.2	◎ -1.0
Top Selectivity	○ 6.5	◎ 10.2	◎ 10.1
Bottom Selectivity	○ 6.0	◎ 10.5	◎ 11.3
Thickness Rate of Top Remaining SiO ₂	○ 0.90	◎ 0.95	◎ 0.95
Thickness Rate of Bottom Remaining SiO ₂	○ 0.90	○ 0.90	○ 0.90

◎: (Excellent)

○: (Good)

△: (Satisfactory),

×: (Unsatisfactory)

As shown in Table 1-4, it was found that, in terms of the etching amount of the silicon nitride films 103 in each of the slit samples, as the time of the methanol gas flow was increased, the etching amount increased to be almost saturated when the time of the methanol gas flow was 120 s or longer. It was found that, even

when the time of the methanol gas flow was increased, the thickness of the remaining SiO₂ in the bottom was 0.90 or more, and the top-bottom etching amount difference was as small as 2.0 nm or less, and an excellent etching result as illustrated in FIG. 14 was shown.

[0065]

[Composition of Reacting layer and Effect of Methanol Gas Flow]

Experiment was performed in which, in the single-layer silicon nitride film 103, under the conditions illustrated in Table 1-2 in Example 1, instead of removing the reacting layer using the IR heating, the reacting layer was positively left in the case of the presence and absence of the methanol gas flow at a flow rate of 0.40 L/min.

[0066]

Using the etching apparatus 100 illustrated in FIG. 3 and using the single-layer silicon nitride film, first, at a stage temperature of -30°C, Ar was caused to flow at a flow rate of 1.4 L/min and under 900 Pa for 60 seconds to cool the wafer. Then, in a state where the pressure was kept at 900 Pa, irradiation using the IR lamp 60 with an output of 60% was simultaneously performed for 60 seconds, while HF was introduced at 0.40 L/min and Ar serving as the dilution gas was introduced at 0.20 L/min. As a result, on the silicon nitride film 103, the reacting layer was formed. Then, in a state where the exhaust valve was 100% open, exhaust was performed for 120 seconds. By the exhaust operation, the fluorine gas and a reaction product are partially exhausted.

[0067]

Then, in a state where the stage 3 was kept at the set temperature, the methanol gas was caused to flow as the polar solvent gas at a flow rate of 0.40 L/min and under a pressure of 300 Pa for 120 seconds. By causing the methanol gas to flow, the reacting layer was modified, while being partly removed.

[0068]

Thereafter, the removal of the reacting layer by the heating was not performed, the process returned to the wafer cooling, and the sequential process was performed in 8 cycles. In the flow, the removal of the reacting layer by the heating (S105) in the flow shown in FIG. 5-1 was not performed, and S101 to S104 were repeated eight times. The reacting layer formed by this process is assumed to be a reacting layer B (with the methanol gas flow).

[0069]

Meanwhile, by way of comparison, the reacting layer was formed without the flow of the methanol gas serving as the polar solvent gas and without performing the removal of the reacting layer by the heating. As the flow, of the flow shown in FIG. 5-1, S101 to S103 were repeated eight times without performing the modification and removal of the reacting layer using the polar solvent (S104) and without performing the removal of the reacting layer by the heating (S105). The reacting layer formed by this process is assumed to be a reacting layer A (without the methanol gas flow).

[0070]

With respect to these two reacting layers, observation of a cross section and a surface using a scanning electron microscope

(SEM), composition analysis according to X-ray photoelectron spectroscopy (XPS), and desorbed gas analysis by thermal desorption spectrometry (TDS) were performed.

[0071]

As a result of performing observation of the cross section and the surface by the SEM with respect to the reacting layer A (without the methanol gas flow), a film thickness of the reacting layer in the cross section was 61 nm, the unreacted silicon nitride film 103 was present in a layer therebelow, and a film thickness of that portion was 281 nm. By contrast, in the reacting layer B (with the methanol gas flow), a film thickness of the reacting layer in the cross section was 65 nm, and a film thickness of the portion with the unreacted silicon nitride film 103 in a layer therebelow was 285 nm. The numerical value of the film thickness of the reacting layer remained unchanged regardless of the presence or absence of the methanol gas flow but, in a case of the reacting layer B (with the methanol gas flow), compared to the reacting layer A (without the methanol gas flow), surface roughness was considerable, the reacting layer partly aggregated, and the reacting layer was partly missing. From the foregoing, it has been found that the methanol gas flow has an effect of partially removing the reacting layer.

[0072]

Then, with respect to the reacting layer A (without the methanol gas flow) and the reacting layer B (with the methanol gas flow), composition analysis was performed according to the X-ray photoelectron spectroscopy (XPS). In the composition analysis, an

outermost surface (a) in an as-is state, an inner portion (b) obtained by performing sputtering with Ar for 10 seconds, and an inner portion (c) obtained by further performing sputtering with Ar for 10 seconds were compared to each other.

[0073]

It was found that the outermost surface (a) of the reacting layer A (without the methanol gas flow) had only a peak of 401 eV of nitrogen (N1s), and 395 eV of silicon nitride was not observed therein. It was found that the peak of 401 eV was attributed to an ammonium salt. In the inner portion (b) obtained by performing sputtering with Ar for 10 seconds, the peak of 395 eV of the silicon nitride appeared, and the peak of 401 eV of the ammonium salt and 395 eV of the silicon nitride were at about 1:1. In the inner portion (c) obtained as a result of further performing sputtering with Ar for 10 seconds, a peak of 401 eV of the ammonium salt was not observed, and there was only the peak of 395 eV of the silicon nitride.

[0074]

With regard to silicon (Si2P), in the outermost surface (a) of the reacting layer A (without the methanol gas flow), a peak of 99 eV of the silicon nitride and a peak of 102 eV of silicate, i.e., a peak attributable to hexafluorosilicate SiF_6^{2-} were observed at about 1:1. In the inner portion (b) obtained by performing sputtering with Ar for 10 seconds, a peak of 99 eV of the silicon nitride and a peak of 102 eV of the silicate were also observed at about 1:1. In the inner portion (c) obtained by further performing sputtering with Ar for 10 seconds, a peak of 102 eV of the silicate

was no longer observed, and there was only a peak of 99 eV of the silicon nitride .

[0075]

By contrast, in the outermost surface (a) of the reacting layer B (with the methanol gas flow), as nitrogen (N1s), a peak of 401 eV of the ammonium salt and a peak of 395 eV of the silicon nitride were observed at about 2:1 and, since the silicon nitride film in the layer therebelow was seen, it can be considered that the reacting layer B was thinner than the reacting layer A. It was found that the peak of 401 eV was attributed to an ammonium salt. In the inner portion (b) obtained by performing sputtering with Ar for 10 seconds, a peak of 395 eV of the silicon nitride appeared large, and the peak of 401 eV of the ammonium salt and 395 eV of the silicon nitride were at about 1:4. In the inner portion (c) obtained as a result of further performing sputtering with Ar for 10 seconds, a peak of 401 eV of the ammonium salt was not observed, and there was only the peak of 395 eV of the silicon nitride.

[0076]

With regard also to silicon (Si2P), in the outermost surface (a) of the reacting layer B (with the methanol gas flow), a peak of 99 eV of the silicon nitride and a peak of 102 eV of silicate, i.e., a peak attributable to hexafluorosilicate SiF_6^{2-} were observed at about 1:1. In the inner portion (b) obtained by performing sputtering with Ar for 10 seconds, 99 eV of the silicon nitride and 102 eV of the silicate were observed at about 1:4, and it was also understood from the result that the reacting layer B was thinner than the reacting layer A. In the inner portion (c) obtained by

further performing sputtering with Ar for 10 seconds, a peak of 102 eV of the silicate was no longer observed, and there was only a peak of 99 eV of the silicon nitride .

[0077]

Thus, as a result of the analysis of the reacting layer according to the XPS, a remarkable composition difference between the reacting layer A (without the methanol gas flow) and the reacting layer B (with the methanol gas flow) could not be recognized from the peaks thereof, but it was confirmed that, in the case where there was the methanol gas flow, the thickness of the reacting layer was obviously smaller.

[0078]

In a case of ammonium hexafluorosilicate $[(\text{NH}_4)_2\text{SiF}_6]$, an element ratio Si:F:N=1:6:2 was satisfied. An element ratio of the uppermost surface (a) of the reacting layer A (without the methanol gas flow) according to the XPS was Si:F:N=1:1.25:0.58, while an element ratio according to the XPS of the uppermost surface (a) of the reacting layer B (with the methanol gas flow) was Si:F:N=1:1.46:0.88, and it was found that, in either case, fluorine and nitrogen were insufficient. It was found that the reacting layer B (with the methanol gas flow) had more fluorine and nitrogen, though slightly.

[0079]

The HF and NH_3 each produced when a compound similar to ammonium hexafluorosilicate $[(\text{NH}_4)_2\text{SiF}_6]$, which is a component generated as the reacting layer, is decomposed and evaporated etch the adjacent silicon oxide film depending on conditions, which is

considered to be related to the top-bottom difference and thinning of the oxide film in the bottom. A conceivable reason for an improved shape is the partial removal of the reacting layer by the methanol gas flow.

[0080]

Next, with regard to these reacting layer A (without the methanol gas flow) and reacting layer B (with the methanol gas flow), the desorbed gas analysis was performed by the thermal desorption spectroscopy (TDS). The TDS analysis raises a temperature of a 1 cm square sample formed with the reacting layer in a vacuum state at a vacuum degree of 5.0×10^{-7} Pa at $10^\circ\text{C}/\text{minute}$ in a temperature range of 80°C to 500°C , and analyzes a pressure increase at that time and a gas desorbed at that time by using a mass spectrometer (quadrupole mass spectrometer).

[0081]

In the reacting layer A (without the methanol gas flow), there was a pressure increase from around 150°C , there was one peak, and a temperature indicating a maximum pressure was 182°C . It was found that, as a mass at this time, F^+ had a high peak intensity satisfying $m/z=19$, followed by NH_2^+ and NH_3^+ having intensities of about one-fiftieth thereof satisfying $m/z=16$ and 17 and further followed by SiF^+ having an intensity of about one-fifth thereof satisfying $m/z=47$. In addition, there was no peak resulting from methanol. The result of the analysis according to the TDS also indicated that the reacting layer contained ammonium hexafluorosilicate.

[0082]

It was found that the reacting layer B (with the methanol gas flow) had two pressure peaks, and maximum temperatures were 176°C and 208°C. From this, it is understood that, when there is the methanol gas flow, components which are decomposed and evaporated at high temperatures are generated. It was found that, as masses at this time, the same result was obtained as in the case of the reacting layer A (without the methanol gas flow) except that there were two peaks in either case and, as a mass at this time, F^+ had a high peak intensity satisfying $m/z=19$, followed by NH_2^+ and NH_3^+ having intensities of about one-fiftieth thereof satisfying $m/z=16$ and 17 and further followed by SiF^+ having an intensity of about one-fifth thereof satisfying $m/z=47$. In addition, there was no peak resulting from methanol. In addition, no peak resulting from the methanol was observed, which seemed unchanged from the case without the methanol gas flow. A detailed reason for two degassing peaks is unknown but, due to the methanol gas flow, a component having a high decomposition/evaporation temperature was consequently obtained. When considered in conjunction with the earlier XPS result, it is presumed that, due to dissipation of excessive HF, the composition is similar to that of ammonium hexafluorosilicate. However, since a high-temperature-side peak shifted by the methanol gas flow seems to cause no change in the formed masses, details are currently unknown.

[0083]

Note that, when peak areas of pressures at 150°C to 250°C are compared to each other, the peak area in the reacting layer A (without the methanol gas flow) was $4.72e-14$ (Pa·°C), while the

peak area in the reacting layer B (with the methanol gas flow) was 4.15×10^{-14} (Pa $\cdot$ °C), and it was found that there was a reduction of about 15%. From this also, it was found that the methanol gas flow had partly removed the reacting layer.

[0084]

(Comparative Example)

To confirm the effect of the polar solvent gas flow of the present invention in greater detail, experiment was performed in which the removal of the reaction by the IR heating was not performed under a condition of the methanol gas flow rate of 0.40 L/min illustrated in Table 1-2 in Example 1.

[0085]

Using the etching apparatus 100 illustrated in FIG. 3, at a stage temperature of -30°C, for wafer cooling, Ar was caused to flow first at a flow rate of 1.4 L/min and under 900 Pa for 60 seconds. Then, in a state where the pressure was kept at 900 Pa, irradiation using the IR lamp 60 with an output of 60% was simultaneously performed for 60 seconds, while HF was introduced at 0.40 L/min and Ar serving as the dilution gas was introduced at 0.20 L/min. As a result, on the silicon nitride film 103, the reacting layer was formed. Then, in a state where the exhaust valve was 100% open, exhaust was performed for 120 seconds. By the exhaust operation, the fluorine gas and a reaction product are partially exhausted.

[0086]

Then, in a state where the stage was kept at the set temperature, as the polar solvent gas, a methanol gas was caused to

flow at a flow rate of 0.40 L/min and under a pressure of 300 Pa for 60 seconds. By causing the methanol gas to flow, the reacting layer was modified, while being partly removed.

[0087]

Then, the removal of the reacting layer by the heating was not performed, a process flow returned to the wafer cooling, and the sequential process was performed in 10 cycles. As the flow, S101 to S104 were repeated without the removal of the reacting layer by the heating in the flow shown in FIG. 5-1 (S105).

[0088]

Using a sample obtained by forming, by the etching process described above, a slit-shaped space of 200 nm in the sample used in Example 1 in which a total of 40 layers of the silicon nitride films 103 (each having a film thickness of 30 nm) and the silicon oxide films 102 (each having a film thickness of 30 nm) which were alternately deposited, etching characteristics in a miniaturized pattern were evaluated.

[0089]

As a result, it was found that etching of the silicon nitride portions had begun to occur, but there was a large amount of the deposit in the portions. This deposit is thought to be a compound similar to ammonium hexafluorosilicate, as shown in the composition of the reacting layer and the effect of methanol gas flow in Example 1, and was found to volatilize when irradiated with an electron beam during observation with a scanning electron microscope (SEM). Table 1-5 shows an etching amount of the silicon nitride films when a portion with the deposit assumed to be the

ammonium hexafluorosilicate was ignored, which was found to be smaller than that when the removal of the reacting layer by the IR heating was performed illustrated in Table 1-2. From the foregoing, it was found that, by merely modifying and removing the reacting layer with the polar solvent gas, the silicon nitride films 103 could not sufficiently be etched, and the step of removing the reacting layer by the heating was necessary.

[0090]

(Table 1-5)

Table 1-5: Etching Result in Absence of Removal of Reacting layer by Heating

Etching Amount A of Top Nitride film (nm)	15.6
Etching Amount B of Bottom Nitride film (nm)	19.8
Top Selectivity	3.8
Bottom Selectivity	6.1

Example 2

[0091]

A description will be given of another mode of the etching process using the hydrogen fluoride gas and using no plasma of the present invention. Using the etching apparatus 100 illustrated in FIG. 3 in Example 1, flows shown in FIG. 5-2 and FIG. 7-2 are described herein.

[0092]

[Flow 2 of Etching Process]

First, after the wafer 2 was transported to the process chamber 1 through the transportation port (not shown) provided in

the process chamber 1, the wafer 2 was left in place over the projections 56 of the wafer stage 3. In this case, as a stage temperature, 40°C was used.

[0093]

Then, an Ar gas for conducting heat to the wafer 2 was supplied via the mass flow controller 52, the gas distributor 51, and the shower plate 23 to perform wafer heating using the stage temperature in S101 in FIG. 5-2. S101 is described herein as heating/cooling to mean that the wafer temperature is to be matched to the stage temperature and, since the wafer temperature is higher than the stage temperature after S105 described later, cooling is performed.

[0094]

The Ar gas functions to conduct heat to the wafer 2 and functions as the dilution gas for diluting the HF gas, and accordingly S101 and S102 in FIG. 5-2 are simultaneously performed herein. Note that the flow rate of the Ar gas can be changed when the Ar gas is used to conduct heat to the wafer 2 and used as the dilution gas. It is possible to allow the dilution Ar gas to flow continuously until the etching process is ended or alternatively prevent the dilution Ar gas from flowing. Instead of the Ar gas, an N₂ gas can also be used as the inert gas.

[0095]

Subsequently, as S103 in FIG. 5-2, the HF gas was supplied in a predetermined amount and for a predetermined time to the process chamber 1 to form the reacting layer. Only a temperature of the heat transmission by the stage 3 is used herein without using the

heating with the IR (infrared) lamp 60 as shown in the flow in FIG. 5-2. As the stage temperature, 40°C was used herein, but the stage temperature, i.e., the wafer temperature is preferably 30°C or more and 55°C or less, and is more preferably 35°C or more and 50°C or less. By using the stage temperature, a total pressure or the HF partial pressure, a time period, the number of repetitions, and the like, it is possible to control the film thickness of the reacting layer.

[0096]

In the present invention, a pressure to be used is preferably from about 10 Pa to 1000 Pa, and particularly preferably from 300 Pa to 1000 Pa. As the pressure is higher, the reaction layer is more easily formed on the silicon nitride film 103, and a temperature required for the formation decreases. After the reacting layer is formed for the predetermined time, the supply of the HF gas is stopped, and the HF gas remaining in the vapor phase is exhausted, though not shown in FIG. 5-2. In a case of performing vacuum exhaust, the pressure is preferably adjusted to 5 Pa or less. In other words, the step of exhausting the HF gas, while causing the inert gas to flow, is inserted between S103 and S104 subsequent thereto.

[0097]

Then, in S104 in FIG. 5-2, the polar solvent gas is caused to flow to modify the reacting layer, while the reacting layer is partly removed. As the polar solvent gas, alcohol such as methanol, ethanol, or isopropanol or water can be used herein. An amount of the polar solvent gas caused to flow is preferably 0.1 to

3.0 L/min, and a time during which the polar solvent gas is caused to flow is preferably about 30 s to 300 s. A pressure at this time is preferably adjusted to about 10 to 1000 Pa. Note that, when the polar solvent gas is caused to flow, it is also possible to simultaneously cause an inert gas such as an Ar or nitrogen gas to flow as the dilution gas.

[0098]

After the reacting layer is formed for the predetermined time, the supply of the polar solvent gas is stopped, and the polar solvent gas remaining in the vapor phase is exhausted, though not shown in FIG. 5-2. In a case of performing vacuum exhaust, the pressure is preferably adjusted to 5 Pa or less. In other words, a step of exhausting the polar solvent gas, while causing the inert gas to flow, is inserted herein between S104 and S105 subsequent thereto.

[0099]

Then, in a state where the HF gas and the polar solvent gas are not allowed to flow, heating is performed to remove the reacting layer (S105 in FIG. 5-2). A temperature of the heating performed herein is preferably 70°C to 110°C (is 70°C or more and 110°C or less), and is more preferably 70°C to 100°C. As a heating method, the IR lamp 60 was used herein. The heating method is not limited thereto and, e.g., a method of heating the wafer stage 3 or a method of separately transporting the wafer 2 to an apparatus that performs only heating and performing a heating process may also be used. In addition, during irradiation with the IR lamp, the Ar gas or nitrogen gas can be introduced. The heating process

can also be performed a plurality of times as necessary. After the heating, the process flow returns to S101, where the wafer cooling using the stage is performed. Thereafter, on the assumption that steps from S101 to S105 are included in one cycle, the cycle is repeated N times. The cycle is repeated until a required etching amount is obtained, and is then ended. The step S103 and the step S105 set herein the stage to a low temperature of -50°C or more and 0°C or less, perform lamp heating thereon to obtain a temperature of 30°C or more and 55°C or less for the stage in the step S103, and can further obtain a temperature of 70°C or more and 110°C or less as the stage temperature in Step S105.

[0100]

FIG. 7-2 illustrates a time chart according to the flow shown in FIG. 5-2. The step of causing the HF gas and Ar to flow (step of forming the reacting layer), the step of causing the polar solvent gas to flow, and the step of performing the IR lamp heating in a state where the HF gas is not allowed to flow are included in one cycle, and the cycle is repeated N times to cause etching of the silicon nitride film.

[0101]

[Etching Result 2]

Using the etching apparatus 100 and the etching process flow 2 (FIG. 5-2 and FIG. 7-2) in FIG. 3, a process was examined in which the stage temperature was set to 40°C , and, in the step of causing the HF/Ar to flow, the IR heating was not performed. First, for heat conduction to the wafer 2, Ar was caused to flow at a flow rate of 1.4 L/min and under 900 Pa for 60 seconds. Then,

while being controlled under a pressure of 900 Pa, HF was introduced at 0.40 L/min, while Ar serving as the dilution gas was introduced at 0.20 L/min, for 60 seconds. As a result, on the silicon nitride film 103, the reacting layer was formed.

[0102]

Then, in a state where the exhaust valve was 100% open, exhaust was performed for 120 seconds. By the exhaust operation, the fluorine gas and a reaction product are partially exhausted. Then, in a state where the stage 3 was kept at the set temperature, the methanol gas serving as the polar solvent gas was caused to flow at a flow rate of 0.40 L/min and under a pressure of 300 Pa for 120 seconds. By causing the methanol gas to flow, the reacting layer was modified, while being partly removed.

[0103]

Then, in a state where the stage 3 was kept at the set temperature, Ar was caused to flow at 0.50 L/min, and the exhaust valve was 100% open, heating was performed with a lamp intensity of 70% for 40 seconds. By the process, the reacting layer modified by the polar solvent gas flow was removed. Then, back to the beginning, cooling was performed in a state where Ar was caused to flow at 1.4 L/min and under a pressure of 900 Pa for 60 seconds. According to the flow of FIG. 5-2, the sequential process was performed herein in 10 cycles.

[0104]

In the same manner as in Example 1, by using a sample obtained by forming a slit-like space of 200 nm in a sample including a total of 40 layers of the silicon nitride films 103

(each having a film thickness of 30 nm) and the silicon oxide films 102 (each having a film thickness of 30 nm) which are alternately stacked, etching characteristics were evaluated with a miniaturized pattern. A result thereof is shown in Table 2.

[0105]

[Table 2]

Table 2: Methanol Gas Flow Time and Etching Result

Methanol Gas Flow Time (s)	120
Etching Amount A of Top Nitride Film (nm)	31.5
Etching Amount B of Bottom Nitride Film(nm)	33.3
Etching Amount Difference A-B(nm)	◎ -1.8
Top Selectivity	◎ 10.6
Bottom Selectivity	◎ 12.4
Thickness Rate of Top Remaining SiO ₂	○ 0.90
Thickness Rate of Bottom Remaining SiO ₂	○ 0.90

◎: (Excellent)

○: (Good)

△: (Satisfactory),

×: (Unsatisfactory)

It was found that, even when the IR heating was not performed in the step of causing HR/Ar to flow, the methanol gas flow was effective, a thickness of each of the top remaining SiO₂ and the bottom remaining SiO₂ was 0.90 or more, and a top-bottom etching amount difference was as small as 2.0 nm or less as in Table 2, and an excellent etching result as illustrated in FIG. 14 was obtained.

Example 3

[0106]

A description will be given of another mode of the etching

process using the hydrogen fluoride gas and using no plasma of the present invention. Using the etching apparatus 100 in FIG. 3 shown in Example 1, flows shown in FIG. 6-2 and FIG. 8 will be described.

[0107]

[Flow 3 of Etching Process]

First, after the wafer 2 is transported to the process chamber 1 via a transportation port (not shown) provided in the process chamber 1, the wafer 2 is left in place on the projections 56 provided at the wafer stage 3. In this case, as a stage temperature, 30°C was used.

[0108]

Then, the Ar gas for conducting heat to the wafer 2 was supplied via the mass flow controller 52, the gas distributor 51, and the shower plate 23 to perform wafer heating/cooling using the stage 3 in S111 in FIG. 6-2. The wording "heating/cooling" is used herein to mean that the wafer temperature is to be matched to the stage temperature and, since after S114 described later, the wafer temperature is higher than the stage temperature, and consequently cooling is performed.

[0109]

Since the Ar gas functions to conduct heat to the wafer and functions as the dilution gas for diluting the HF gas, S111 and S112 in FIG. 6-2 are simultaneously performed. Note that the flow rate of the Ar gas can be changed when the Ar gas is used to conduct heat to the wafer 2 and used as the dilution gas. It is possible to allow the dilution Ar gas to flow continuously until the etching process is ended or alternatively prevent the dilution

Ar gas from flowing. Instead of the Ar gas, an N₂ gas can also be used as the inert gas.

[0110]

Subsequently, in S113 in FIG. 6-2, the HF gas was supplied in a predetermined amount and for a predetermined time period to the process chamber 1 mentioned above to form the reacting layer. The heating using the IR (infrared) lamp 60 shown in the flow in FIG. 6-2 is not used herein, and only a temperature resulting from the heat conduction using the stage 3 is used. As a stage temperature, 30°C was used herein, but the stage temperature, i.e., the wafer temperature is preferably 30°C or more and 55°C or less, and is more 35°C or more and 50°C or less. By using the stage temperature, a total pressure or the HF partial pressure, a time period, the number of repetitions, and the like, it is possible to control the film thickness of the reacting layer.

[0111]

In the present invention, a pressure to be used is preferably from about 10 Pa to 1000 Pa, and particularly preferably from 300 Pa to 1000 Pa. As the pressure is higher, the reaction layer is more easily formed on the silicon nitride film 103, and a temperature required for the formation decreases. After the reacting layer is formed for a predetermined time, the supply of the HF gas is stopped, and the HF gas remaining in the vapor phase is exhausted, though not shown in FIG. 6-2. In a case of performing vacuum exhaust, the pressure is preferably adjusted to 5 Pa or less. In other words, the step of exhausting the HF gas, while causing the inert gas to flow, is inserted herein between

S113 and S114 subsequent thereto.

[0112]

Next, in S114 in FIG. 6-2, heating is performed, while the polar solvent gas is introduced, to modify and simultaneously remove the reacting layer. As the polar solvent gas, alcohol such as methanol, ethanol, or isopropanol or water can be used. An amount of the polar solvent gas to be caused to flow is preferably 0.1 to 3.0 L/min. A heating temperature used herein is preferably from 70°C to 110°C, and more preferably from 70°C to 100°C. As a heating method, the IR lamp 60 was used herein. A heating method is not limited thereto, and it may also be possible to use, e.g., a method of heating the wafer stage 3 or a method of separately transporting the wafer 2 to an apparatus that performs only heating and performing a heating process. In the step of performing heating, while introducing the polar solvent gas, and modifying and simultaneously removing the reacting layer, it is possible to introduce an inert gas such as the Ar gas or nitrogen gas. In addition, this step can also be performed a plurality of times as necessary.

[0113]

Then, the heating and the supply of the polar solvent gas is stopped, and the polar solvent gas remaining in the vapor phase is exhausted, though not shown in FIG. 6-2. In a case of performing vacuum exhaust, the pressure is preferably adjusted to 5 Pa or less. In other words, the step of exhausting the polar solvent gas, while causing the inert gas to flow, is added after S114.

[0114]

Then, the process flow returns to the wafer heating/cooling using the stage 3 in S111. S111 is a step of matching the stage temperature to the wafer temperature and, since the wafer 2 is heated by S114, cooling is performed in S111 subsequent thereto. Thereafter, on the assumption that S111 to S114 are included in one cycle, the cycle is repeated N times. The cycle is repeated until a required etching amount is obtained, and is then ended. In the step in S113 and the step in S114, by setting the stage to a low temperature of -50°C or more and 0°C or less and performing lamp heating thereon, it is possible to obtain a temperature of 30°C or more and 55°C or less for the stage in the step in S113 and further obtain a temperature of 70°C or more and 110°C or less for the stage in the step in S114.

[0115]

FIG. 8 illustrates a time chart according to the flow shown in FIG. 6-2. The step of causing the HF gas and Ar to flow (step of forming the reacting layer), the step of causing the polar solvent gas to flow, and the step of performing the IR lamp heating in a state where the HF gas is not allowed to flow are included in one cycle, and the cycle is repeated N times to cause etching of the silicon nitride film.

[0116]

[Etching Result 3]

A process was studied in which, by using the etching apparatus 100 in FIG. 3 and an etching process flow 3 (FIG. 6-2 and FIG. 8) each described in Example 1, the stage temperature was set to 30°C and, in the step of causing HF/Ar to flow, the IR heating

was not performed. First, for heat conduction to the wafer 2, Ar was caused to flow at a flow rate of 1.4 L/min and under 900 Pa for 60 seconds. Then, while being controlled under a pressure of 900 Pa, HF was introduced at 0.40 L/min, while Ar serving as the dilution gas was introduced at 0.20 L/min, for 60 seconds. As a result, on the silicon nitride film 103, the reacting layer was formed.

[0117]

Then, in a state where the exhaust valve was 100% open, exhaust was performed for 120 seconds. By the exhaust operation, the fluorine gas and a reaction product are partially exhausted. Then, in a state where the stage 3 was kept at the set temperature and the methanol gas was caused to flow at 0.40 L/min, a pressure was controlled to 300 Pa, and heating was performed for 30 s to 50 s with an IR lamp output of 70%. Thus, the reacting layer was removed, while the methanol gas was flowing. Then, the process returned to the beginning and, in a state where Ar was caused to flow under a pressure of 900 Pa and at 1.4 L/min for 60 seconds, the wafer 2 was cooled to reach the same temperature as the stage temperature. The sequential process was performed in 10 cycles according to the flow in FIG. 6-2.

[0118]

FIG. 2 illustrates respective etching film thicknesses of the single-layer silicon nitride film (PE-SiN) 103 and the single-layer silicon oxide film (PE-SiO₂, which is PE-SiO₂ in FIG. 2) 102 each obtained after 10 cycles since a time during which the IR lamp irradiation was to be performed was changed simultaneously with the

methanol gas flow as well as a selectivity of the silicon nitride film 103 to the silicon oxide film 102.

[0119]

As illustrated in FIG. 2, it was found that, in this process also, the silicon nitride films 103 were etched, and the etching amount of the silicon nitride films 103 was saturated when the time during which the IR lamp irradiation was performed simultaneously with the methanol gas flow was about 40 s. As a result, the etching amount of the silicon oxide film 102 remained substantially unchanged, while the selectivity of the single-layer film was higher as the time during which the IR lamp irradiation was performed simultaneously with the methanol gas flow was shorter.

[0120]

In the same manner as in Example 1, by using a sample obtained by forming a slit-like space of 200 nm in a sample including a total of 40 layers of the silicon nitride films 103 (each having a film thickness of 30 nm) and the silicon oxide films 102 (each having a film thickness of 30 nm) which were alternately stacked, etching characteristics were evaluated herein with a miniaturized pattern. A result thereof is shown in Table 3.

[0121]

[Table 3]

Table 3: Time of IR Irradiation Simultaneous with Methanol Gas Flow and Etching Result

Time of IR Irradiation Simultaneous with Methanol Gas Flow (s)	30	40	50
Etching Amount A of Top Nitride Film (nm)	14.4	22.1	26.0

Etching Amount B of Bottom Nitride Film (nm)	18.9	22.8	25.5
Etching Amount Difference A-B (nm)	◎ -4.5	◎ -0.7	◎ 0.5
Top Selectivity	× 4.4	◎ 10.9	◎ 11.3
Bottom Selectivity	○ 5.3	◎ 12.1	◎ 11.9
Thickness Rate of Top Remaining SiO ₂	◎ 0.95	◎ 0.95	◎ 0.95
Thickness Rate of Bottom Remaining SiO ₂	× 0.85	○ 0.90	○ 0.90

◎: (Excellent)

○: (Good)

△: (Satisfactory),

×: (Unsatisfactory)

As shown in Table 3, it was found that, in terms of an etching amount of the silicon nitride films 103 in the slit sample also, as the time of the IR irradiation simultaneous with the methanol gas flow was increased, the etching amount increased. Note that, for easier understanding of a result of the evaluation, in Table 3, symbols such as ◎ (Excellent), ○ (Good), △ (Satisfactory), and × (Unsatisfactory) each shown in Table 1-3 previously described are used.

[0122]

It was found that, even when the IR irradiation was performed simultaneously with the methanol gas flow as in the present example also, an effect was achieved and, except when the time period was as short as 30 s in Table 3, the thickness of the remaining SiO₂ in the bottom had improved to 0.90 or more, the top-bottom etching amount difference was as small as 2.0 nm or less, and a satisfactory etching result as illustrated in FIG. 14 was obtained. It was found that, by performing the methanol gas flow

simultaneously with the heating process, a reaction product was inhibited from functioning to increase the etching amount in a bottom portion, while being inhibited from conversely functioning to reduce the etching amount in the top.

Example 4

[0123]

A description will be given of another mode of the etching process using the hydrogen fluoride gas and using no plasma of the present invention. Using an etching apparatus 100A in FIG. 4, flows shown in FIG. 5-1 and FIG. 9-1 are described herein.

[0124]

[Configuration Example 2 of Etching Apparatus]

Next, referring to FIG. 4, an outline of the etching apparatus 100A according to Example 4 of the present invention, including an overall configuration thereof, will be described. The process chamber 1 of the etching apparatus 100A is configured to include the base chamber 11, and the wafer stage 3 for mounting the wafer 2 is disposed therein. In an upper portion of the process chamber 1, a plasma source is disposed, and an ICP (Inductively Coupled Plasma) discharge method is used. The ICP plasma source can be used to clean an inner wall of the chamber 11 with a plasma and generate a reactive gas by using the plasma. A cylindrical quartz chamber 12 included in the ICP plasma source is disposed in the upper portion of the process chamber 1, and an ICP coil 20 is disposed outside the quartz chamber 12. To the ICP coil 20, a high frequency power source 21 for generating the plasma is connected via a matching device 22. It is assumed that, as a frequency of

high frequency power, a frequency band of several tens of megahertz, including 13.56 MHz or the like, is used. Over the quartz chamber 12, a ceiling plate 25 is disposed. Below the ceiling plate 25, a gas dispersion plate 24 and the shower plate 23 are disposed, and a process gas is introduced into the quartz chamber 12 via the gas dispersion plate 24 and the shower plate 23.

[0125]

A flow rate of the supplied process gas is adjusted by the mass flow controller 52 in the mass flow box 50 disposed for each gas species. On a downstream side of the mass flow controller 52, the gas distributor 51 is disposed to be able to independently control flow rates and compositions of a gas to be supplied to the vicinity of a center of the quartz chamber 12 and a gas to be supplied to the vicinity of an outer circumference thereof and supply the gases, thereby allowing a space distribution of partial pressures of the process gas to be controlled in detail. Note that, in FIG. 4, Ar, N₂, NF, O₂, and methanol (CH₃OH), which is alcohol serving as the polar solvent gas, are shown. Note that another process gas other than these can also be supplied. In particular, as the polar solvent, water, ethanol, isopropanol, or the like can also be used. However, when water is to be used, water is frozen at 0°C or lower, and therefore, as the stage temperature, a temperature higher than 0°C needs to be used.

[0126]

For a pressure reduction in the process chamber 1, a lower portion of the process chamber 1 is connected to the exhaust means (exhaust device) 15 via the vacuum exhaust pipe 16. It is assumed

that the exhaust means is formed of, e.g., a turbo molecular pump, a mechanical booster pump, or a dry pump. In addition, to adjust the pressure in the process chamber 1, a pressure adjustment means (pressure adjustment device) 14 is disposed on an upstream side of the exhaust means 15.

[0127]

Above the wafer stage 3, an IR lamp unit for heating the wafer 2 is disposed. The IR lamp unit mainly includes the IR lamp 60, the reflecting plate 61, and the IR light transmission window 72. As the IR lamp 60, a circle-type (circular or annular) lamp is used. It is assumed that that light emitted from the IR lamp 60 is light (referred to as IR light herein) which is mainly in visible to infrared light regions. In the present embodiment, as the IR lamp 60, the lamps 60-1, 60-2, and 60-3 for three laps are disposed, but lamps for two laps, four laps, or the like may also be disposed. Over the IR lamp 60, the reflecting plate 61 for reflecting the IR light downward (in a direction in which the wafer is disposed) is disposed. Preferably, a material of the IR transmission window 72 does not include alkali metal ions or the like, transmits light in the infrared region, and has a heat resistance and, as a specific material, quartz is preferred.

[0128]

To the IR lamp 60, the IR lamp power source 73 is connected, the high frequency cut filter 74 is disposed midway therebetween to prevent noise of the high frequency power from flowing into the IR lamp power source. The IR lamp power source 73 also has a function of being able to independently control power to be supplied to the

IR lamps 60-1, 60-2, and 60-3 to allow a radial distribution of an amount of heating of the wafer 2 to be adjusted (illustration of wiring is partly omitted).

[0129]

At a center of the IR lamp unit, a flow path 27 is formed. In the flow path 27, a slit plate 26 for blocking ions and electrons each generated in the plasma, which has a plurality of holes for transmitting only a neutral gas and neutral radicals and applying the neutral gas and neutral radicals to the wafer 2 opened therein, is disposed. As the slit plate 26, a material not including alkali metal ions or the like and resistant to heat is preferred and, as a specific material, alumina or quartz can be used.

[0130]

Inside the wafer stage 3, a flow path 39 for a refrigerant for cooling the stage 3 is formed, and the chiller 38 circulates and supplies the refrigerant. As the chiller 38, in the present invention, a chiller that could be controlled to a temperature of -50°C to 50°C was used. To fix the wafer 2 by electrostatic adsorption, a plate-like electrode plate 30 is embedded in the stage 3, and a DC (direct-current) power source 31 is connected thereto. To efficiently cool the wafer 2, a He gas can be supplied between the back surface of the wafer 2 and the wafer stage 3. To protect the back surface of the wafer 2 from damage even when heating and cooling is performed while the wafer 2 is adsorbed, the surface (surface mounting the wafer 2) of the wafer stage 3 is assumedly coated with a resin such as polyimide. Inside the wafer

stage 3, the thermocouple 70 for measuring a temperature of the stage 3 is disposed, and the thermocouple 70 is connected to the thermocouple thermometer 71.

[0131]

The temperature of the wafer stage 3 measured by the thermocouple thermometer 71 using thermocouple 70 was within $\pm 1^{\circ}\text{C}$ difference from the set temperature of the chiller 38, and the wafer temperature separately measured with the thermocouple 70 was within $\pm 3^{\circ}\text{C}$ difference (within $\pm 2^{\circ}\text{C}$ difference with respect to the stage temperature).

[0132]

Note that, as a mechanism for cooling the wafer stage 3 to be used in the etching apparatus 100A of the present invention, not only a mechanism that circulates the refrigerant, but also a Peltier element, which is a thermoelectric conversion device, or the like can also be used.

[0133]

The etching apparatus 100A used in the present invention can heat the inside of the chamber except for the wafer stage exposed to the hydrogen fluoride gas, such as the process chamber 1. For example, as the temperature, about 40°C to 120°C can be used. Thus, it is possible to prevent the hydrogen fluoride gas from adsorbing to the inside of the chamber 11 and minimize corrosion of the inside of the chamber 11.

[0134]

[Flow 4 of Etching Process]

Next, a description will be given of an etching process using

a hydrogen fluoride gas and using no plasma, which is proposed in the present invention. A flow used herein is basically the same as that used in Example 1, but is partially different from Flow 1 of the etching process in Example 1, since the etching apparatus 100A illustrated in FIG. 4 is used. Referring to FIG. 5-1, FIG. 9-1, and FIG. 4 (apparatus diagram), the flow will be described.

[0135]

First, after the wafer 2 is transported to the process chamber 1 via the transportation port provided in the process chamber 1, the wafer 2 is fixed to the wafer stage 3 with a DC power source 31 for electrostatic adsorption, while a He gas 55 for wafer cooling is supplied to the back surface of the wafer 2, and the wafer cooling in S101 in FIG. 5-1 is thus performed.

[0136]

Subsequently, according to the flow chart in FIG. 5-1 described in Example 1, etching is performed. A repetitive description of the flow in FIG. 5-1 is omitted.

[0137]

FIG. 9-1 illustrates a time chart according to the flow shown in FIG. 5-1 when the etching apparatus 100A illustrated in FIG. 4 is used. The stage 3 was for electrostatic adsorption, and a portion that supplies the He gas 55 for wafer cooling to the back surface of the wafer 2 was added. One cycle includes a step of performing the IR lamp heating, while causing the HF gas to flow, a step of causing the polar solvent gas to flow, and the step of performing the IR lamp heating in a state where the HF gas and the polar solvent gas are not allowed to flow and, by repeating the

cycle N times, the etching of the silicon nitride film is caused.

[0138]

[Etching Resul 4]

Using the etching apparatus 100A illustrated in FIG. 4, etching was performed by using the process flow in FIG. 5-1 and FIG. 9-1. In the etching apparatus 100A in FIG. 4, a voltage of ± 1200 V was applied during etching to electrostatically adsorb the wafer 2. To improve heat conduction of the stage 3, He was caused to flow from the back surface to achieve a pressure of 1.0 kPa.

[0139]

After a pressure of Ar was set to 900 Pa at 1.4 L/min with a stage temperature of -30°C , the pressure of 900 Pa was maintained, and irradiation was performed for 60 seconds with a 60% output of the IR lamp 60 while simultaneously introducing HF at 0.40 L/min and Ar serving as the dilution gas at 0.20 L/min. As a result, on the silicon nitride film 103, the reacting layer was formed.

[0140]

Then, in a state where the exhaust valve was 100% open, exhaust was performed for 60 seconds. By the exhaust operation, the fluorine gas and a reaction product are partially exhausted. Then, in a state where the stage 3 was kept at the set temperature, methanol serving as the polar solvent gas was caused to flow at a flow rate of 0.4 L/min under a pressure of 300 Pa, 450 Pa, and 600 Pa each for 60 seconds. By causing the polar solvent gas to flow, the reacting layer was modified, while being partly removed.

[0141]

Then, in a state where the stage 3 was kept at the set

temperature, Ar was caused to flow at 0.50 L/min, and the exhaust valve was 100% open, heating was performed with a lamp intensity of 70% for 40 seconds. Thus, the reacting layer modified by the polar solvent gas flow is removed. Then, back to the beginning, cooling was performed in a state where Ar was caused to flow at 1.4 L/min and under a pressure of 900 Pa for 60 seconds. According to the flow in FIG. 5-1, the sequential process was performed herein in 10 cycles.

[0142]

Table 4 shows a result of experiment using the slit sample evaluated in the same mode as those shown in Table 1-2 and Table 1-4.

[0143]

[Table 4]

Table 4: Pressure of Methanol Gas Flow and Etching Result

Methanol Gas Flow Pressure (Pa)	300	450	600
Etching Amount A of Top Nitride Film (nm)	34.0	42.4	41.9
Etching Amount B of Bottom Nitride Film (nm)	35.5	43.9	43.0
Etching Amount Difference A-B (nm)	◎ -1.5	◎ -1.5	◎ -1.1
Top Selectivity	○ 6.5	◎ 10.8	◎ 10.1
Bottom Selectivity	○ 6.0	◎ 15.0	◎ 13.2
Thickness Rate of Top Remaining SiO ₂	○ 0.90	◎ 0.95	◎ 0.95
Thickness Rate of Bottom Remaining SiO ₂	○ 0.90	○ 0.90	○ 0.90

◎: (Excellent)

○: (Good)

△: (Satisfactory),

×: (Unsatisfactory)

As shown in Table 4, it was found that, in terms of the etching amount of the silicon nitride films 103 in the slit sample, as the pressure of the methanol gas flow was increased, the etching amount increased to be almost saturated under 450 Pa or higher. Note that, for easier understanding of a result of the evaluation, in Table 4, symbols such as ◎ (Excellent), ○ (Good), △ (Satisfactory), and × (Unsatisfactory) each shown in Table 1-3 previously described are used.

[0144]

Even when the pressure of the methanol gas flow was increased, a thickness of SiO₂ remaining in the bottom was 0.90 or more and a top-bottom etching amount difference was as small as 2.0 nm or more, and it was found that a satisfactory etching result as shown in FIG. 14 was obtained.

[0145]

In the etching apparatus 100A used in the present embodiment in FIG. 4, an ICP plasma generation mechanism was mounted and accordingly, before an etching process, chamber cleaning using an oxygen plasma was performed for 300 seconds under conditions of O₂=1.0 L/min, 50 Pa, and 1500 W. Thus, it was possible to reduce a foreign substance in the chamber or the like.

Example 5

[0146]

A description will be given of another mode of the etching process using the hydrogen fluoride gas and using no plasma of the present invention. Using the etching apparatus 100A in FIG. 4, flows shown in FIG. 6-1 and FIG. 9-2 are described.

[0147]

[Flow 5 of Etching Process]

Next, a description will be given of an etching process using a hydrogen fluoride gas and using no plasma, which is proposed in the present invention. The flow is basically similar to the flow shown in the previous example, but is partly different from Flow 1 of the etching process in Example 1, since the etching apparatus 100A illustrated in FIG. 4 is used.

[0148]

First, the wafer 2 is transported to the process chamber 1 via the transportation port (not shown) provided in the process chamber 1, and then the wafer 2 is fixed to the wafer stage 3 with the DC power source 31 for electrostatic adsorption, while the He gas 55 for wafer cooling is supplied to the back surface of the wafer 2 to perform wafer cooling in S101 in FIG. 6-1.

[0149]

Using the etching apparatus 100A illustrated in FIG. 4 and the process flow in each of FIG. 6-1 and FIG. 9-2, etching was performed. In the etching apparatus 100A in FIG. 4, a voltage of ± 1200 V was applied during etching to electrostatically adsorb the wafer 2. The stage temperature was set to -30°C herein. In addition, to improve the heat conduction of the stage 3, He was caused to flow from the back surface so as to achieve a pressure of 1.0 kPa. Thus, the stage cooling in S111 was performed.

[0150]

Then, in Step S112, the Ar gas was introduced. The Ar gas was the dilution gas, and was used herein to increase the pressure.

Since cooling using the electrostatically adsorbing stage 3 and He from the back surface is used herein, the step can also be omitted. [0151]

Subsequently, in S113 in FIG. 6-1, the HF gas and the Ar gas were supplied in predetermined amounts and for predetermines time periods to the process chamber 1, while heating was simultaneously performed, to form the reacting layer. As a heating type, heating using the IR (infrared) lamp 60 is used herein. A wafer temperature obtained as a result of the cooling using the stage 3 and the heating using the IR lamp 60 is preferably 30°C or more and 55°C or less, and is more preferably 35°C or more and 50°C or less. The film thickness of the reacting layer can be controlled by using a total pressure or a HF partial pressure and a heating temperature, and by using herein an output of the IR lamp, a time period, the number of repetitions, and the like. When the wafer temperature described previously is lower than 30°C, the reacting layer is not sufficiently formed, and therefore etching is less likely to occur. Conversely, when the wafer temperature described previously is higher than 55°C, the reacting layer is excessively formed and, accordingly, when the reacting layer is to be decomposed to be evaporated, the silicon oxide film 102 adjacent thereto is undesirably etched, and therefore the selectivity tends to decrease.

[0152]

In the present invention, a pressure to be used is preferably from about 10 Pa to 100 Pa, and is particularly preferably from 100 Pa to 1000 Pa. As the pressure is higher, the reaction layer is

more easily formed on the silicon nitride film 103, and a temperature required for the formation decreases. Even when the pressure is increased, by controlling the output of the IR lamp 60, it is possible to form the reacting layer on the silicon nitride film 103 without affecting the silicon oxide film 102.

[0153]

After the formation of the reacting layer, the supply of the HF gas is stopped, and the HF gas remaining in a vapor phase is exhausted, though not shown in FIG. 6-1. In a case of performing vacuum exhaust, the pressure is preferably adjusted to 5 Pa or less. In other words, the step of exhausting the HF gas, while causing the inert gas to flow, is inserted herein between S113 and S114 subsequent thereto.

[0154]

Then, in S114 in FIG. 6-1, heating is performed, while a polar solvent gas is introduced, to thereby modifying the reacting layer and simultaneously removing the reacting layer. As the polar solvent gas, alcohol such as methanol, ethanol, or isopropanol or water can be used. An amount of the polar solvent gas to be caused to flow is preferably 0.1 to 3.0 L/min. A heating temperature used herein is preferably from 70°C to 110°C, and more preferably from 70°C to 100°C. As a heating method, the IR lamp 60 was used herein. A heating method is not limited thereto, and it may also be possible to use, e.g., a method of heating the wafer stage 3 or a method of separately transporting the wafer 2 to an apparatus that performs only heating and performing a heating process. In the step of performing heating, while introducing the polar solvent

gas, and modifying and simultaneously removing the reacting layer, it is possible to introduce an inert gas such as the Ar gas or nitrogen gas. In addition, this step can also be performed a plurality of times as necessary.

[0155]

Then, the heating and the supply of the polar solvent gas is stopped, and the polar solvent gas remaining in the vapor phase is exhausted, though not shown in FIG. 6-1. In a case of performing vacuum exhaust, the pressure is preferably adjusted to 5 Pa or less. In other words, the step of exhausting the polar solvent gas, while causing the inert gas to flow, is added after S114.

[0156]

Then, the process flow returns to the wafer cooling using the stage 3 in S111. Thereafter, on the assumption that the steps from S111 to S115 are included in one cycle, the cycle is repeated N times. The cycle is repeated until a required etching amount is obtained, and is then ended.

[0157]

FIG. 9-2 illustrates a time chart based on the flow shown in FIG. 6-1. The step of causing the HF gas and Ar to flow (step of forming the reacting layer), the step of causing the polar solvent gas to flow, and the step of performing the IR lamp heating in a state where the HF gas is not allowed to flow are included in one cycle, and the cycle is repeated N times to cause etching of the silicon nitride film.

[0158]

[Etching Result 5]

Using the etching apparatus 100A illustrated in FIG. 4 and the process flow in each of FIG. 6-1 and FIG. 9-2, etching was performed. In the etching apparatus 100A in FIG. 4, a voltage of ± 1200 V was applied during etching to electrostatically adsorb the wafer 2. In addition, to improve heat conduction of the stage 2, He was allowed to flow from the back surface to achieve a pressure of 1.0 kPa.

[0159]

After a pressure of Ar was set to 900 Pa at 1.4 L/min with a stage temperature of -30°C , the pressure of 900 Pa was maintained, and irradiation was performed for 60 seconds with a 60% output of the IR lamp 60 while simultaneously introducing HF at 0.40 L/min and Ar serving as the dilution gas at 0.20 L/min. As a result, on the silicon nitride film 103, the reacting layer was formed.

[0160]

Then, in a state where the exhaust valve was 100% open, exhaust was performed for 120 seconds. By the exhaust operation, the fluorine gas and a reaction product are partially exhausted.

[0161]

Next, in a state where the stage was kept at the set temperature and a methanol gas was caused to flow at 0.40 L/min, a pressure was controlled to 300 Pa, and heating was performed for 30 s to 50 s with an IR lamp output of 70%. Thus, the reacting layer was removed, while the methanol gas was flowing. Then, the process returned to the beginning and, in a state where Ar was caused to flow under a pressure of 900 Pa and at 1.4 L/min for 60 seconds, the wafer was cooled to reach the same temperature as the stage

temperature. The sequential process was performed in 10 cycles according to the flow in FIG. 6-1.

[0162]

In the same manner as in Example 1, by using a sample obtained by forming a slit-like space of 200 nm in a sample including a total of 40 layers of the silicon nitride films 103 (each having a film thickness of 30 nm) and the silicon oxide films 102 (each having a film thickness of 30 nm) which were alternately stacked, etching characteristics were evaluated herein with a miniaturized pattern. A result thereof is shown in Table 5.

[0163]

[Table 5]

Table 5: Time of IR Irradiation Simultaneous with Methanol Gas Flow and Etching Result

Time of IR Irradiation Simultaneous with Methanol Gas Flow (s)	30	40	50
Etching Amount A of Top Nitride Film (nm)	26.5	38.7	42.7
Etching Amount B of Bottom Nitride Film (nm)	38.0	36.2	44.2
Etching Amount Difference A-B (nm)	× -11.5	◎ -2.5	◎ -0.6
Top Selectivity	○ 5.0	◎ 10.9	◎ 12.3
Bottom Selectivity	○ 13.5	◎ 8.9	◎ 16.9
Thickness Rate of Top Remaining SiO ₂	◎ 0.95	◎ 0.95	◎ 0.95
Thickness Rate of Bottom Remaining SiO ₂	◎ 0.95	◎ 0.95	◎ 0.95

◎: (Excellent)

○: (Good)

△: (Satisfactory),

×: (Unsatisfactory)

As shown in Table 5, it was found that, in terms of the etching amount of the silicon nitride film 103 in each of the slit samples also, the etching amount increased as the time during which IR irradiation was performed simultaneously with the methanol gas flow was increased. Note that, for easier understanding of a result of evaluation, in Table 5, symbols such as ◎ (Excellent), ○ (Good), △ (Satisfactory), and × (Unsatisfactory) each shown in Table 1-3 previously described are used.

[0164]

It was found that, even when the IR irradiation was performed simultaneously with the methanol gas flow as in the present example, an effect was achieved and, except when the time was as short as 30 s in Table 5, the top-bottom etching amount difference was as small as 2.5 nm or less, each of the remaining SiO₂ thicknesses was 0.95, and a satisfactory etching result as illustrated in FIG. 14 was obtained. It was found that, by performing the methanol gas flow simultaneously with the heating process, a reaction product was inhibited from functioning to increase the etching amount in a bottom portion, while being inhibited from conversely functioning to reduce the etching amount in the top.

[0165]

While the invention achieved by the present inventor has specifically been described on the basis of the examples, it will be appreciated that the present invention is not limited to the embodiments and examples described above, and can variously be

changed.

List of Reference Signs

[0166]

- | | |
|----|--|
| 1 | Process chamber |
| 2 | Wafer |
| 3 | Wafer stage |
| 11 | Base chamber |
| 12 | Quartz chamber |
| 13 | Discharge region |
| 14 | Pressure adjusting means |
| 15 | Exhaust means |
| 16 | Vacuum exhaust pipe |
| 20 | ICP coil |
| 21 | High frequency power source |
| 22 | Matching device |
| 23 | Shower plate |
| 24 | High gas dispersion plate |
| 25 | Ceiling plate |
| 26 | Slit plate |
| 27 | Flow path |
| 30 | Electrostatic adsorption electrode |
| 31 | Electrostatic adsorption DC power source |
| 38 | Chiller |
| 39 | Refrigerant flow path |
| 50 | Mass flow box |
| 51 | Gas distributor |
| 52 | Mass flow controller |

- 54 Valve
- 55 He gas
- 56 Proximity cooling projection
- 60, 60-1, 60-2, 60-3 IR lamp
- 61 Reflecting plate
- 64 IR lamp power source
- 70 Thermocouple
- 71 Thermocouple thermometer
- 72 IR light transmission window
- 73 IR lamp power source
- 74 High frequency cut filter
- 100, 100A Etching apparatus
- 101 Substrate
- 102 Silicon nitride film
- 103 Silicon oxide film
- 104 Opening portion
- 105 Layered films
- 106 Etching amount of silicon oxide film relative to silicon nitride film
- 109 Etching amount of silicon oxide films relative to silicon nitride films
- 111 End portion of silicon oxide film after etching when selectivity is low
- 112 Diagram illustrating example of end portion of silicon oxide film after etching in which film thickness of portion with silicon oxide film is small, while corner of silicon oxide film retains rectangular shape

113 Diagram illustrating example of end portion of silicon oxide film after etching when selectivity is high and film thickness is retained

Claims

[Claim 1]

An etching method, which is a dry etching method that supplies a process gas into a process chamber to etch, without using a plasma, a film structure formed in advance on a wafer placed in the process chamber to include stacked layers of silicon oxide films and a silicon nitride film vertically sandwiched between the silicon oxide films such that an end portion of each of the stacked layers forms a sidewall of a trench or a hole, the etching method comprising the steps of:

(a) causing a hydrogen fluoride gas to react at a predetermined temperature to form a reacting layer on the silicon nitride film;

(b) causing a polar solvent gas to flow to process the reacting layer formed in the step (a); and

(c) performing heating at a temperature higher than that in the step (a) in a state where the hydrogen fluoride gas is not allowed to flow, to evaporate and remove the reacting layer formed in the step (a) and processed in the step (b), wherein

the step (a), the step (b), and the step (c) are repeatedly performed a plurality of times to laterally etch the silicon nitride film from the end portion.

[Claim 2]

An etching method, which is a dry etching method that supplies a process gas into a process chamber to etch, without using a plasma, a film structure formed in advance on a wafer placed in the process chamber to include stacked layers of silicon

oxide films and a silicon nitride film vertically sandwiched the silicon oxide films such that an end portion of each of the stacked layers forms a sidewall of a trench or a hole, the etching method comprising the steps of:

(a) causing a hydrogen fluoride gas to react at a predetermined temperature to form a reacting layer on the silicon nitride film; and

(d) performing heating at a temperature higher than that in the step (a) in a state where a polar solvent gas is caused to flow while the hydrogen fluoride gas is not allowed to flow, to evaporate and remove the reacting layer formed in the step (a), wherein

the step (a) and the step (d) are repeatedly performed a plurality of times to laterally etch the silicon nitride film from the end portion.

[Claim 3]

The etching method according to claim 1, wherein the temperature in the step (a) is 30°C or more and 55°C or less.

[Claim 4]

The etching method according to claim 1, wherein a temperature in the step (c) is 70° or more and 110°C or less.

[Claim 5]

The etching method according to claim 1, wherein the polar solvent in the step (b) is alcohol.

[Claim 6]

The etching method according to claim 1, wherein the heating in the step (c) is lamp heating.

[Claim 7]

The etching method according to claim 1, wherein in the step (a) and the step (c), a stage is set to a low temperature of -50°C or more and 0°C or less, and lamp heating is performed thereon to obtain a temperature of 30°C or more and 55°C or less for the stage in the step (a) and further obtain a temperature of 70°C or more and 110°C or less for the stage in the step (c).

[Claim 8]

The etching method according to claim 1, wherein a pressure in the step (a) is 50 Pa or more and 1000 Pa or less.

[Claim 9]

The etching method according to claim 1, wherein between each of the steps (a) and (b) and the step (c), a step of performing exhaust, while causing an inert gas to flow, is inserted.

[Claim 10]

The etching method according to claim 2, wherein the temperature in the step (a) is 30°C or more and 55°C or less.

[Claim 11]

The etching method according to claim 2, wherein a temperature in the step (d) is 70°C or more and 110°C or less.

[Claim 12]

The etching method according to claim 2, wherein
the polar solvent in the step (d) is alcohol.

[Claim 13]

The etching method according to claim 2, wherein
the heating in the step (d) is lamp heating.

[Claim 14]

The etching method according to claim 2, wherein
in the step (a) and the step (d), a stage is set to a low
temperature of -50°C or more and 0°C or less, and lamp heating is
performed thereon to obtain a temperature of 30°C or more and 55°C
less for the stage in the step (a) and further obtain a temperature
of 70°C or more and 110°C or less for the stage in the step (d).

[Claim 15]

The etching method according to claim 2, wherein
a pressure in the step (a) is 50 Pa or more and 1000 Pa or
less.

[Claim 16]

The etching method according to claim 2, wherein
between the step (a) and the step (d), a step of performing
exhaust, while causing an inert gas to flow, is inserted.