

ETCHING METHOD AND PLASMA PROCESSING APPARATUS

FIELD

[0001] Exemplary embodiments of the present disclosure relate to an etching method and
5 a plasma processing apparatus.

BACKGROUND

[0002] Patent Literature 1 describes a method for etching a film in a substrate. The film
contains silicon. The substrate further includes a mask on the film. The mask contains
10 amorphous carbon or organic polymers. The etching performed with the method uses a
plasma generated from a processing gas including a hydrocarbon gas and a hydrofluorocarbon
gas.

CITATION LIST

PATENT LITERATURE

15 [0003] Patent Literature 1: Japanese Unexamined Patent Application Publication No. 2016-
39310

BRIEF SUMMARY

TECHNICAL PROBLEM

20 [0004] One or more aspects of the present disclosure are directed to a technique for
reducing irregular features during etching.

SOLUTION TO PROBLEM

[0005] An etching method according to one exemplary embodiment of the present
25 disclosure includes (a) providing a substrate onto a substrate support, and (b) generating a
plasma from a processing gas including a hydrogen fluoride gas and a bromine-containing gas.
The substrate includes a silicon-containing film and a mask on the silicon-containing film.
The mask includes a sidewall defining at least one opening to expose the silicon-containing
film. The generating the plasma includes forming a first protective film containing bromine

on the sidewall to a lower portion of the sidewall and forming a recess in the silicon-containing film.

ADVANTAGEOUS EFFECTS

5 [0006] The technique according to one exemplary embodiment of the present disclosure can reduce irregular features during etching.

BRIEF DESCRIPTION OF DRAWINGS

[0007] FIG. 1 is a diagram of a plasma processing system, illustrating an example structure.

10 FIG. 2 is a diagram of a capacitively coupled plasma processing apparatus, illustrating an example structure.

FIG. 3 is a flowchart of an example of an etching method.

FIG. 4 is a diagram of a substrate W provided in step ST1, illustrating an example cross-sectional structure.

15 FIG. 5 is a diagram of the substrate W during step ST2, illustrating an example cross-sectional structure.

DETAILED DESCRIPTION

[0008] One or more embodiments of the present disclosure will be described below.

20 [0009] In one exemplary embodiment, an etching method includes (a) providing a substrate onto a substrate support, and (b) generating a plasma from a processing gas including a hydrogen fluoride gas and a bromine-containing gas. The substrate includes a silicon-containing film and a mask on the silicon-containing film. The mask includes a sidewall defining at least one opening to expose the silicon-containing film. The generating the plasma
25 includes forming a first protective film containing bromine on the sidewall to a lower portion of the sidewall and forming a recess in the silicon-containing film.

[0010] In one exemplary embodiment, the lower portion of the sidewall includes a boundary with the silicon-containing film.

[0011] In one exemplary embodiment, the bromine-containing gas includes a bromine-

containing unsaturated halon gas.

[0012] In one exemplary embodiment, the bromine-containing gas includes an unsaturated halon represented by $R^1R^2C=CR^3R^4$, where R^1 , R^2 , R^3 , and R^4 each independently represent a hydrogen atom or a halogen atom, and at least one of R^1 , R^2 , R^3 , or R^4 represents a bromine atom.

[0013] In one exemplary embodiment, the unsaturated halon includes C_2BrF_3 .

[0014] In one exemplary embodiment, (b) further includes forming a second protective film on at least a part of the sidewall defining the recess.

[0015] In one exemplary embodiment, the second protective film is free of bromine or contains bromine with a lower concentration than the first protective film.

[0016] In one exemplary embodiment, the etching method further includes (c) controlling a temperature of the substrate support to be lower than or equal to 0 °C between (a) and (b).

[0017] In one exemplary embodiment, the processing gas further includes at least one gas selected from the group consisting of a phosphorus-containing gas, a carbon-containing gas, a halogen-containing gas different from the bromine-containing unsaturated halon gas, and a metal-containing gas.

[0018] In one exemplary embodiment, the phosphorus-containing gas includes at least one of PF_3 or $POCl_3$.

[0019] In one exemplary embodiment, the carbon-containing gas includes at least one selected from the group consisting of a CF-based gas, a CHF-based gas, and a CH-based gas.

[0020] In one exemplary embodiment, the halogen-containing gas includes at least one selected from the group consisting of Cl_2 , HCl, and HBr.

[0021] In one exemplary embodiment, the metal-containing gas includes at least one of WF_6 or MoF_6 .

[0022] In one exemplary embodiment, the silicon-containing film includes at least one selected from the group consisting of a silicon oxide film, a silicon nitride film, and a polycrystalline silicon film.

[0023] In one exemplary embodiment, the mask includes at least one selected from the group consisting of a carbon-containing film, a metal-containing film, and another silicon-

containing film.

[0024] In one exemplary embodiment, the metal-containing film includes a tungsten-containing film.

[0025] In one exemplary embodiment, the other silicon-containing film includes a BSi film.

5 [0026] In one exemplary embodiment, a plasma processing apparatus includes a chamber, a substrate support in the chamber, a gas supply that supplies a processing gas into the chamber, a plasma generator that generates a plasma from the processing gas, and a controller that performs, with the gas supply and the plasma generator, control operations including (a) providing a substrate onto a substrate support, and (b) generating a plasma from a processing
10 gas including a hydrogen fluoride gas and a bromine-containing gas. The substrate includes a silicon-containing film and a mask on the silicon-containing film. The mask includes a sidewall defining at least one opening to expose the silicon-containing film. The generating the plasma includes forming a first protective film containing bromine on the sidewall to a lower portion of the sidewall and forming a recess in the silicon-containing film.

15 [0027] One or more embodiments of the present disclosure will now be described with reference to the drawings. In the drawings, like reference numerals denote the same or like components. Such components will not be described repeatedly. Unless otherwise specified, the positional relationships shown in the drawings are used to describe the vertical, lateral, and other positions. The drawings are not drawn to scale relative to the actual ratio of each
20 component, and the actual ratio is not limited to the ratio in the drawings.

Example of Plasma Processing System

[0028] FIG. 1 is a diagram of a plasma processing system, illustrating an example structure. In one embodiment, the plasma processing system includes a plasma processing apparatus 1 and a controller 2. The plasma processing system is an example of a substrate processing
25 system. The plasma processing apparatus 1 is an example of a substrate processing apparatus. The plasma processing apparatus 1 includes a plasma processing chamber 10, a substrate support 11, and a plasma generator 12. The plasma processing chamber 10 has a plasma processing space. The plasma processing chamber 10 also has at least one gas inlet for supplying at least one processing gas into the plasma processing space and at least one gas

outlet for exhausting the gas from the plasma processing space. The gas inlet is connected to a gas supply 20 (described later). The gas outlet is connected to an exhaust system 40 (described later). The substrate support 11 is located in the plasma processing space and has a substrate support surface for supporting a substrate.

5 [0029] The plasma generator 12 generates a plasma from at least one processing gas supplied into the plasma processing space. The plasma generated in the plasma processing space may be, for example, a capacitively coupled plasma (CCP), an inductively coupled plasma (ICP), an electron cyclotron resonance (ECR) plasma, a helicon wave plasma (HWP), or a surface wave plasma (SWP). The plasma generator 12 may be one of various plasma
10 generators including an alternating current (AC) plasma generator and a direct current (DC) plasma generator. In one embodiment, an AC signal (AC power) used in the AC plasma generator has a frequency in a range of 100 kHz to 10 GHz. Thus, the AC signal may be a radio-frequency (RF) signal or a microwave signal. In one embodiment, the RF signal has a frequency in a range of 100 kHz to 150 MHz.

15 [0030] The controller 2 processes computer-executable instructions that cause the plasma processing apparatus 1 to perform various steps described in one or more embodiments of the present disclosure. The controller 2 may cause the components of the plasma processing apparatus 1 to perform the various steps described herein. In one embodiment, some or all of the components of the controller 2 may be included in the plasma processing apparatus 1. The
20 controller 2 is implemented by, for example, a computer 2a. The controller 2 may include a processor 2a1, a storage 2a2, and a communication interface 2a3. The functions of the processor 2a1 described herein may be implemented by circuitry or processing circuitry including at least one or any combination of a general-purpose processor, a specific-purpose processor, integrated circuits, application-specific integrated circuits (ASICs), a central
25 processing unit (CPU), and conventional circuitry, which are programmed to implement the described functions. The processor serves as circuitry or processing circuitry including a transistor and other circuitry. The processor may be programmed to execute a program stored in the storage 2a2. The program may be prestored in the storage 2a2 or may be obtained through a medium as appropriate. The obtained program is stored into the storage 2a2 to be

loaded from the storage 2a2 and executed by the processor 2a1. The medium may be one of various storage media readable by the computer 2a or a communication line connected to the communication interface 2a3. The storage 2a2 may include a random-access memory (RAM), a read-only memory (ROM), a hard disk drive (HDD), a solid-state drive (SSD), or a combination of these. The communication interface 2a3 may communicate with the plasma processing apparatus 1 through a communication line such as a local area network (LAN). In one or more embodiments of the present disclosure, circuitry, units, and means are hardware programmed to implement the described functions or configured to perform the described functions. The hardware may be any hardware described in one or more embodiments of the present disclosure or any hardware programmed to implement the described functions or known to perform the described functions. For the hardware being a processor that is substantially one type of circuitry, the circuitry, means, or units are a combination of hardware and software used to configure the hardware or the processor, or both.

[0031] An example structure of a capacitively coupled plasma processing apparatus as an example of the plasma processing apparatus 1 will now be described. FIG. 2 is a diagram of the capacitively coupled plasma processing apparatus, illustrating an example structure.

[0032] The capacitively coupled plasma processing apparatus 1 includes the plasma processing chamber 10, the gas supply 20, a power supply system 30, and the exhaust system 40. The plasma processing apparatus 1 further includes the substrate support 11 and a gas guide unit. The gas guide unit allows at least one processing gas to be introduced into the plasma processing chamber 10. The gas guide unit includes a showerhead 13. The substrate support 11 is located in the plasma processing chamber 10. The showerhead 13 is located above the substrate support 11. In one embodiment, the showerhead 13 defines at least a part of the ceiling of the plasma processing chamber 10. The plasma processing chamber 10 has a plasma processing space 10s defined by the showerhead 13, a sidewall 10a of the plasma processing chamber 10, and the substrate support 11. The plasma processing chamber 10 is grounded. The showerhead 13 and the substrate support 11 are electrically insulated from the housing of the plasma processing chamber 10.

[0033] The substrate support 11 includes a body 111 and a ring assembly 112. The body

111 includes a central portion 111a for supporting a substrate W and an annular portion 111b for supporting the ring assembly 112. A wafer is an example of the substrate W. The annular portion 111b of the body 111 surrounds the central portion 111a of the body 111 as viewed in plan. The substrate W is placeable on the central portion 111a of the body 111. The ring assembly 112 is located on the annular portion 111b of the body 111 to surround the substrate W on the central portion 111a of the body 111. Thus, the central portion 111a is also referred to as a substrate support surface for supporting the substrate W. The annular portion 111b is also referred to as a ring support surface for supporting the ring assembly 112.

[0034] In one embodiment, the body 111 includes a base 1110 and an electrostatic chuck (ESC) 1111. The base 1110 includes a conductive member. The conductive member in the base 1110 may function as a lower electrode. The ESC 1111 is located on the base 1110. The ESC 1111 includes a ceramic member 1111a and an ESC electrode 1111b located inside the ceramic member 1111a. The ESC electrode 1111b is also referred to as a clamping electrode. In one embodiment, the ESC electrode 1111b is electrically connected or coupled to a chuck power supply. The chuck power supply may be a DC power supply or an AC power supply. The ceramic member 1111a includes the central portion 111a. In one embodiment, the ceramic member 1111a also includes the annular portion 111b. The annular portion 111b may be included in another member surrounding the ESC 1111, such as an annular ESC or an annular insulating member. In this case, the ring assembly 112 may be located on the annular ESC or the annular insulating member, or may be located on both the ESC 1111 and the annular insulating member. At least one bias electrode electrically connected or coupled to a power supply 31 or a power supply 32, or both (described later) may be located inside the ceramic member 1111a. In this case, the at least one bias electrode functions as a lower electrode. The conductive member in the base 1110 and the bias electrode inside the ceramic member 1111a may function as multiple lower electrodes. In one embodiment, the bias electrode inside the ceramic member 1111a is electrically connected or coupled to a first voltage generator 32a, which functions as a voltage pulse generator (described later). The conductive member in the base 1110 is electrically connected or coupled to a first RF generator 31a (described later). The ESC electrode 1111b may also function as a lower electrode. The substrate support 11

thus includes at least one lower electrode.

[0035] The ring assembly 112 includes one or more annular members. In one embodiment, the one or more annular members include one or more edge rings and at least one cover ring. The edge rings are formed from a conductive material or an insulating material.

5 The cover ring is formed from an insulating material.

[0036] The substrate support 11 may include a temperature controller that adjusts the temperature of at least one of the ESC 1111, the ring assembly 112, or the substrate to a target temperature. The temperature controller may include a heater, a heat transfer medium, a channel 1110a, or a combination of these. The channel 1110a carries a heat transfer fluid such
10 as brine or a gas. In one embodiment, the channel 1110a is defined inside the base 1110, and one or more heaters are located inside the ceramic member 1111a in the ESC 1111. The substrate support 11 may include a heat transfer gas supply to supply a heat transfer gas into a space between the back surface of the substrate W and the central portion 111a.

[0037] The showerhead 13 introduces at least one processing gas from the gas supply 20
15 into the plasma processing space 10s. The showerhead 13 includes at least one gas inlet 13a, at least one gas-diffusion compartment 13b, and multiple gas guides 13c. The processing gas supplied to the gas inlet 13a passes through the gas-diffusion compartment 13b and is introduced into the plasma processing space 10s through the multiple gas guides 13c. The showerhead 13 further includes at least one upper electrode. In addition to the showerhead 13,
20 the gas guide unit may include one or more side gas injectors (SGIs) installed in one or more openings in the sidewall 10a.

[0038] The gas supply 20 may include at least one gas source 21 and at least one flow controller 22. In one embodiment, the gas supply 20 supplies at least one processing gas from each gas source 21 to the showerhead 13 through the corresponding flow controller 22. The
25 flow controller 22 may be, for example, a mass flow controller or a pressure-based flow controller. The gas supply 20 may further include at least one flow rate modulator that causes at least one processing gas to be supplied at a modulated flow rate or in a pulsed manner.

[0039] The power supply system 30 includes the power supply 31 electrically connected or coupled to the plasma processing chamber 10. In one embodiment, the power supply 31 is

electrically connected or coupled to the plasma processing chamber 10 through at least one impedance matcher. The impedance matcher may be a mechanical- or an electronic-controlled matcher. The power supply 31 provides at least one RF signal (RF power) to at least one lower electrode or at least one upper electrode, or both. This generates plasma from at least one processing gas supplied into the plasma processing space 10s. The power supply 31 may thus function as at least a part of the plasma generator 12. A bias RF signal is provided to at least one lower electrode to generate a bias potential in the substrate W, thus drawing ion components in the generated plasma toward the substrate W.

[0040] The power supply 31 includes the first RF generator 31a and a second RF generator 31b. The first RF generator 31a is electrically connected or coupled to at least one lower electrode or at least one upper electrode, or both to generate a source RF signal (source RF power) for generating plasma in the plasma processing space 10s. In one embodiment, the first RF generator 31a is electrically connected or coupled to at least one lower electrode or at least one upper electrode, or both through at least one impedance matcher. In one embodiment, the source RF signal has a frequency in a range of 10 to 150 MHz. In one embodiment, the first RF generator 31a may generate multiple source RF signals with different frequencies. The one or more generated source RF signals are provided to at least one lower electrode or at least one upper electrode, or both.

[0041] The second RF generator 31b is electrically connected or coupled to at least one lower electrode to generate a bias RF signal (bias RF power). In one embodiment, the second RF generator 31b is electrically connected or coupled to at least one lower electrode through at least one impedance matcher. When the first RF generator 31a is electrically connected or coupled to a lower electrode, the second RF generator 31b may be electrically connected or coupled to the same lower electrode or to another lower electrode. The frequency of the bias RF signal may be the same as or different from the frequency of the source RF signal. In one embodiment, the bias RF signal has a lower frequency than the source RF signal. In one embodiment, the bias RF signal has a frequency in a range of 100 kHz to 60 MHz. In one embodiment, the second RF generator 31b may generate multiple bias RF signals with different frequencies. The one or more generated bias RF signals are provided to at least one lower

electrode. In various embodiments, at least one of the source RF signal or the bias RF signal may be pulsed.

[0042] The power supply system 30 may include the power supply 32 electrically connected or coupled to the plasma processing chamber 10. The power supply 32 includes the first voltage generator 32a and a second voltage generator 32b. In one embodiment, the first voltage generator 32a is electrically connected or coupled to at least one lower electrode to generate a first voltage signal. The generated first voltage signal is applied to at least one lower electrode. In one embodiment, the second voltage generator 32b is electrically connected or coupled to at least one upper electrode to generate a second voltage signal. The generated second voltage signal is applied to at least one upper electrode.

[0043] In various embodiments, the first voltage signal or the second voltage signal, or both may be pulsed. In this case, the first voltage generator 32a or the second voltage generator 32b, or both function as a voltage pulse generator that generates a sequence of voltage pulses. The sequence of voltage pulses is thus applied to at least one lower electrode or at least one upper electrode, or both. In one embodiment, the sequence of voltage pulses includes multiple cycles each including a burst of voltage pulses in a first period and a constant reference voltage in a second period. In other words, bursts of voltage pulses are repeated in the sequence of voltage pulses. The absolute value of the voltage level of the voltage pulses is greater than the absolute value of the voltage level of the reference voltage. The voltage pulses may have any of rectangular, trapezoidal, and triangular pulse waveforms, or a combination of these. The pulse waveforms may change over time. The voltage pulses may have positive polarity or negative polarity. The sequence of voltage pulses may include one or more positive voltage pulses and one or more negative voltage pulses within one cycle. The power supply system 30 may include the first voltage generator 32a and the second voltage generator 32b in addition to the power supply 31 or may include the first voltage generator 32a in place of the second RF generator 31b.

[0044] The exhaust system 40 is connectable to, for example, a gas outlet 10e in the bottom of the plasma processing chamber 10. The exhaust system 40 may include a pressure control valve and a vacuum pump. The pressure control valve regulates the pressure in the plasma

processing space 10s. The vacuum pump may be a turbomolecular pump, a dry pump, or a combination of these.

Example of Etching Method

[0045] FIG. 3 is a flowchart of an etching method (hereafter also referred to as the method) according to an exemplary embodiment. The method includes step ST1 of preparing a substrate and step ST2 of generating a plasma. Each step may be performed using any one or more of the plasma processing systems (refer to FIGs. 1 and 2) described above. For example, the method may be implemented using the plasma processing system illustrated in FIG. 1. In the example described below, the controller 2 causes the components of the plasma processing apparatus 1 illustrated in FIG. 2 to implement the method on the substrate W.

Step ST1: Providing Substrate

[0046] In step ST1, the substrate W is provided onto the substrate support 11. In one embodiment, the substrate W is loaded into the chamber 10 with a transfer arm, placed onto the substrate support 11 with a lifter, and clamped on the substrate support 11 as illustrated in, for example, FIG. 2.

[0047] FIG. 4 is a diagram of the substrate W provided in step ST1, illustrating an example cross-sectional structure. As illustrated in FIG. 4, the substrate W may include a silicon-containing film SF and a mask MK stacked on a given underlying film UF in this order. The substrate W includes the silicon-containing film SF and the mask MK on the silicon-containing film SF. The mask MK includes at least one opening OP to expose the silicon-containing film SF. The substrate W may be used for manufacturing semiconductor devices. Examples of the semiconductor devices include a memory device such as a dynamic RAM (DRAM) and a three-dimensional NOT-AND (3D-NAND) flash memory, and a logic device.

[0048] The underlying film UF may be, for example, a silicon wafer or an organic film, a dielectric film, a metal film, or a semiconductor film on the silicon wafer. The underlying film UF may include multiple films stacked on one another.

[0049] Examples of the silicon-containing film SF include a spin-on-glass (SOG) film, a silicon-containing antireflective coating (SiARC), a silicon oxide film, a silicon nitride film, a silicon oxynitride film, a silicon carbon film, a silicon carbonitride film, a polycrystalline silicon

film, and an amorphous silicon film. In one embodiment, the silicon-containing film SF includes at least one selected from the group consisting of a silicon oxide film, a silicon nitride film, and a polycrystalline silicon film. In one example, the silicon-containing film may be a film stack including a silicon oxide film and a silicon nitride film or a film stack including a silicon oxide film and a polycrystalline silicon film. For example, the silicon-containing film SF may include silicon oxide films and silicon nitride films alternately stacked on one another. For example, the silicon-containing film SF may include silicon oxide films and polycrystalline silicon films alternately stacked on one another. For example, the silicon-containing film SF may be a film stack including a silicon nitride film, a silicon oxide film, and a polycrystalline silicon film. In one embodiment, the silicon-containing film SF may contain at least one element selected from the group consisting of H, P, N, and B.

[0050] The silicon-containing film SF and the underlying film UF may be formed by, for example, chemical vapor deposition (CVD), atomic layer deposition (ALD), molecular layer deposition (MLD), physical vapor deposition (PVD), or spin coating. The silicon-containing film SF and the underlying film UF may each be a flat film or an uneven film.

[0051] The mask MK on the silicon-containing film SF includes a sidewall Wa defining at least one opening OP. The mask MK may include at least one selected from the group consisting of a carbon-containing film, a metal-containing film, and another silicon-containing film (a silicon-containing film different from the silicon-containing film SF). In one embodiment, the carbon-containing film may be a spin-on carbon (SOC) film, an amorphous carbon (ACL) film, a photoresist film, a tungsten carbide film, or a boron carbide film. In one example, the carbon-containing film includes an ACL film. In one embodiment, the metal-containing film may contain at least one metal selected from the group consisting of tungsten, molybdenum, ruthenium, titanium, tin, and aluminum. In one example, the metal-containing film includes a tungsten-containing film. In one embodiment, the other silicon-containing film may be a silicon oxide film, a silicon nitride film, a silicon carbonitride film, a polycrystalline silicon film, and a carbon-containing silicon film. The other silicon-containing film may be doped with an element such as phosphorus, boron, or nitrogen. In one example, the other silicon-containing film includes a boron-doped silicon (BSi) film. In one

embodiment, the mask MK may be a single layer mask including one layer or a multilayer mask including two or more layers. In one embodiment, the mask MK may be a photoresist. In one embodiment, the mask MK may be a photoresist exposed to extreme ultraviolet (EUV). In one example, a metal-containing resist may be exposed to EUV. In one embodiment, the mask MK may be a chemically amplified resist (CAR). In one example, the CAR may be exposed to EUV.

[0052] In the example in FIG. 4, the mask MK includes the sidewall Wa and an upper surface Wb. The sidewall Wa defines at least one opening OP. The opening OP may have any feature in a plan view of the substrate W, or in other words, when the substrate W is viewed from the top to the bottom in FIG. 4. The opening feature may be, for example, a circle, an oval, a rectangle, a line, or a combination of one or more of these features. The mask MK may include multiple sidewalls, which may define multiple openings OP. The openings OP may be slits arranged in a pattern of lines and spaces at regular intervals. The openings OP may be holes in a patterned array. In one embodiment, each opening OP may have a dimension of 100 nm or less, 50 nm or less, or 30 nm or less. In one embodiment, the opening OP may be formed by lithography. In one example, the opening OP may be formed by exposing and developing the photoresist on the silicon-containing film SF. For the photoresist being an EUV resist, the exposure may be EUV exposure using an EUV exposure device. The development may be dry development or wet development.

[0053] The process of forming the underlying film UF, the silicon-containing film SF, and the mask MK in the substrate W may be at least partially performed in the chamber 10 as part of step ST1. When, for example, the opening OP in the mask MK is formed by etching, the etching in step ST1 and the processing in step ST2 may be performed sequentially in the chamber 10. In one embodiment, all or some of the substrate W may be formed in an apparatus or a chamber external to the plasma processing apparatus 1 and then provided into the chamber 10.

[0054] In one embodiment, after the substrate W is provided onto the central portion 111a of the substrate support 11, the temperature of the substrate support 11 is controlled to a set temperature by the temperature controller. The set temperature may be, for example, 0 °C or

lower, $-10\text{ }^{\circ}\text{C}$ or lower, $-20\text{ }^{\circ}\text{C}$ or lower, $-30\text{ }^{\circ}\text{C}$ or lower, $-40\text{ }^{\circ}\text{C}$ or lower, $-50\text{ }^{\circ}\text{C}$ or lower, $-60\text{ }^{\circ}\text{C}$ or lower, or $-70\text{ }^{\circ}\text{C}$ or lower. In one example, controlling the temperature of the substrate support 11 to the set temperature includes causing the temperature of the heat transfer fluid flowing through the channel 1110a and the temperature of the heater to be the respective set temperatures, or to be temperatures different from the respective set temperatures. The heat transfer fluid may start to flow through the channel 1110a before, after, or at the same time as the substrate W is placed onto the substrate support 11. The temperature of the substrate support 11 may be controlled to the set temperature before step ST1. In other words, the substrate W may be provided onto the substrate support 11 after the temperature of the substrate support 11 is controlled to the set temperature.

[0055] In one embodiment, the temperature of the substrate W, in place of the temperature of the substrate support 11, may be controlled to the set temperature. Controlling the temperature of the substrate W to the set temperature includes causing at least one of the temperature of the substrate support 11, the temperature of the heat transfer fluid flowing through the channel 1110a, or the temperature of the heater to be the set temperature, or to be a temperature different from the set temperature.

Step ST2: Generating Plasma

[0056] In step ST2, a plasma is generated from a processing gas including a hydrogen fluoride gas (hereafter also referred to as an HF gas) and a bromine-containing gas. In step ST2, the plasma generation forms a first protective film PM containing bromine on the sidewall Wa to a lower portion of the sidewall Wa. In step ST2, the plasma generation also forms a recess RC in the silicon-containing film SF. In one embodiment, the first protective film PM and the recess RC are formed in parallel. In one embodiment, the recess RC is formed after the first protective film PM is formed. In one embodiment, the first protective film PM is formed after the recess RC is formed. In one embodiment, step ST2 includes supplying the processing gas into the chamber 10 and generating a plasma from the processing gas.

[0057] In step ST2, the processing gas is supplied into the chamber 10. The processing gas may be supplied into the chamber 10 from, for example, the gas supply 20 through the gas guide 13c in a central gas inlet 13. The processing gas includes an HF gas and a bromine-

containing gas. The temperature of the substrate support 11 or the substrate W may be controlled to the set temperature as in step ST1.

[0058] The HF gas may have the highest flow rate (partial pressure) among components of the processing gas excluding an inert component. In one example, the flow rate of the HF gas may be 50 vol% or more, 60 vol% or more, 70 vol% or more, 80 vol% or more, 90 vol% or more, or 95 vol% or more of the total flow rate of all components of the processing gas (all components of the processing gas excluding an inert component when the processing gas includes an inert gas). The flow rate of the HF gas may be less than 100 vol%, 99.5 vol% or less, 98 vol% or less, or 96 vol% or less of the total flow rate of all components of the processing gas. In one example, the flow rate of the HF gas is 70 to 96 vol% inclusive of the total flow rate of all components of the processing gas.

[0059] In one embodiment, the bromine-containing gas includes a bromine-containing unsaturated halon gas. In one embodiment, the bromine-containing unsaturated halon gas contains an unsaturated halon represented by $R^1R^2C=CR^3R^4$, where R^1 , R^2 , R^3 , and R^4 each independently represent a hydrogen atom or a halogen atom, and at least one of R^1 , R^2 , R^3 , or R^4 represents a bromine atom. In one embodiment, the unsaturated halon contains at least one of C_2BrF_3 or C_2H_2BrF . In one example, the unsaturated halon contains C_2BrF_3 . In addition to the above, the bromine-containing gas may further contain HBr.

[0060] In one embodiment, the processing gas further includes at least one gas selected from the group consisting of a phosphorus-containing gas, a carbon-containing gas, a halogen-containing gas different from the bromine-containing unsaturated halon gas, and a metal-containing gas.

[0061] In one example, the phosphorus-containing gas may be a phosphorus halide gas. The phosphorus halide gas may be a phosphorus fluoride gas containing fluorine as a halogen element, such as a PF_3 gas or a PF_5 gas. The phosphorus halide gas may be a phosphorus chloride gas containing fluorine as a halogen element, such as a PCl_3 gas or a PCl_5 gas. The phosphorus halide gas may contain bromine or iodine as a halogen element, such as a PBr_3 gas, a PBr_5 gas, or a PI_3 gas. The phosphorus halide gas may contain, two or more halogen elements, such as a $PClF_2$ gas, a PCl_2F gas, or a PCl_2F_3 gas. The phosphorus halide gas may

be, for example, a phosphorus oxyfluoride gas or a phosphorus oxychloride gas. The phosphorus halide gas may be, for example, a POF_3 gas, a POCl_3 gas, a POF_2Cl_2 gas, a POFCl_2 gas, or a POF_2Cl gas.

[0062] In one embodiment, the carbon-containing gas includes at least one selected from the group consisting of a CF-based gas, a CHF-based gas, and a CH-based gas. In one example, the CF-based gas may be at least one selected from the group consisting of a CF_4 gas, a C_2F_2 gas, a C_2F_4 gas, a C_3F_6 gas, a C_3F_8 gas, a C_4F_6 gas, a C_4F_8 gas, and a C_5F_8 gas. In one example, the CHF-based gas may be at least one selected from the group consisting of a CHF_3 gas, a CH_2F_2 gas, a CH_3F gas, a C_2HF_5 gas, and a hydrofluorocarbon gas having three or more carbon atoms (e.g., a $\text{C}_3\text{H}_2\text{F}_4$ gas, a $\text{C}_3\text{H}_2\text{F}_6$ gas, or a $\text{C}_4\text{H}_2\text{F}_6$ gas).

[0063] In one embodiment, the halogen-containing gas different from the bromine-containing unsaturated halon gas contains at least one selected from the group consisting of Cl_2 , HCl , and HBr .

[0064] In one embodiment, the metal-containing gas contains at least one metal selected from the group consisting of tungsten, titanium, ruthenium, and molybdenum. In one embodiment, the metal-containing gas may further contain halogen. The metal-containing gas may be, for example, a WF_2 gas, a WF_4 gas, a WF_5 gas, a WF_6 gas, a WCl_2 gas, a WCl_4 gas, a WCl_5 gas, a WCl_6 gas, a MoF_4 gas, a MoF_6 gas, a MoCl_6 gas, or a TiCl_4 gas.

[0065] In one embodiment, the processing gas may further include an inert gas. In one example, the inert gas may be a noble gas such as an Ar gas, a He gas, and a Kr gas, or an N_2 gas.

[0066] In one embodiment, the processing gas may include, in place of part or all of the HF gas, a gas that can generate an HF species in the plasma. The HF species includes at least any of a gas, radicals, or ions of HF. The gas that can generate an HF species may be, for example, a CHF-based gas. The CHF-based gas may have two or more, three or more, or four or more carbon atoms.

[0067] The gas that can generate an HF species may be a mixture gas including, for example, a hydrogen source and a fluorine source. The hydrogen source may be at least one selected from the group consisting of an H_2 gas, an NH_3 gas, an H_2O gas, an H_2O_2 gas, and a

CH-based gas. The fluorine source may be a carbon-free fluorine-containing gas, such as an NF_3 gas, an SF_6 gas, a WF_6 gas, or an XeF_2 gas. The fluorine source may be a fluorine-containing gas containing carbon, such as a CF-based gas or a CHF-based gas.

[0068] A plasma is then generated from the processing gas in the chamber 10. In one embodiment, a source RF signal is provided to the lower electrode of the substrate support 11 or the upper electrode of the showerhead 13, or both. An RF electric field between the showerhead 13 and the substrate support 11 is generated to generate a plasma from the processing gas in the plasma processing space 10s. In this case, a bias signal may be provided to the substrate support 11. The bias signal may be a bias RF signal provided from the RF power supply 31 or a bias DC signal provided from the DC power supply 32. In this case, a bias potential is generated between the plasma and the substrate W.

[0069] FIG. 5 is a diagram of the substrate W during step ST2, illustrating an example cross-sectional structure. In step ST2, bromine dissociated from the bromine-containing gas in the processing gas into a plasma is deposited on the mask MK. This forms the first protective film PM on the mask MK. The first protective film PM contains bromine. In one embodiment, the first protective film PM is formed on the sidewall Wa of the mask MK from an upper portion (hereafter also referred to as a second portion R2) to a lower portion (hereafter also referred to as a first portion R1) of the sidewall Wa. In one embodiment, the first portion R1 of the sidewall Wa may extend from a boundary P1 between the mask MK and the silicon-containing film SF to a position P2 at half (50%) of the thickness of the mask MK. The second portion R2 may extend from the position P2 to a position P3 on the upper surface of the mask MK. In one embodiment, the first protective film PM may be formed partially or entirely on the first portion R1. In one embodiment, the first protective film PM may be formed partially or entirely on the second portion R1. In one embodiment, the first protective film PM may also be formed on the upper surface Wb of the mask MK as illustrated in FIG. 5.

[0070] Active species such as ions and radicals in the plasma are drawn toward the substrate W. In this case, the mask MK functions as a mask, and a portion of the silicon-containing film SF exposed to the opening OP is selectively etched with the active species (e.g., HF species) in the plasma. This forms the recess RC as illustrated in FIG. 5. The first

protective film PM functions as a protective film for the sidewall Wa of the mask MK. The first protective film PM is formed on the sidewall Wa of the mask MK from the upper portion (second portion R2) to the lower portion (first portion R1) of the sidewall Wa. This structure may reduce etching of the sidewall Wa in the lateral direction (the left-right direction in FIG. 5) with the active species in the plasma in the lower portion of the sidewall Wa of the mask MK as well as the upper portion. This may reduce irregular features such as bowing in the recess RC.

[0071] When the bromine-containing gas includes a bromine-containing unsaturated halon gas, the first protective film PM may extend more downward on the sidewall Wa, for example, to or close to the boundary P1 with the silicon-containing film. This structure may further reduce irregular features such as bowing. In one embodiment, when the bromine-containing gas includes a bromine-containing unsaturated halon gas and a hydrogen bromide gas, the bromine-containing unsaturated halon gas may have a higher flow rate than the hydrogen bromide gas. In one example, when the bromine-containing gas includes a C_2BrF_3 gas and a hydrogen bromide gas, the chlorine-containing gas may include the C_2BrF_3 gas at a higher flow rate than the hydrogen bromide gas.

[0072] In one embodiment, step ST2 may further include forming a second protective film (not shown) on at least a part of a sidewall Wc defining the recess RC. In one embodiment, the second protective film may include a reaction product generated by etching. For example, when the silicon-containing film includes a silicon nitride film, the second protective film may contain a silicofluoride ammonium salt ($(NH_4)_2SiF_6$ (AFS)). In one embodiment, the second protective film may be free of bromine or contain bromine with a lower concentration than the first protective film PM.

[0073] In one embodiment, the bottom of the recess reaches the underlying film UF during formation of the recess RC. This may expose at least a part of the underlying film UF to the opening OP. Step ST2 may end after or before (e.g., immediately before) at least a part of the underlying film UF is exposed. Step ST2 may end when a given stop condition is satisfied. The stop condition may be, for example, an etching time or the depth of the recess RC. Etching may end when supply of the source RF signal, the bias RF signal, the bias DC signal,

or the first processing gas is stopped.

Examples

[0074] Examples of evaluating a pattern shape with the method will now be described. One or more embodiments of the present disclosure are not limited to the examples described below.

First Reference Example

[0075] An apparatus with the same structure as the plasma processing apparatus 1 illustrated in FIG. 2 was prepared. A substrate was placed onto the substrate support 11 in the apparatus. The substrate had the same structure as the substrate W shown in FIG. 4. The silicon-containing film SF was a film stack including a silicon oxide film and a silicon nitride film. The mask MK was an amorphous carbon film. The mask MK included multiple openings OP to expose the silicon-containing film SF. More specifically, the openings OP were arranged to form a pattern of contact holes.

[0076] The plasma processing apparatus was used for etching to form a pattern of the contact holes. Etching was performed using a processing gas including an HF gas, an HBr gas, and a PF₃ gas.

[0077] The etching results revealed that a recess in the silicon-containing film had bowing (hereafter also referred to as a bowing feature). A protective film formed from a bromine-containing gas (HBr gas) was observed on an upper portion of a sidewall defining the opening OP of the mask in addition to the upper surface of the mask.

Second Reference Example

[0078] A pattern of contact holes was formed in the same manner as in the first reference example except that the amount of an HBr gas was 2.5 times the amount of the HBr gas under an etching condition in the first reference example.

[0079] The etching results revealed that a recess on the silicon-containing film had the same bowing feature as in the first reference example. More specifically, the maximum opening dimension of the bowing (hereafter also referred to as BCD) in the second reference example was 95.2% of the BCD in the first reference example. In the second reference example, a protective film formed from a bromine-containing gas (HBr gas) was observed on

the upper portion of the sidewall defining the opening OP of the mask in addition to the upper surface of the mask, as in the first reference example.

First Example

[0080] A pattern of contact holes was formed in the same manner as in the first reference example except that a C_2BrF_3 gas was also used as a processing gas under the etching condition in the first reference example.

[0081] The etching results revealed improvement in the bowing feature of the recess in the silicon-containing film. More specifically, the BCD in the first example was 92.6% of the BCD in the first reference example. In the first example, a protective film formed from a bromine-containing gas (C_2BrF_3 gas) extended entirely from the upper portion to the lower portion of the sidewall of the mask (the boundary between the mask and the silicon-containing film) in addition to the upper surface of the mask. In this manner, the protective film formed from the bromine-containing gas extending to the lower portion of the sidewall defining the opening OP of the mask tended to reduce bowing. When an unsaturated halon, such as C_2BrF_3 , was used as a bromine-containing gas, the protective film formed from the bromine-containing gas tended to extend to the lower portion of the sidewall.

[0082] The embodiments of the present disclosure further include the aspects described below.

Appendix 1

[0083] An etching method, comprising:

(a) providing a substrate onto a substrate support, the substrate including a silicon-containing film and a mask on the silicon-containing film, the mask including a sidewall defining at least one opening to expose the silicon-containing film; and

(b) generating a plasma from a processing gas including hydrogen fluoride and a bromine-containing gas, the generating including forming a first protective film comprising bromine on the sidewall to a lower portion of the sidewall and forming a recess in the silicon-containing film.

Appendix 2

[0084] The etching method according to appendix 1, wherein

the lower portion of the sidewall includes a boundary with the silicon-containing film.

Appendix 3

[0085] The etching method according to appendix 1 or appendix 2, wherein the bromine-containing gas includes a bromine-containing unsaturated halon gas.

5 Appendix 4

[0086] The etching method according to any one of appendixes 1 to 3, wherein the bromine-containing gas includes an unsaturated halon represented by $R^1R^2C=CR^3R^4$, where R^1 , R^2 , R^3 , and R^4 each independently represent a hydrogen atom or a halogen atom, and at least one of R^1 , R^2 , R^3 , or R^4 represents a bromine atom.

10 Appendix 5

[0087] The etching method according to appendix 4, wherein the unsaturated halon includes C_2BrF_3 .

Appendix 6

[0088] The etching method according to any one of appendixes 1 to 5, wherein

15 (b) further includes forming a second protective film on at least a part of the sidewall defining the recess.

Appendix 7

[0089] The etching method according to appendix 6, wherein

the second protective film is free of bromine or comprises bromine with a lower
20 concentration than the first protective film.

Appendix 8

[0090] The etching method according to any one of appendixes 1 to 8, further comprising:

(c) controlling a temperature of the substrate support to be lower than or equal to 0 °C between (a) and (b).

25 Appendix 9

[0091] The etching method according to appendix 3, wherein

the processing gas further includes at least one gas selected from the group consisting of a phosphorus-containing gas, a carbon-containing gas, a halogen-containing gas different from the bromine-containing unsaturated halon gas, and a metal-containing gas.

Appendix 10

[0092] The etching method according to appendix 9, wherein
the phosphorus-containing gas includes at least one of PF_3 or POCl_3 .

Appendix 11

5 [0093] The etching method according to appendix 9 or appendix 10, wherein
the carbon-containing gas includes at least one selected from the group consisting of a CF-based gas, a CHF-based gas, and a CH-based gas.

Appendix 12

[0094] The etching method according to any one of appendixes 9 to 11, wherein
10 the halogen-containing gas includes at least one selected from the group consisting of Cl_2 , HCl , and HBr .

Appendix 13

[0095] The etching method according to any one of appendixes 9 to 12, wherein
the metal-containing gas includes at least one of WF_6 or MoF_6 .

15 Appendix 14

[0096] The etching method according to any one of appendixes 1 to 13, wherein
the silicon-containing film includes at least one selected from the group consisting of a silicon oxide film, a silicon nitride film, and a polycrystalline silicon film.

Appendix 15

20 [0097] The etching method according to any one of appendixes 1 to 14, wherein
the mask includes at least one selected from the group consisting of a carbon-containing film, a metal-containing film, and another silicon-containing film.

Appendix 16

[0098] The etching method according to appendix 15, wherein
25 the carbon-containing film includes an amorphous carbon film.

Appendix 17

[0099] The etching method according to appendix 15 or appendix 16, wherein
the metal-containing film includes a tungsten-containing film.

Appendix 18

[0100] The etching method according to any one of appendixes 15 to 17, wherein the other silicon-containing film includes a BSi film.

Appendix 19

[0101] A plasma processing apparatus, comprising:

- 5 a chamber;
a substrate support in the chamber;
a gas supply configured to supply a processing gas into the chamber;
a plasma generator configured to generate a plasma from the processing gas; and
a controller configured to perform, with the gas supply and the plasma generator, control
10 operations including

(a) providing a substrate onto a substrate support, the substrate including a silicon-containing film and a mask on the silicon-containing film, the mask including a sidewall defining at least one opening to expose the silicon-containing film, and

- (b) generating a plasma from a processing gas including hydrogen fluoride and a bromine-
15 containing gas, the generating including forming a first protective film comprising bromine on the sidewall to a lower portion of the sidewall and forming a recess in the silicon-containing film.

Appendix 20

[0102] The plasma processing apparatus according to appendix 19, wherein
20 the bromine-containing gas includes a bromine-containing unsaturated halon gas.

Appendix 21

[0103] The plasma processing apparatus according to appendix 19 or appendix 20, wherein the bromine-containing gas includes an unsaturated halon represented by $R^1R^2C=CR^3R^4$, where R^1 , R^2 , R^3 , and R^4 each independently represent a hydrogen atom or a halogen atom, and
25 at least one of R^1 , R^2 , R^3 , or R^4 represents a bromine atom.

Appendix 22

[0104] The plasma processing apparatus according to appendix 21, wherein the unsaturated halon includes C_2BrF_3 .

Appendix 23

[0105] The plasma processing apparatus according to any one of appendixes 19 to 22, further comprising:

a temperature controller configured to control a temperature of the substrate, wherein the controller further controls, with the temperature controller, a temperature of the substrate support to be lower than or equal to 0 °C.

[0106] The above embodiments are mere examples described for illustrative purposes and are not intended to limit the scope of the present disclosure. The embodiments may be modified in various manners without departing from the spirit and scope of the present disclosure. For example, one or more components in one embodiment may be added to the structure according to another embodiment. One or more components in one embodiment may be replaced with the corresponding one or more components in another embodiment.

REFERENCE SIGNS LIST

[0107]

- 15 1 Plasma processing apparatus
- 2 Controller
- 10 Plasma processing chamber
- 11 Substrate support
- W Substrate
- 20 SF Silicon-containing film
- MK Mask
- OP Opening
- Wa Sidewall
- RC Recess
- 25 R1 First portion
- R2 Second portion
- PM First protective film

CLAIMS

1. An etching method, comprising:

(a) providing a substrate onto a substrate support, the substrate including a silicon-containing film and a mask on the silicon-containing film, the mask including a sidewall

5 defining at least one opening to expose the silicon-containing film; and

(b) generating a plasma from a processing gas including a hydrogen fluoride gas and a bromine-containing gas, the generating including forming a first protective film comprising bromine on the sidewall to a lower portion of the sidewall and forming a recess in the silicon-containing film.

10 2. The etching method according to claim 1, wherein

the lower portion of the sidewall includes a boundary with the silicon-containing film.

3. The etching method according to claim 1, wherein

the bromine-containing gas includes a bromine-containing unsaturated halon gas.

4. The etching method according to claim 1, wherein

15 the bromine-containing gas includes an unsaturated halon represented by $R^1R^2C=CR^3R^4$,

where R^1 , R^2 , R^3 , and R^4 each independently represent a hydrogen atom or a halogen atom, and at least one of R^1 , R^2 , R^3 , or R^4 represents a bromine atom.

5. The etching method according to claim 4, wherein

the unsaturated halon includes C_2BrF_3 .

6. The etching method according to claim 1, wherein

(b) further includes forming a second protective film on at least a part of the sidewall defining the recess.

7. The etching method according to claim 6, wherein

5 the second protective film is free of bromine or comprises bromine with a lower concentration than the first protective film.

8. The etching method according to claim 1, further comprising:

(c) controlling a temperature of the substrate support to be lower than or equal to 0 °C between (a) and (b).

10 9. The etching method according to claim 3, wherein

the processing gas further includes at least one gas selected from the group consisting of a phosphorus-containing gas, a carbon-containing gas, a halogen-containing gas different from the bromine-containing unsaturated halon gas, and a metal-containing gas.

10. The etching method according to claim 9, wherein

15 the phosphorus-containing gas includes at least one of PF_3 or POCl_3 .

11. The etching method according to claim 9, wherein

the carbon-containing gas includes at least one selected from the group consisting of a CF-based gas, a CHF-based gas, and a CH-based gas.

12. The etching method according to claim 9, wherein

the halogen-containing gas includes at least one selected from the group consisting of Cl_2 , HCl , and HBr .

13. The etching method according to claim 9, wherein

the metal-containing gas includes at least one of WF_6 or MoF_6 .

5 14. The etching method according to claim 1, wherein

the silicon-containing film includes at least one selected from the group consisting of a silicon oxide film, a silicon nitride film, and a polycrystalline silicon film.

15. The etching method according to claim 1, wherein

10 the mask includes at least one selected from the group consisting of a carbon-containing film, a metal-containing film, and another silicon-containing film.

16. The etching method according to claim 15, wherein

the carbon-containing film includes an amorphous carbon film.

17. The etching method according to claim 15, wherein

the metal-containing film includes a tungsten-containing film.

15 18. The etching method according to claim 15, wherein

the other silicon-containing film includes a BSi film.

19. A plasma processing apparatus, comprising:

a chamber;

a substrate support in the chamber;

a gas supply configured to supply a processing gas into the chamber;

a plasma generator configured to generate a plasma from the processing gas; and

a controller configured to perform, with the gas supply and the plasma generator, control operations including

- 5 (a) providing a substrate onto a substrate support, the substrate including a silicon-containing film and a mask on the silicon-containing film, the mask including a sidewall defining at least one opening to expose the silicon-containing film, and
- (b) generating a plasma from a processing gas including a hydrogen fluoride gas and a bromine-containing gas, the generating including forming a first protective film comprising
- 10 bromine on the sidewall to a lower portion of the sidewall and forming a recess in the silicon-containing film.

20. The plasma processing apparatus according to claim 19, wherein

the bromine-containing gas includes a bromine-containing unsaturated halon gas.

21. The plasma processing apparatus according to claim 19, wherein

- 15 the bromine-containing gas includes an unsaturated halon represented by $R^1R^2C=CR^3R^4$, where R^1 , R^2 , R^3 , and R^4 each independently represent a hydrogen atom or a halogen atom, and at least one of R^1 , R^2 , R^3 , or R^4 represents a bromine atom.

22. The plasma processing apparatus according to claim 21, wherein

the unsaturated halon includes C_2BrF_3 .

23. The plasma processing apparatus according to claim 19, further comprising:

a temperature controller configured to control a temperature of the substrate,

wherein the controller further controls, with the temperature controller, a temperature of the substrate support to be lower than or equal to 0 °C.