

DESCRIPTION

DRY ETCHING METHOD, METHOD FOR MANUFACTURING SEMICONDUCTOR ELEMENT, AND CLEANING METHOD

5

Technical Field

[0001]

The present invention relates to a dry etching method,
a method for manufacturing a semiconductor element, and a
10 cleaning method.

Background Art

[0002]

Copper (Cu) is widely used as a wiring material for
semiconductor elements because of low electrical resistance
15 in addition to high electromigration resistance. However,
many of reaction products between copper and etching gas have
little vapor pressure, so that dry etching of copper is not
easy.

Citation List

20 Patent Literature

[0003]

PTL 1: JP 3381076 B

Summary of Invention

Technical Problem

25 [0004]

For example, PTL 1 proposes a method for plasma etching
copper using iodine halide as the etching gas. However, in
the technology disclosed in PTL 1, etching using plasma is

needed, which is a problem in terms of requiring an expensive plasma generation device.

It is an object of the present invention to provide a dry etching method capable of etching an etching target
5 containing copper without using plasma, a method for manufacturing a semiconductor element, and a cleaning method.

Solution to Problem

[0005]

In order to achieve the above object, an aspect of the
10 present invention is as follows: [1] to [15].

[1] A dry etching method including a dry etching step in which an etching gas containing a halogen fluoride being a compound of bromine or iodine and fluorine is brought into contact with a member to be etched including an etching target
15 being a target of etching with the etching gas to etch the etching target without using plasma, the etching target containing copper, and the dry etching step being performed under temperature conditions of from 140°C to 300°C.

[0006]

20 [2] The dry etching method according to [1], in which the etching gas is a gas comprising only a gas of the halogen fluoride or is a mixed gas containing the halogen fluoride and inert gas.

[3] The dry etching method according to [2], in which
25 the inert gas is at least one selected from nitrogen gas, helium, argon, neon, krypton, and xenon.

[4] The dry etching method according to any one of [1] to [3], in which an amount of the halogen fluoride contained in the etching gas is from 1% by volume to 90% by volume.
[0007]

5 [5] The dry etching method according to any one of [1] to [4], in which the halogen fluoride is at least one of bromine pentafluoride or iodine heptafluoride.

[6] The dry etching method according to any one of [1] to [5], in which an amount of oxygen gas contained in the
10 etching gas is 1% by volume or less.

[7] The dry etching method according to any one of [1] to [6], in which the dry etching step is performed under pressure conditions of from 50 Pa to 80 kPa.
[0008]

15 [8] The dry etching method according to any one of [1] to [7], in which the etching target contains at least one of a copper compound containing at least one type of atom among oxygen, nitrogen, and halogen atoms and copper or elemental copper.

20 [9] The dry etching method according to any one of [1] to [8], in which the dry etching step is performed under temperature conditions of from 210°C to 280°C.

[10] The dry etching method according to any one of [1] to [9], in which the member to be etched includes a non-etching
25 target not being the target of the etching with the etching gas and the etching target, the etching target being selectively etched compared to the non-etching target.
[0009]

[11] The dry etching method according to [10], in which the non-etching target is at least one selected from silicon oxide, photoresist, and amorphous carbon.

[12] The dry etching method according to [10] or [11],
5 in which an etching selectivity ratio being a ratio of an etching rate of the etching target to an etching rate of the non-etching target is 5 or more.

[0010]

[13] A method for manufacturing a semiconductor element,
10 the method using the dry etching method according to any one of [1] to [12] to manufacture the semiconductor element, in which the member to be etched is a semiconductor substrate including the etching target, and which manufacturing method includes a processing step of removing at least a part of the
15 etching target from the semiconductor substrate by the dry etching method.

[14] The method for manufacturing a semiconductor element according to [13], in which copper wiring is formed on the semiconductor substrate by the processing step.

20 [0011]

[15] A cleaning method for cleaning an inner surface of a chamber of a semiconductor element manufacturing device using the dry etching method according to any one of [1] to [12], in which the member to be etched is the chamber, the
25 chamber having, on the inner surface, a deposit adhered due to operation of the semiconductor element manufacturing device, and the deposit being the etching target, and which cleaning method includes a cleaning step of removing the

deposit from the inner surface of the chamber by the dry etching method.

Advantageous Effects of Invention

[0012]

5 According to the present invention, an etching target containing copper can be etched without using plasma.

Brief Description of Drawings

[0013]

10 FIG. 1 is a schematic diagram of an example of an etching device illustrating an embodiment of a dry etching method according to the present invention; and

 FIG. 2 is a diagram illustrating a test piece used in Example 1 and the like.

Description of Embodiments

15 [0014]

 An embodiment of the present invention will be described below. It should be noted that the present embodiment is illustrative of an example of the present invention, and the present invention is not limited thereto. Additionally, 20 various changes or improvements can be added to the present embodiment, and embodiments added with such changes or improvements may also be included in the present invention.

[0015]

25 A dry etching method according to the present embodiment includes a dry etching step in which an etching gas containing a halogen fluoride being a compound of bromine (Br) or iodine (I) and fluorine (F) is brought into contact with a member to be etched including an etching target being a target of

etching with the etching gas to etch the etching target without using plasma. The etching target contains copper (Cu). Additionally, in the dry etching method according to the present embodiment, the dry etching step is performed
5 under temperature conditions of from 140°C to 300°C. Hereinafter, the etching method not using plasma may also be referred to as "plasmaless etching".

[0016]

When the etching gas is brought into contact with the
10 member to be etched, the halogen fluoride in the etching gas reacts with the copper in the etching target to generate copper fluoride. Copper fluoride is volatile, so that the generated copper fluoride volatilizes, causing etching of the etching target to proceed.

15 [0017]

Therefore, the dry etching method according to the present embodiment allows the etching target containing copper to be etched selectively and at a sufficient etching rate without using plasma. In other words, the etching target
20 can be selectively etched compared to a non-etching target that is not the target of the etching with the etching gas. The non-etching target will be described in detail later.

[0018]

Additionally, since the dry etching method according to
25 the present embodiment allows for etching of the etching target without using plasma, it is unnecessary to etch using an expensive plasma generation device. Thus, etching of the member to be etched can be performed at low cost. In addition,

since plasma is not used, it is less likely to cause corrosion in a member forming the etching device (for example, a chamber), a pipe connected to the etching device, a member forming a semiconductor element manufacturing device
5 described later (for example, a chamber), a pipe connected to the semiconductor element manufacturing device described later, and the like.

[0019]

It should be noted that the etching meant in embodiments
10 of the present invention includes processing the member to be etched into a predetermined shape (for example, a three-dimensional shape) by removing a part or all of the etching target included in the member to be etched (for example, processing the etching target in film form
15 comprising copper into a predetermined film thickness) and cleaning or etching back the member to be etched by removing a residue or deposit comprising the etching target from the member to be etched.

[0020]

20 The dry etching method according to the present embodiment can be used to manufacture semiconductor elements and clean the inner surfaces of chambers of semiconductor element manufacturing devices.

In other words, a method for manufacturing a
25 semiconductor element according to the present embodiment is a method for manufacturing a semiconductor element, which uses the dry etching method according to the present embodiment to manufacture the semiconductor element, in which

the member to be etched is a semiconductor substrate including the etching target, and which manufacturing method includes a processing step of removing at least a part of the etching target from the semiconductor substrate by the dry etching method according to the above-described present embodiment.
5 [0021]

For example, the dry etching method according to the present embodiment can be used to form copper wiring on a semiconductor substrate of a semiconductor element or etch
10 back for removal of an excessive copper film. Conventionally, copper wirings have often been formed by a wet process using a chemical mechanical polishing (CMP) slurry or a wet etching solution. However, dry etching with etching gas is superior to wet processes in terms of micro-machinability. Therefore,
15 the dry etching method according to the present embodiment can be expected to contribute to further miniaturization and higher integration of semiconductor elements.

[0022]

Additionally, in manufacturing a semiconductor element
20 using the dry etching method according to the present embodiment, when the non-etching target itself described later is used as a structural body of the semiconductor element or a resist, a material that does not substantially react with halogen fluoride or a material that is extremely
25 late to react with halogen fluoride is used as the non-etching target. Specific examples of such a non-etching target usable herein include at least one selected from silicon oxide

(for example, silicon dioxide (SiO_2)), photoresist, and amorphous carbon.

[0023]

Furthermore, the dry etching method according to the
5 present embodiment can also be used for cleaning, as described
above. Specifically, a cleaning method according to the
present embodiment is a cleaning method for cleaning an inner
surface of a chamber of a semiconductor element manufacturing
device using the dry etching method according to the present
10 embodiment, in which the member to be etched is the chamber.
The chamber has a deposit, on the inner surface, adhered due
to operation of the semiconductor element manufacturing
device, and the deposit is the etching target. Additionally,
the cleaning method according to the present embodiment
15 includes a cleaning step of removing the deposit from the
inner surface of the chamber by the dry etching method
according to the above-described present embodiment.

[0024]

For example, after performing a step of forming a film
20 comprising the etching target containing copper on the
semiconductor substrate and a step of etching the film
comprising the etching target containing copper and formed
on the semiconductor substrate in a chamber whose inner
surface is made of a material not containing copper, cleaning
25 can be performed by removing a deposit containing copper
adhered onto the inner surface of the chamber using the dry
etching method according to the present embodiment.

[0025]

Hereinafter, a more detailed description will be given of the dry etching method, the method for manufacturing a semiconductor element, and the cleaning method according to the present embodiment.

5 [Halogen Fluoride]

The type of the halogen fluoride is not particularly limited as long as it is a compound of bromine or iodine and fluorine. Preferred is at least one selected from bromine monofluoride (BrF), bromine trifluoride (BrF_3), bromine
10 pentafluoride (BrF_5), iodine monofluoride (IF), iodine trifluoride (IF_3), iodine pentafluoride (IF_5), and iodine heptafluoride (IF_7). Among these halogen fluorides, more preferred is at least one selected from bromine trifluoride, bromine pentafluoride, iodine pentafluoride, and iodine
15 heptafluoride, and still more preferred is at least one selected from bromine pentafluoride and iodine heptafluoride, in terms of stability and ease of vaporization.

[0026]

[Etching Gas]

20 The etching gas is a halogen fluoride containing gas. The etching gas may be a gas comprising only halogen fluoride or a mixed gas containing halogen fluoride and another type of gas. When the etching gas is a mixed gas containing halogen fluoride and another type of gas, the amount of the halogen
25 fluoride contained in the etching gas is preferably 1% by volume or more, more preferably 5% by volume or more, and still more preferably 10% by volume or more, in order to etch the etching target at a sufficient etching rate. In addition,

in terms of etching stability and ease of exhaust gas processing, the amount of the halogen fluoride contained in the etching gas is preferably 90% by volume or less, more preferably 60% by volume or less, and still more preferably
5 40% by volume or less.

[0027]

When the etching gas is a mixed gas containing halogen fluoride and another type of gas, inert gas is preferably used as the other type of gas. In other words, the etching gas
10 may be a mixed gas containing halogen fluoride and inert gas. As the inert gas, at least one selected from nitrogen gas (N_2), helium (He), argon (Ar), neon (Ne), krypton (Kr), and xenon (Xe) can be used. The amount of the insert gas contained in the etching gas is not particularly limited, but may be more
15 than 0% by volume and 99% by volume or less, and more preferably from 60% by volume to 97% by volume in terms of ease of handling of the etching gas.

[0028]

The amount of oxygen gas (O_2) contained in the etching
20 gas is preferably 1% by volume or less, more preferably less than 1000 ppm by volume, and still more preferably less than 300 ppm by volume. When the amount of the oxygen gas contained is 1% by volume or less, a copper oxide film is unlikely to be formed on a copper surface, so that the etching rate of
25 copper is likely to be high. It is also unlikely that the diffusion of oxygen atoms inside from the copper oxide film causes problems such as the occurrence of an etching residue and increased wiring resistance.

[0029]

[Pressure Conditions for Dry Etching Step]

Pressure conditions for the dry etching step in the dry etching method according to the present embodiment are not particularly limited as long as halogen fluoride can be present in a gaseous form at the temperature and pressure during etching, but are preferably from 50 Pa to 80 kPa, more preferably from 200 Pa to 70 kPa, and still more preferably from 500 Pa to 60 kPa.

10 [0030]

For example, the member to be etched is placed in the chamber, and etching can be performed while distributing the etching gas in the chamber. The pressure in the chamber during the distribution of the etching gas can be from 10 Pa to 100 kPa. The flow rate of the etching gas may be appropriately set according to the size of the chamber and the capacity of an exhaust system for reducing the pressure in the chamber so that the pressure in the chamber is maintained constant.

20 [0031]

[Temperature Conditions for Dry Etching Step]

Temperature conditions for the dry etching step in the dry etching method according to the present embodiment are needed to be from 140°C to 300°C. Here, although the temperature of the temperature conditions refers to the temperature of the member to be etched, the temperature of the stage supporting the member to be etched placed in the chamber of the etching device can also be used.

[0032]

When the temperature condition for the dry etching step is 140°C or more, halogen fluoride can be present in the gaseous form, and the etching rate of copper is likely to be higher. Note that the temperature condition for the dry etching step is preferably 160°C or more, and more preferably more than 200°C. Particularly, at 210°C or more, the etching rate of a copper compound increases, facilitating a significant contribution to improvement of efficiency of the etching step.

[0033]

On the other hand, when the temperature condition for the dry etching step is 300°C or less, there are advantages such as that etching can be performed without requiring excessive time and energy, that load on the etching device and the semiconductor element manufacturing device is small, and that it is possible to suppress etching of a portion that should originally not be etched (for example, the non-etching target described later). Note that the temperature condition for the dry etching step is preferably 280°C or less, and more preferably 260°C or less.

[0034]

Halogen fluoride hardly reacts with the non-etching target such as at least one of silicon oxide, photoresist, or amorphous carbon in the absence of plasma and under the temperature conditions of 300°C or less. Therefore, when the member to be etched includes both the etching target and the non-etching target, using the dry etching method according

to the present embodiment allows the etching target to be selectively etched without hardly etching the non-etching target. Thus, the dry etching method according to the present embodiment can be used for methods of processing an etching
5 target into a predetermined shape by using a patterned non-etching target as a mask, and the like.

[0035]

Furthermore, when temperatures of the etching target and the non-etching target are 300°C or less, etching selectivity
10 ratio is likely to be high. For example, the etching selectivity ratio, which is a ratio of an etching rate of the etching target to an etching rate of the non-etching target, is likely to be 5 or more. The etching selectivity ratio is more preferably 10 or more, and still more preferably 20 or
15 more.

[0036]

[Member to be Etched]

The member to be etched that is subjected to etching by the dry etching method according to the present embodiment
20 includes an etching target being the target of etching with the etching gas, but may or may not include a non-etching target not being the target of the etching with the etching gas.

[0037]

25 When the member to be etched includes the etching target and the non-etching target, the member to be etched may be a member that includes a portion formed by the etching target and a portion formed by the non-etching target or a member

formed by a mixture of the etching target and the non-etching target. The member to be etched may also include a material other than the etching target and the non-etching target.

In addition, the shape of the member to be etched is not particularly limited, and, for example, may be in plate, foil, film, powder, or lump form. An example of the member to be etched is the above-mentioned semiconductor substrate.

[0038]

[Etching Target]

The etching target to be etched with the etching gas contains copper, but may contain at least one of a copper compound containing at least one type of atom among oxygen, nitrogen, and halogen atoms and copper (for example, a copper oxide, a copper nitride, a copper oxynitride, or a copper halide) or elemental copper. More specifically, the etching target may be, for example, one comprising elemental copper, one comprising the copper compound, one comprising a mixture containing elemental copper, or one comprising a mixture containing the copper compound.

[0039]

The etching target has a copper content of preferably 1% by mole or more, more preferably 10% by mole or more, and still more preferably 40% by mole or more. Additionally, the shape of the etching target and the shape of a portion of the etching target formed by only elemental copper are not particularly limited, and for example, may be in foil, film, powder, or lump form.

[0040]

[Non-Etching Target]

As described above, the member to be etched may include a non-etching target not being the target of etching with the etching gas. The non-etching target is hardly etched by the etching method according to the present embodiment, so that the etching of the etching target with the etching gas can be suppressed by the non-etching target.

[0041]

Thus, the etching method according to the present embodiment can be used for methods such as processing an etching target into a predetermined shape (for example, processing a film-formed etching target included in a member to be etched into a predetermined film thickness) by using a patterned non-etching target as a mask, and therefore can be suitably used to manufacture semiconductor elements.

[0042]

Furthermore, since the non-etching target is hardly etched, etching of a portion that should originally not be etched in a semiconductor element can be suppressed by the non-etching target, which can prevent characteristics of the semiconductor element from being lost due to etching.

The non-etching target is a material that does not substantially react with halogen fluoride or a material that is extremely late to react with halogen fluoride, and for example, is at least one selected from silicon oxide, photoresist, and amorphous carbon.

[0043]

Photoresist means a photosensitive composition whose physical properties such as solubility are changed by light, electron beams, or the like. Examples of the photoresist include photoresists for g-line, h-line, i-line, KrF, ArF, F₂, EUV, and the like. The composition of the photoresist is not particularly limited as long as it is commonly used in semiconductor element manufacturing processes. Examples of the composition thereof include compositions containing polymers synthesized from at least one monomer selected from chain olefins, cyclic olefins, styrene, vinylphenols, (meth)acrylic acids, (meth)acrylates, epoxies, melamines, and glycols. Note that (meth)acrylic acid means one or both of acrylic acid and methacrylic acid, and (meth)acrylate means one or both of acrylate and methacrylate.

[0044]

Next will be a description of a configuration example of an etching device capable of performing the dry etching method according to the present embodiment and an example of a copper dry etching method using the etching device with reference to FIG. 1. The etching device of FIG. 1 is a plasmaless etching device not using plasma. First will be a description of the etching device of FIG. 1.

[0045]

The etching device of FIG. 1 includes a chamber 10 inside which etching is performed, a stage 11 that supports, in the chamber 10, a member to be etched 12 that is subjected to etching, a thermometer 14 that measures temperature of the member to be etched 12, an exhaust pipe 13 for exhausting a

gas in the chamber 10, a vacuum pump 15 provided on the exhaust pipe 13 to reduce pressure in the chamber 10, and a pressure gauge 16 that measures the pressure in the chamber 10.

[0046]

5 The etching device of FIG. 1 also includes an etching gas supply unit that supplies an etching gas into the chamber 10. The etching gas supply unit includes a halogen fluoride gas supply unit 1 that supplies halogen fluoride gas, an inert gas supply unit 2 that supplies inert gas, a halogen fluoride
10 gas supply pipe 5 that connects the halogen fluoride gas supply unit 1 to the chamber 10, and an inert gas supply pipe 6 that connects the inert gas supply unit 2 to an intermediate portion of the halogen fluoride gas supply pipe 5.

[0047]

15 Furthermore, the halogen fluoride gas supply pipe 5 is provided with a pressure gauge 7 that measures pressure of the halogen fluoride gas and a halogen fluoride gas flow rate control device 3 that controls flow rate of the halogen fluoride gas. Still furthermore, the inert gas supply pipe
20 6 is provided with an inert gas pressure control device 8 that controls pressure of the inert gas and an inert gas flow rate control device 4 that controls flow rate of the inert gas.

[0048]

 Then, when the halogen fluoride gas is supplied as the
25 etching gas to the chamber 10, the halogen fluoride gas is supplied to the chamber 10 via the halogen fluoride gas supply pipe 5 by sending the halogen fluoride gas out from the halogen

fluoride gas supply unit 1 to the halogen fluoride gas supply pipe 5.

[0049]

5 Additionally, when the mixed gas of the halogen fluoride gas and the inert gas is supplied as the etching gas, the halogen fluoride gas is sent out from the halogen fluoride gas supply unit 1 to the halogen fluoride gas supply pipe 5, and also the inert gas is sent out from the inert gas supply unit 2 to the halogen fluoride gas supply pipe 5 via the inert
10 gas supply pipe 6. As a result, the halogen fluoride gas and the inert gas are mixed together at the intermediate point of the halogen fluoride gas supply pipe 5 to form a mixed gas, and the mixed gas is supplied to the chamber 10 via the halogen fluoride gas supply pipe 5.

15 [0050]

 Note that configurations of the halogen fluorine gas supply unit 1 and the inert gas supply unit 2 are not particularly limited, and, for example, they may be tanks, cylinders, or the like. In addition, examples of the halogen
20 fluoride gas flow rate control device 3 and the inert gas flow rate control device 4 usable herein include mass flow controllers and flow meters.

[0051]

 When supplying the etching gas to the chamber 10, it is
25 preferable to supply the etching gas while maintaining supply pressure of the etching gas (i.e., a value of the pressure gauge 7 in FIG. 1) at a predetermined value. Specifically, the supply pressure of the etching gas is preferably from 1

kPa to 1.0 MPa, more preferably from 10 kPa to 0.5 MPa, and still more preferably from 30 kPa to 0.3 MPa. When the supply pressure of the etching gas is within the above range, the etching gas is smoothly supplied to the chamber 10, and load
5 on components (for example, the various devices and the pipes) included in the etching device of FIG. 1 is small.

[0052]

Additionally, the pressure of the etching gas supplied into the chamber 10 is preferably from 50 Pa to 80 kPa, and
10 more preferably from 500 Pa to 60 kPa, from the viewpoint of uniform etching of a surface of the member to be etched 12. When the pressure of the etching gas in the chamber 10 is within the above range, a sufficient etching rate can be obtained, and an etching rate ratio with the non-etching target, i.e.,
15 the etching selectivity ratio is likely to be high.

[0053]

The pressure in the chamber 10 before supplying the etching gas is not particularly limited as long as it is equal to or lower than the supply pressure of the etching gas or
20 lower than the supply pressure of the etching gas. However, for example, the pressure in the chamber 10 is preferably from 1 Pa to less than 10 kPa, and more preferably from 10 Pa to 5 kPa.

[0054]

25 A differential pressure between the supply pressure of the etching gas and the pressure in the chamber 10 before supplying the etching gas is preferably 1.0 MPa or less, more preferably 0.5 MPa or less, and still more preferably 0.3 MPa

or less. When the differential pressure is within the above range, smooth supply of the etching gas to the chamber 10 is facilitated.

[0055]

5 When supplying the etching gas to the chamber 10, it is preferable to supply the etching gas while maintaining the temperature of the etching gas at a predetermined value. Specifically, the supply temperature of the etching gas is preferably from 10°C to 150°C.

10 The temperature of the member to be etched 12 during etching is from 140°C to 300°C. When the temperature thereof is within the above temperature range, the etching of the etching target included in the member to be etched 12 proceeds smoothly, and the load on the etching device is small, which
15 facilitates life extension of the etching device.

[0056]

 The processing time for etching (hereinafter may be referred to as "etching time") can be set optionally depending on how much the etching of the etching target included in the
20 member to be etched 12 is desired. However, considering the production efficiency of semiconductor element manufacturing processes, the etching time is preferably within 30 minutes, more preferably within 20 minutes, and still more preferably within 10 minutes. Note that the
25 processing time for etching refers to a time from when the etching gas is introduced into the chamber 10 to when the etching gas in the chamber 10 is exhausted in order to finish etching.

[0057]

The dry etching method according to the present embodiment can be performed using a common plasmaless etching device used in the semiconductor element manufacturing processes, such as the etching device of FIG. 1, and the configuration of the etching device usable herein is not particularly limited.

For example, a positional relationship between the halogen fluoride gas supply pipe 5 and the member to be etched 12 is not particularly limited as long as the etching gas can be brought into contact with the member to be etched 12. It also suffices that the configuration of a temperature control mechanism of the chamber 10 allows the temperature of the member to be etched 12 to be controlled to any temperature. Accordingly, the temperature control mechanism may be directly provided on the stage 11, or the chamber 10 may be heated or cooled by an external temperature controller from outside the chamber 10.

[0058]

In addition, the material of the etching device of FIG. 1 is not particularly limited as long as it has a corrosion resistance to a halogen fluoride to be used and allows depressurization to a predetermined pressure. For example, a portion of the etching device brought into contact with the etching gas can be made of a metal such as nickel, a nickel-based alloy, aluminum, stainless steel, or platinum, a ceramic such as alumina, a fluororesin, or the like. Specific examples of the nickel-based alloy include INCONEL

(registered trademark), HASTELLOY (registered trademark), and MONEL (registered trademark). Additionally, examples of the fluororesin include polytetrafluoroethylene (PTFE), polychlorotrifluoroethylene (PCTFE), tetrafluoroethylene
5 perfluoroalkoxyethylene copolymer (PFA), polyvinylidene fluoride (PVDF), TEFLON (registered trademark), VITON (registered trademark), and KALREZ (registered trademark).

Examples

[0059]

10 A more detailed description of the present invention will be given by illustrating Examples and Comparative Examples below. Additionally, purities of bromine pentafluoride and iodine heptafluoride used in the following Examples and Comparative Examples were analyzed by a Fourier-transform
15 infrared spectrophotometer Nicolet iS5 manufactured by Thermo Fisher Scientific Inc., a double beam spectrophotometer U-2900 manufactured by Hitachi High-Tech Science Corporation, and a gas chromatography GC-2014 manufactured by Shimadzu Corporation, and were all confirmed
20 to be 99% by mass or more.

[0060]

(Example 1)

Using an etching device having substantially the same configuration as that of the etching device of FIG. 1, etching
25 (plasmaless etching) of a member to be etched was performed. A test piece (the member to be etched) used in Example 1 will be described with reference to FIG. 2.

[0061]

There was prepared a square silicon substrate 21 having a 2 inch side length formed with a titanium (Ti) film 22 having a film thickness of 100 nm thereon and then a copper film 23 having a film thickness of 600 nm on the titanium film 22 (manufactured by KST World Corporation). A rectangular silicon dioxide substrate 24 having a size of 1 inch × 2 inch was glued onto the copper film 23 using grease (DEMNUM GREASE L-200 manufactured by Daikin Industries, Ltd.), and this laminate was used as the test piece. As illustrated in FIG. 2, the silicon dioxide substrate 24 was glued to cover approximately a half portion of the copper film 23.

[0062]

The test piece was placed on a stage in a chamber of the etching device, and the temperature of the stage was raised to 160°C. Next, bromine pentafluoride gas at a flow rate of 50 mL/min and argon at a flow rate of 450 mL/min were mixed together to form a mixed gas, and the mixed gas was used as an etching gas. Then, the etching gas was supplied into the chamber at a flow rate of 500 mL/min and distributed for 10 minutes for etching. As a result, an exposed portion of the copper film 23 not covered by the silicon dioxide substrate 24 was etched. The pressure in the chamber during the distribution of the etching gas was 10 kPa, and the bromine pentafluoride gas had a partial pressure of 1 kPa. After completion of the distribution of the etching gas, the heating of the stage was stopped, and the atmosphere in the chamber was replaced with argon.

[0063]

Additionally, the amount of oxygen gas contained in the etching gas was measured by the gas chromatography, and found to be less than 100 ppm by volume. Conditions for the measurement were as follows:

5 Measurement instrument: GC-2014 manufactured by Shimadzu Corporation

GC column: ShinCarbon ST 6m

Carrier gas: He (20 mL/min)

GC sample loop: 5 mL

10 Injection temperature: 150°C

Column temperature: 50°C

Detector: thermal conductivity detector (TCD)

Detection temperature: 200°C

Electric current: 180 mA

15 [0064]

After the etching finished, the chamber was opened to take out the test piece. The silicon dioxide substrate 24 was removed from the test piece taken out, and the glued surface thereof was washed with ethanol to remove the grease. 20 Then, using an atomic force microscope VN-8010 manufactured by Keyence Corporation, the size of a step difference between a covered surface 23a of the copper film 23 covered by the silicon dioxide substrate 24 and not etched and an etched surface 23b of the copper film 23 not covered by the silicon 25 dioxide substrate 24 and etched was measured. The size (nm) of the measured step difference was divided by the etching time (min) to calculate the etching rate of copper (nm/min). Table 1 illustrates the result.

[0065]

Note that conditions for measuring the size of the step difference using the atomic force microscope were as follows:

Measurement pressure: atmospheric pressure (101.3 kPa)

5 Measurement temperature: 28°C

Measurement atmosphere: air atmosphere

Scanning range: 80.0 μm in width, 20.0 μm in height, 0° in angle.

[0066]

10 Table 1

	Etching target	Non-etching target	Stage temperature (°C)	Etching gas				Pressure (kPa)		Etching time (min)	Etching rate ²⁾ (nm/min)
				Halogen fluoride	Inert gas	Other gas	Volume ratio ¹⁾	In-chamber	Halogen fluoride		
Ex. 1	Copper	—	160	BrF ₅	Ar	—	10/90/0	10	1	10	9
Ex. 2	Copper	—	210	BrF ₅	Ar	—	10/90/0	10	1	10	23
Ex. 3	Copper	—	280	BrF ₅	Ar	—	10/90/0	10	1	10	38
Ex. 4	Copper	—	210	BrF ₅	Ar	—	20/80/0	10	2	10	56
Ex. 5	Copper	—	210	BrF ₅	Ar	—	3/97/0	10	0.3	10	10
Ex. 6	Copper	—	210	BrF ₅	Ar	—	10/90/0	1	0.1	10	10
Ex. 7	Copper	—	210	BrF ₅	Ar	—	10/90/0	30	3	10	32
Ex. 8	Copper	—	210	BrF ₅	N ₂	—	10/90/0	10	1	10	24
Ex. 9	Copper	—	210	BrF ₅	He	—	10/90/0	10	1	10	24
Ex. 10	Copper	—	210	IF ₇	Ar	—	10/90/0	10	1	10	25
Ex. 11	Copper	Silicon oxide	210	BrF ₅	Ar	—	10/90/0	10	1	10	27/1
Ex. 12	Copper	Photoresist	210	BrF ₅	Ar	—	10/90/0	10	1	10	27/2
Ex. 13	Copper	Amorphous carbon	210	BrF ₅	Ar	—	10/90/0	10	1	10	27/2
Ex. 14	Copper(I) oxide	—	280	BrF ₅	Ar	—	10/90/0	10	1	10	5

Ex. 15	Copper(II) oxide	–	280	BrF ₅	Ar	–	10/90/0	10	1	10	2
Ex. 16	Copper nitride	–	210	BrF ₅	Ar	–	10/90/0	10	1	10	17
Ex. 17	Copper	–	210	BrF ₅	Ar	O ₂	10/89/1	10	1	10	9
Comp. Ex. 1	Copper	–	130	BrF ₅	Ar	–	10/90/0	10	1	10	Less than 0.1
Comp. Ex. 2	Copper	–	210	F ₂	Ar	–	10/90/0	10	1	10	Less than 0.1
Comp. Ex. 3	Copper	Silicon oxide/photoresist/amorphous carbon	30	BrF ₅	Ar	–	10/90/0	3×10 ⁻³	3×10 ⁻⁴	10	3/20/57/49
Comp. Ex. 4	Copper	Silicon oxide/photoresist/amorphous carbon	30	IF ₇	Ar	–	10/90/0	3×10 ⁻³	3×10 ⁻⁴	10	2/25/58/51

1) A volume ratio of halogen fluoride gas to inert gas and other gas. For example, when halogen fluoride gas:inert gas:other gas = 10:90:0, it is described as 10/90/0.

2) An etching rate of the etching target. When two or more numerical values are listed, they indicate the etching rates of the etching target and the non-etching target. For example, in Comparative Example 4, the etching rates of copper/silicon oxide/photoresist/amorphous carbon are listed in this order.

[0067]

(Examples 2 to 10)

Etching of the test piece was performed in the same manner as in Example 1 except that the conditions were set as listed in Table 1 to calculate the etching rate of copper. Table 1 illustrates the results.

(Example 11)

There was prepared a square silicon substrate having a 2 inch side length formed with a silicon oxide film having a film thickness of 2000 nm thereon (manufactured by KST World Corporation). Then, a rectangular silicon dioxide substrate having a size of 1 inch $\times$ 2 inch was glued onto the silicon oxide film using grease (DEMNUM GREASE L-200 manufactured by Daikin Industries, Ltd) so that approximately a half portion of the silicon oxide film was covered, and the resulting laminate was used as a test piece. Additionally, a test piece including the same copper film as that of Example 1 was prepared. Then, these two test pieces were placed on the stage in the chamber of the etching device, and the two test pieces were simultaneously etched under the same conditions as those of Example 1 to calculate the etching rates of copper and silicon oxide. Table 1 illustrates the results.

[0068]

(Example 12)

Etching of the test piece was performed in the same manner as in Example 11 except that the silicon oxide film having the film thickness of 2000 nm in Example 11 was replaced by a photoresist cured product film having a film thickness of

300 nm to calculate the etching rates of copper and a photoresist cured product. Table 1 illustrates the results. Note that the photoresist cured product film formed on the copper film 23 was formed by coating a photoresist TSCR
5 (registered trademark) manufactured by Tokyo Ohka Kogyo Co., Ltd., on the copper film 23 and then exposing and curing it.
[0069]

(Example 13)

Etching of the test piece was performed in the same manner
10 as in Example 11 except that the silicon oxide film having the film thickness of 2000 nm in Example 11 was replaced by an amorphous carbon film having a film thickness of 500 nm to calculate the etching rates of copper and amorphous carbon. Table 1 illustrates the results.
15 [0070]

(Example 14)

Etching of the test piece was performed in the same manner as in Example 1 except that a copper oxide film having a film thickness of 50 nm was formed instead of the copper film 23
20 on the titanium film 22 to calculate the etching rate of copper oxide. Table 1 illustrates the result. Note that the copper oxide in Example 14 was copper(I) oxide (Cu_2O).

(Example 15)

Etching of the test piece was performed in the same manner
25 as in Example 1 except that a copper oxide film having a film thickness of 50 nm was formed instead of the copper film 23 on the titanium film 22 to calculate the etching rate of copper

oxide. Table 1 illustrates the result. Note that the copper oxide in Example 15 was copper(II) oxide (CuO).

[0071]

(Example 16)

5 Etching of the test piece was performed in the same manner as in Example 1 except that a copper nitride (Cu_3N) film having a film thickness of 100 nm was formed instead of the copper film 23 on the titanium film 22 to calculate the etching rate of copper nitride. Table 1 illustrates the result.

10 [0072]

(Example 17)

Etching of the test piece was performed in the same manner as in Example 1 except that a mixed gas obtained by mixing bromine pentafluoride gas at a flow rate of 50 mL/min, argon
15 at a flow rate of 445 mL/min, and oxygen gas at a flow rate of 5 mL/min was used as the etching gas to calculate the etching rate of copper. Table 1 illustrates the result.

[0073]

(Comparative Example 1)

20 Etching of the test piece was performed in the same manner as in Example 1 except that the stage temperature was 130°C to calculate the etching rate of copper. Table 1 illustrates the result.

(Comparative Example 2)

25 Etching of the test piece was performed in the same manner as in Example 1 except that fluorine gas (F_2 gas) was used instead of bromine pentafluoride gas and a mixed gas obtained by mixing fluorine gas at a flow rate of 50 mL/min and argon

at a flow rate of 450 mL/min was used as the etching gas to calculate the etching rate of copper. Table 1 illustrates the result.

[0074]

5 (Comparative Example 3)

Etching of the test piece was performed as in the same manner as in Example 1 except that normal plasma etching was performed by generating a plasma of etching gas in the chamber and etching in the chamber with the plasma of the etching gas
10 and conditions for the etching were set as follows.

[0075]

As test pieces, there were prepared a substrate formed with a copper film having a film thickness of 100 nm (manufactured by KST World Corporation), a substrate formed
15 with a silicon oxide film having a film thickness of 2000 nm (manufactured by KST World Corporation), a substrate including a photoresist cured product film having a film thickness of 300 nm formed by coating a photoresist (TSCR (registered trademark) manufactured by Tokyo Ohka Kogyo Co.,
20 Ltd.) and exposing and curing it, and a substrate formed with an amorphous carbon film having a film thickness of 500 nm (manufactured by KST World Corporation). Then, these four types of test pieces were placed on the stage in the chamber of the etching device and etched simultaneously to measure
25 the etching rates of the four types of films. Table 1 illustrates the results.

[0076]

Conditions for the etching were set as follows. As the etching device, a parallel flat plate type plasma CVD device RIE-800 iPC was used at a source power of 500 W and a bias power of 100 W. The etching gas used was a mixed gas obtained by mixing bromine pentafluoride gas at a flow rate of 5 mL/min and argon at a flow rate of 45 mL/min. The etching time was 30 seconds, the stage temperature was 30°C, and the in-chamber pressure was 3 Pa.

[0077]

10 (Comparative Example 4)

Etching of the test pieces was performed in the same manner as in Comparative Example 4 except that the halogen fluoride was iodine heptafluoride and the etching gas used was a mixed gas obtained by mixing an iodine heptafluoride gas at a flow rate of 5 mL/min and argon at a flow rate of 45 mL/min to calculate the etching rates of the four types of films. Table 1 illustrates the result.

[0078]

(Example 21)

20 Etching was performed in the same manner as in Example 1 except that the etching target was a copper(II) fluoride powder (manufactured by Kanto Chemical Co., Inc., mean particle size: 0.3 μm , purity: 99.5%). After completion of the distribution of the etching gas, the atmosphere in the chamber was replaced with argon, and the etching target was taken out to measure a mass of the etching target.

[0079]

Then, the mass of the etching target reduced due to the etching was divided by a mass of the etching target before the etching to calculate a mass reduction ratio of the etching target. Table 2 illustrates the result.

5 Note that the mean particle size of powder such as the copper(II) fluoride powder was a mean particle size on a volume basis, and was measured using a laser diffraction/scattering particle size distribution analyzer PARTICA LA-960 manufactured by Horiba, Ltd.

10 [0080]

Table 2

	Etching target	Stage temperature (°C)	Etching gas			Pressure (kPa)		Etching time (min)	Mass reduction ratio (%)
			Halogen fluoride or fluorine gas	Inert gas	Volume ratio ¹⁾	In-chamber	Halogen fluoride		
Ex. 21	Copper fluoride	210	BrF ₅	Ar	10/90	10	1	10	53
Ex. 22	Copper fluoride	210	IF ₇	Ar	10/90	10	1	10	61
Comp. Ex. 11	Copper fluoride	210	F ₂	Ar	10/90	10	1	10	Less than 1
Ex. 23	Copper bromide	210	BrF ₅	Ar	10/90	10	1	10	92
Ex. 24	Copper bromide	210	IF ₇	Ar	10/90	10	1	10	93
Comp. Ex. 12	Copper bromide	210	F ₂	Ar	10/90	10	1	10	Less than 1
Ex. 25	Copper iodide	210	BrF ₅	Ar	10/90	10	1	10	93
Ex. 26	Copper iodide	210	IF ₇	Ar	10/90	10	1	10	97
Comp. Ex. 13	Copper iodide	210	F ₂	Ar	10/90	10	1	10	2

1) A volume ratio of halogen fluoride or fluorine gas to inert gas. For example, halogen fluoride or fluorine gas:inert gas = 10:90, it is described as 10/90.

[0081]

(Example 22)

Etching was performed in the same manner as in Example 21 except that the halogen fluoride was iodine heptafluoride and the etching gas used was a mixed gas obtained by mixing
5 iodine heptafluoride gas at a flow rate of 50 mL/min and argon at a flow rate of 450 mL/min to calculate the mass reduction ratio of the etching target. Table 2 illustrates the result.

[0082]

10 (Comparative Example 11)

Etching was performed in the same manner as in Example 21 except that fluorine gas was used instead of bromine pentafluoride gas and the etching gas used was a mixed gas obtained by mixing fluorine gas at a flow rate of 50 mL/min
15 and argon at a flow rate of 450 mL/min to calculate the mass reduction ratio of the etching target. Table 2 illustrates the result.

[0083]

(Example 23)

20 Etching was performed in the same manner as in Example 21 except that instead of the copper(II) fluoride powder, a copper(I) bromide powder (manufactured by Nacalai Tesque, Inc., mean particle size: 0.5 μm , purity: 97.5%) was used as the etching target to calculate the mass reduction ratio of
25 the etching target. Table 2 illustrates the result.

(Example 24)

Etching was performed in the same manner as in Example 23 except that the halogen fluoride was iodine pentafluoride

and the etching gas used was a mixed gas obtained by mixing iodine pentafluoride gas at a flow rate of 50 mL/min and argon at a flow rate of 450 mL/min to calculate the mass reduction ratio of the etching target. Table 2 illustrates the result.

5 [0084]

(Comparative Example 12)

Etching was performed in the same manner as in Example 23 except that fluorine gas was used instead of bromine pentafluoride gas and a mixed gas obtained by mixing fluorine
10 gas at a flow rate of 50 mL/min and argon at a flow rate of 450 mL/min was used as the etching gas to calculate the mass reduction ratio of the etching target. Table 2 illustrates the result.

[0085]

15 (Example 25)

Etching was performed in the same manner as in Example 21 except that instead of the copper(II) fluoride powder, a copper(I) iodine powder (manufactured by Nacalai Tesque, Inc., mean particle size: 0.7 μm , purity: 99.5%) was used as the
20 etching target to calculate the mass reduction ratio of the etching target. Table 2 illustrates the result.

(Example 26)

Etching was performed in the same manner as in Example 25 except that the halogen fluoride was iodine heptafluoride
25 and the etching gas used was a mixed gas obtained by mixing iodine heptafluoride gas at a flow rate of 50 mL/min and argon at a flow rate of 450 mL/min to calculate the mass reduction ratio of the etching target. Table 2 illustrates the result.

[0086]

(Comparative Example 13)

Etching was performed in the same manner as in Example
25 except that fluorine gas was used instead of bromine
5 pentafluoride gas and a mixed gas obtained by mixing fluorine
gas at a flow rate of 50 mL/min and argon at a flow rate of
450 mL/min was used as the etching gas to calculate the mass
reduction ratio of the etching target. Table 2 illustrates
the result.

10 [0087]

The results of Examples 1, 2, and 3 show that the higher
the stage temperature, the higher the copper etching rate.

The results of Examples 2, 4, and 5 show that the higher
the halogen fluoride percentage in the etching gas, the higher
15 the copper etching rate.

The results of Examples 2, 6, and 7 shows that the higher
the in-chamber pressure, the higher the copper etching rate.
The reason for this seems to be that an increased partial
pressure of the halogen fluoride gas in the chamber increased
20 the frequency of contact between a copper surface and the
halogen fluoride, which improved a copper conversion rate
into an etching product (a reaction product produced as a
result of copper etching).

[0088]

25 The results of Examples 8 and 9 show that even with the
use of nitrogen gas or helium as the inert gas, copper etching
proceeds without problems.

The result of Example 10 shows that even with the use of iodine heptafluoride as the etching gas, copper etching proceeds without problems.

The results of Examples 11, 12, and 13 show that copper
5 etching proceeds selectively under the conditions where copper and the non-etching target are present in the same chamber. These results indicate that using the dry etching method according to the present invention allows copper to be selectively etched compared to the non-etching target.
10 [0089]

The results of Examples 14, 15, and 16 show that copper oxide and copper nitride can be etched. The results also show that the dry etching method according to the present invention can also be applied to removal of a natural oxide film or
15 nitride film on the copper surface.

The result of Example 17 shows that when oxygen gas is contained in the etching gas, the copper etching rate is reduced slightly.

[0090]

20 The result of Comparative Example 1 shows that when the stage temperature is outside the range of the present invention, copper etching is less likely to proceed.

The result of Comparative Example 2 shows that when fluorine gas is used as the etching gas, copper etching is
25 less likely to proceed.

The results of Comparative Examples 3 and 4 show that in plasma etching, although copper etching proceeds, etching of the non-etching target also proceeds simultaneously.

[0091]

The results of Examples 21 to 26 show that the dry etching method according to the present invention allows etching of copper halides (copper fluoride, copper bromide, and copper iodide) to proceed without problems.

On the other hand, the results of Comparative Examples 11, 12, and 13 show that when fluorine gas is used as the etching gas, copper halide etching is less likely to proceed.

Reference Signs List

10 [0092]

- 1: Halogen fluoride gas supply unit
- 2: Inert gas supply unit
- 3: Halogen fluoride gas flow rate control device
- 4: Inert gas flow rate control device
- 15 5: Halogen fluoride gas supply pipe
- 6: Inert gas supply pipe
- 7, 16: Pressure gauge
- 8: Inert gas pressure control device
- 10: Chamber
- 20 11: Stage
- 12: Member to be etched
- 13: Exhaust pipe
- 14: Thermometer
- 15: Vacuum pump
- 25 21: Silicon substrate
- 22: Titanium film
- 23: Copper film
- 24: Silicon dioxide substrate

CLAIMS

1. A dry etching method comprising a dry etching step
in which an etching gas containing a halogen fluoride being
5 a compound of bromine or iodine and fluorine is brought into
contact with a member to be etched including an etching target
being a target of etching with the etching gas to etch the
etching target without using plasma,
wherein the etching target contains copper; and
10 wherein the dry etching step is performed under
temperature conditions of from 140°C to 300°C.

2. The dry etching method according to claim 1,
wherein the etching gas is a gas comprising only a gas of the
15 halogen fluoride or is a mixed gas containing the halogen
fluoride and inert gas.

3. The dry etching method according to claim 2,
wherein the inert gas is at least one selected from nitrogen
20 gas, helium, argon, neon, krypton, and xenon.

4. The dry etching method according to any one of
claims 1 to 3, wherein an amount of the halogen fluoride
contained in the etching gas is from 1% by volume to 90% by
25 volume.

5. The dry etching method according to any one of claims 1 to 4, wherein the halogen fluoride is at least one of bromine pentafluoride or iodine heptafluoride.

5 6. The dry etching method according to any one of claims 1 to 5, wherein an amount of oxygen gas contained in the etching gas is 1% by volume or less.

7. The dry etching method according to any one of
10 claims 1 to 6, wherein the dry etching step is performed under pressure conditions of from 50 Pa to 80 kPa.

8. The dry etching method according to any one of claims 1 to 7, wherein the etching target contains at least
15 one of a copper compound containing at least one type of atom among oxygen, nitrogen, and halogen atoms and copper or elemental copper.

9. The dry etching method according to any one of
20 claims 1 to 8, wherein the dry etching step is performed under temperature conditions of from 210°C to 280°C.

10. The dry etching method according to any one of claims 1 to 9, wherein the member to be etched includes a
25 non-etching target not being the target of the etching with the etching gas and the etching target, the etching target being selectively etched compared to the non-etching target.

11. The dry etching method according to claim 10, wherein the non-etching target is at least one selected from silicon oxide, photoresist, and amorphous carbon.

5 12. The dry etching method according to claim 10 or 11, wherein an etching selectivity ratio being a ratio of an etching rate of the etching target to an etching rate of the non-etching target is 5 or more.

10 13. A method for manufacturing a semiconductor element, the method using the dry etching method according to any one of claims 1 to 12 to manufacture the semiconductor element,

wherein the member to be etched is a semiconductor
15 substrate including the etching target; and

wherein the manufacturing method comprises a processing step of removing at least a part of the etching target from the semiconductor substrate by the dry etching method.

20 14. The method for manufacturing a semiconductor element according to claim 13, wherein copper wiring is formed on the semiconductor substrate by the processing step.

15 15. A cleaning method for cleaning an inner surface of a chamber of a semiconductor element manufacturing device using the dry etching method according to any one of claims 1 to 12,

wherein the member to be etched is the chamber, the chamber having, on the inner surface, a deposit adhered due to operation of the semiconductor element manufacturing device, and the deposit being the etching target; and

5 wherein the cleaning method comprises a cleaning step of removing the deposit from the inner surface of the chamber by the dry etching method.