

ETCHING METHOD AND PLASMA ETCHING MATERIAL

5 The present invention relates to an etching method and a plasma etching material.

Background Art

 The step of selectively etching a silicon oxide-containing film is a process step that is widely used in processes for producing integrated circuits (IC),
10 microelectromechanical systems (MEMS), optical devices, and so forth.

 Various fluorocarbon gases have been proposed as materials that carry out the selective plasma etching of, for example, silicon oxide films, and silicon oxynitride films, in comparison with materials such as silicon nitride and photoresists. In addition, oxyfluorocarbon gases, which contain the oxygen atom in the molecule, have also been
15 proposed for the execution of highly selective etching.

Summary of

 By using a fluorocarbon gas in combination with an oxidizer such as oxygen gas, the method disclosed in the PCT application No. 2015-533029 can carry out etching while forming a fluorocarbon polymer at the bottom and sidewalls of a
20 depression (for example, a trench or hole). In accordance with this method, by controlling the amount of introduction of the oxidizer, the thickness of the fluorocarbon polymer deposited on the sidewalls of the depression can be controlled and etching can be carried out vertically while protecting the sidewalls. However, because the fluorocarbon gas and oxidizer are different molecules having different molecular
25 weights and different molecular diameters, the uniform introduction of both the fluorocarbon gas and oxidizer in the desired concentrations all the way to the bottom of

a depression has been problematic. The realization of the selective etching in particular of a high aspect ratio depression has thus been problematic.

The use of an oxyfluorocarbon gas is proposed in the etching method disclosed in JP 2005-39277. However, the oxyfluorocarbon gas disclosed in JP 2005-39277 has not more than two oxygen atoms in the molecule, and the introduction of an additional oxidizer is then required in order to secure a satisfactory etching rate. Thus, the uniform introduction of both the oxyfluorocarbon and the oxidizer—which is a different molecule having a different molecular weight and different molecular diameter from the oxyfluorocarbon—in the desired concentrations all the way to the bottom of a depression has been problematic. Moreover, while etching can be executed with this method, either polymer deposition on the sidewalls of the depression does not occur, or the amount of deposition is scarce, and there is then risk of damage to the depression and substrate. As a result, the etching selectivity between the mask material, which is not the etching target, and the etching target material assumes a declining trend.

As a consequence, there is desire for an etching method that exhibits a fast etching rate for silicon oxide-containing films and that can selectively etch silicon oxide-containing films.

The present inventors have discovered a plasma etching method that uses an oxyfluorocarbon gas and a halogenated hydrocarbon in order to selectively etch silicon oxide-containing films.

The disclosure was achieved in order to solve at least a portion of the problem identified above and can be realized as the aspects or application examples provided below.

As used in this Description, the term “etching” refers to a plasma etching process (i.e., a dry etching process) in which, through the acceleration of the chemical reactions in the vertical direction due to ion bombardment, vertical sidewalls are formed

along the edges of the masked features at right angles to the substrate (Manos and Flamm, Plasma Etching: An Introduction, Academic Press, Inc., 1989 pp. 12-13). The etching process produces an aperture, e.g., a via, trench, channel hole, gate trench, staircase contact, capacitor hole, contact hole, and so forth, or a structure that combines
5 these features, in the substrate. In this Description, this aperture is also referred to as a depression.

The term “selectivity” denotes the ratio between the etching rate of one material to the etching rate of a second material. The term “selective etching” or “selectively etching” means that the etching selectivity between two materials is greater
10 than or less than 1:1.

The term “attachment coefficient” refers to the proportion, of molecules that have reached a film surface, for molecules that have undergone chemical adsorption and/or physical adsorption. The attachment coefficient varies as a function of the surface state of the film and the properties of the attaching molecule. As a general
15 matter, molecules having larger molecular weights and larger molecular diameters tend to have smaller attachment coefficients.

It should be noted that the Si-containing films, e.g., of SiN or SiO, are referenced throughout the Description and claims without consideration of their proper stoichiometries. The silicon-containing film can be exemplified by pure silicon (Si)
20 films such as crystalline Si, polysilicon (poly-Si or polycrystalline Si), and amorphous silicon; silicon nitride (Si_kN_l) films; silicon oxide (Si_nO_m) films; and their mixtures, wherein k, l, m, and n in the formulas are in the range from 1 to 6 inclusive. The silicon nitride is preferably Si_kN_l (k and l in the formula are each in the range from 0.5 to 1.5). The silicon nitride is more preferably Si_1N_1 . The silicon oxide is preferably Si_nO_m
25 (in the formula, n is in the range from 0.5 to 1.5 and m is in the range from 1.5 to 3.5). The silicon oxide is more preferably SiO_2 or SiO_3 . The silicon-containing film may also be a silicon oxide-based dielectric material, for example, an organic-based or silicon

oxide-based low-k dielectric material such as the Black Diamond II material or Black Diamond III material from SKW Associates, Inc. The silicon-containing film may also contain a dopant such as B, C, P, As and/or Ge. The amorphous carbon-containing film may also contain a dopant such as a metal element, B, P, As, and/or Ge.

5 In a first aspect, the present disclosure provides an etching method comprising etching a Si-containing material by introducing a gas containing a halogenated hydrocarbon and a gas containing $C_4F_6O_3$ into a plasma reaction chamber and by forming active species in the plasma reaction chamber by a plasma.

10 In a second aspect, the present disclosure provides plasma etching material comprising $C_4F_6O_3$ and a halogenated hydrocarbon, the halogenated hydrocarbon containing at least one compound selected from the group consisting of CF_4 , CF_3I , C_2F_3I , C_3F_5I , C_3F_7I , C_2F_6 , C_3F_6 , C_3F_8 , C_4F_8 , C_4F_6 , C_5F_8 , C_6F_6 , CH_3F , CHF_3 , CH_2F_2 , C_2HF_5 , C_3HF_5 , $C_3H_2F_4$, $C_3H_2F_6$, C_4HF_7 , and $C_4H_2F_6$.

Application Example 1

15 According to one embodiment of the disclosure, there is provided an etching method comprising etching a Si-containing material by introducing a gas containing a halogenated hydrocarbon and a gas containing trifluoroacetic anhydride ($C_4F_6O_3$) into a plasma reaction chamber and by forming active species in the plasma reaction chamber by a plasma.

20 A highly precise etching can be performed in accordance with this application example through the mixing of a halogenated hydrocarbon-containing gas and a $C_4F_6O_3$ -containing gas in the plasma reaction chamber. In addition, because three oxygen atoms are present in each molecule of $C_4F_6O_3$, the etching target material can be selectively etched in comparison with the mask material without the addition of an
25 oxidizer.

Moreover, due mainly to the effects of the halogenated hydrocarbon, it becomes possible to carry out an etching having a controlled deposition of fluorocarbon

polymer on the sidewalls of the depression, and a highly precise etching in the perpendicular direction with respect to the Si-containing material substrate can then be performed.

5 The flow rate ratio between the halogenated hydrocarbon-containing gas and the $C_4F_6O_3$ -containing gas is not particularly limited, and, for the case of use of C_4F_6 as the halogenated hydrocarbon, it can be, for example, 9 : 1 to 7 : 3 and can preferably be 9 : 1 to 8 : 2. In this Description, “flow rate ratio” is the ratio between volumetric flow rates per unit time.

Application Example 2

In the etching method according to Application Example 1,

the Si-containing material may have a first film made of at least one material selected from the group consisting of SiN, amorphous carbon, amorphous carbon doped with an element other than carbon, Si, metal nitrides, metal oxides, organic photoresists, and metals, and has a second film made of at least one material selected from the group consisting of SiO, SiON, SiOC, SiOH, and SiOCH, and

the second film may be selectively removed from the Si-containing material.

Application Example 3

In the etching method according to Application Example 1 or 2, the halogenated hydrocarbon may be a compound represented by the general formula (1):



(In general formula (1), a is a number from 1 to 5; b is a number from 1 to 9; c is a number from 0 to 4; and X is a halogen atom selected from the group consisting of a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.).

Preferably a is a number from 3 to 5; b is preferably a number from 1 to 9; c is preferably a number from 2 to 3; and X is preferably the fluorine atom and/or iodine atom.

Application Example 4

In the etching method according to any one of Application Examples 1 to 3, the halogenated hydrocarbon may contain at least one compound selected from the group consisting of CF₄, CF₃I, C₂F₃I, C₃F₅I, C₃F₇I, C₂F₆, C₃F₆, C₃F₈, C₄F₈, C₄F₆, C₅F₈, C₆F₆, CH₃F, CHF₃, CH₂F₂, C₂HF₅, C₃HF₅, C₃H₂F₄, C₃H₂F₆, C₄HF₇, and C₄H₂F₆.

In accordance with this application example, because the halogenated hydrocarbon contains the fluorine atom in the molecule, volatile SiF₄ is formed by reaction with the second film, which is the etching target and contains at least one material selected from the group consisting of SiO, SiON, SiOC, SiOH, and SiOCH,

and etching can be performed more efficiently. Moreover, because the halogenated hydrocarbon contains the carbon atom in the molecule, the oxygen atom in the etching target can be removed through the production of volatile carbon oxide compounds (CO, CO₂, and so forth).

5 Application Example 5

In the etching method according to any one of Application Examples 1 to 4, the halogenated hydrocarbon may contain at least one compound selected from the group consisting of C₄F₆ and C₄F₈.

10 In accordance with this application example, the active species produced from the halogenated hydrocarbon and C₄F₆O₃ by excitation by the plasma have a low attachment coefficient and can reach all the way to the bottom of the depression formed in the Si-containing material that is the etching target. A uniform and highly precise etching can thus be achieved all the way to the bottom of the depression.

Application Example 6

15 In the etching method according to any one of Application Examples 1 to 5, an inert gas may be further introduced into the plasma reaction chamber.

In accordance with this application example, the stability of the plasma is increased and control of the plasma conditions is facilitated.

Application Example 7

20 In the etching method according to Application Example 6, the inert gas may contain at least one gas selected from the group consisting of N₂, He, Ar, Ne, Kr, and Xe.

Application Example 8

25 In the etching method according to any one of Application Examples 1 to 7, an oxidizing gas may be further introduced into the plasma reaction chamber.

Application Example 9

In the etching method according to Application Example 8, the oxidizing gas may contain at least one gas selected from the group consisting of O₂, O₃, CO, CO₂, NO, N₂O, NOF, SO₂, and COS.

- 5 In accordance with this application example, the thickness of the polymer deposited in the depression formed in the Si-containing material that is the etching target can be more precisely controlled and etching can be more precisely controlled.

Application Example 10

- 10 In the etching method according to any one of Application Examples 1 to 9, the Si-containing material may have a depression with a depth-to-width aspect ratio of from 0.5 : 1 to 20 : 1.

Application Example 11

- 15 In the etching method according to any one of Application Examples 1 to 9, the Si-containing material may have a depression with a depth-to-width aspect ratio of from 21 : 1 to 300 : 1.

- 20 In accordance with Application Examples 10 and 11, the halogen atom content per the predetermined gas flow rate introduced into the plasma reaction chamber is larger than for the introduction of a fluorocarbon gas and oxidizer. That is, the amount of halogen atom in the overall amount of introduced gas is larger for the introduction of a halogenated hydrocarbon and trifluoroacetic anhydride (C₄F₆O₃), which has the oxygen atom in the molecule, than for the introduction of fluorocarbon gas plus oxidizer.

- 25 A faster etching rate is provided by having a larger halogen atom content per unit flow rate. In addition, this application example, because it also has a high etching selectivity, is particularly advantageous for the etching of a relatively deep depression having a large aspect ratio. Because it can perform a highly precise etching at a high rate, this application example is also advantageous for etching a shallow depression having a relatively small aspect ratio.

Application Example 12

In the etching method according to any one of Application Examples 1 to 11, the $C_4F_6O_3$ may have a purity of at least 99.9 wt% and less than 100 wt%, and may have a content of an oxygen-containing impurity of from 0 weight-ppm to 100 weight-ppm.

5 Application Example 13

In the etching method according to Application Example 12, the oxygen-containing impurity may contain H_2O , and the content of the H_2O may range from 0.1 weight-ppb to 20 weight-ppm.

10 In accordance with this application example, due to the low oxygen-containing impurity content (particularly the H_2O content), the decomposition reaction of the $C_4F_6O_3$ is inhibited and the decline in the etching capacity associated with $C_4F_6O_3$ decomposition can then be reduced.

Application Example 14

15 In the etching method according to Application Example 12 or 13, the oxygen-containing impurity may contain trifluoroacetic acid, and the content of the trifluoroacetic acid may range from 0.1 weight-ppb to 20 weight-ppm.

20 In accordance with this application example, the occurrence of the decline in the etching selectivity due to etching of the mask material (particularly SiN) by the hydrogen atom present in trifluoroacetic acid can be inhibited. In addition, due to the low oxygen-containing impurity content (particularly the H_2O content) in this application example, the decomposition reaction of the $C_4F_6O_3$ is inhibited and the decline in the etching capacity associated with $C_4F_6O_3$ decomposition can then also be reduced.

Application Example 15

25 In the etching method according to any one of Application Examples 1 to 14, prior to being introduced into the plasma reaction chamber, the $C_4F_6O_3$ may be stored in a metal container having an inner surface with a surface roughness of 0 to 6 μm . The

surface roughness can be measured using atomic force microscopy (AFM) or a laser microscope.

In accordance with this application example, there is little risk that impurities attached to the inner surface of the container can become admixed into the $C_4F_6O_3$ that is supplied into the plasma chamber. In addition, the decomposition of $C_4F_6O_3$ caused by impurities attached to the container inner surface can be reduced, as can the production of trifluoroacetic acid that accompanies this decomposition. Reductions in the etching capacity can thereby be controlled.

Application Example 16

According to one embodiment of the disclosure, there is provided a plasma etching material comprising $C_4F_6O_3$ and a halogenated hydrocarbon,

the halogenated hydrocarbon containing at least one compound selected from the group consisting of CF_4 , CF_3I , C_2F_3I , C_3F_5I , C_3F_7I , C_2F_6 , C_3F_6 , C_3F_8 , C_4F_8 , C_4F_6 , C_5F_8 , C_6F_6 , CH_3F , CHF_3 , CH_2F_2 , C_2HF_5 , C_3HF_5 , $C_3H_2F_4$, $C_3H_2F_6$, C_4HF_7 , and $C_4H_2F_6$.

In accordance with this application example, a highly precise etching can be performed through the mixing of a halogenated hydrocarbon-containing gas and a $C_4F_6O_3$ -containing gas in the plasma reaction chamber. In addition, because the oxygen atom is present in the $C_4F_6O_3$ molecule, the etching target material can be selectively etched in comparison with a mask material. Moreover, because etching is performed while causing the deposition of fluorocarbon polymer on the sidewalls of the depression formed in the Si-containing material that is the etching target, a highly precise etching in the perpendicular direction with respect to the Si-containing material substrate can be performed.

In accordance with the etching method according to the disclosure, a highly precise etching can be performed at a fast etching rate through the mixing of a halogenated hydrocarbon-containing gas and a $C_4F_6O_3$ -containing gas to uniformity in

the plasma reaction chamber. In addition, because the oxygen atom is present in the $C_4F_6O_3$ molecule, the etching target material can be selectively etched in comparison with the mask material even under conditions in which an oxidizing gas is not introduced. Moreover, because etching is performed while causing the deposition of a fluorocarbon polymer on the sidewalls of the depression, a highly precise etching in the perpendicular direction with respect to the Si-containing material substrate can be performed.

Brief Description of Drawings

Fig. 1 is a schematic structural diagram of an etching apparatus that is preferably used in one embodiment of the invention.

Description of Embodiments

Preferred embodiments according to the invention are described in detail in the following. The invention is not limited to only the embodiments described in the following and should be understood as also encompassing various modification examples executed in a range in which the essential elements of the invention are not altered.

1. Etching method

The etching method according to one embodiment of the invention is a method in which a Si-containing material is etched by introducing a gas containing a halogenated hydrocarbon and a gas containing $C_4F_6O_3$ into a plasma reaction chamber and forming active species in the plasma reaction chamber by a plasma. In addition, in the etching method, an inert gas may be further introduced into the plasma reaction chamber and an oxidizing gas may be further introduced into the plasma reaction chamber. The halogenated hydrocarbon-containing gas, the $C_4F_6O_3$ -containing gas, the inert gas, and the oxidizing gas may be intermixed prior to introduction into the plasma reaction chamber or may be intermixed in the plasma reaction chamber.

The etching method according to one embodiment of the invention is described below.

1.1. Etching method using a halogenated hydrocarbon-containing gas and a $C_4F_6O_3$ -containing gas

5 The etching method can be used to etch a Si-containing material. This Si-containing material is the etching workpiece, but may be a combination of this etching workpiece with a material relatively resistant to etching (for example, a mask material). The Si-containing material that is the etching workpiece should be a material that contains the silicon atom, but is not otherwise particularly limited, and may be a
10 material that contains the silicon atom and the oxygen atom (for example, a silicon oxide-containing film). A portion of the silicon atom- and oxygen atom-containing material may be coated by a first film made of at least one material selected from the group consisting of silicon nitride, amorphous carbon, doped amorphous carbon, Si, metal nitrides, metal oxides, organic photoresists, and metals. The silicon atom- and
15 oxygen atom-containing material may be a second film made of at least one material selected from the group consisting of SiO , $SiON$, $SiOC$, $SiOH$, and $SiOCH$. When the etching workpiece is silicon oxide, SiN , amorphous carbon, and/or polysilicon is particularly advantageous for the first film.

20 The etching method is described below with reference to Fig. 1. Fig. 1 is a schematic structural diagram of an apparatus that is preferably used in one embodiment of the invention.

As illustrated in Fig. 1, an etching workpiece 11 that is Si-containing material is first placed in a plasma reaction chamber 21. The Si-containing material will vary depending on the application, but can contain a first film and a second film. The first
25 film can be specifically exemplified by SiN , amorphous carbon, doped amorphous carbon, Si, metal nitrides, metal oxides, organic photoresists, metals, and materials containing any combination of the preceding materials, but is not limited to the

preceding. The second film can be specifically exemplified by silicon atom- and oxygen atom-containing materials. The silicon atom- and oxygen atom-containing material can be exemplified by SiO, SiON, SiOC, SiOH, SiOCH, and materials containing any combination of the preceding materials, but is not limited to the preceding. A portion of the etching workpiece 11 may be coated by the second film. The etching workpiece 11 can be placed on an etching workpiece holder 12. From approximately 1 to 200 of the etching workpieces for carrying out the etching process can be placed within the plasma reaction chamber 21.

Here, the pressure within the plasma reaction chamber 21 is brought to the predetermined pressure using a vacuum pump 45 and a pressure-regulating mechanism 22, and the temperature within the plasma reaction chamber 21 is brought to the predetermined temperature using a temperature-regulating mechanism 23. A backpressure valve or pressure-regulating valve can be used for the pressure-regulating mechanism 22, but there is no limitation to these. A circulation-type cooling apparatus (chiller) and/or an electric heater-based temperature-regulating mechanism can be used for the temperature-regulating mechanism 23, but there is no limitation to these.

Using the temperature-regulating mechanism 23, the temperature in the plasma reaction chamber 21 can be set to a temperature in the range from -20°C to 200°C. The lower limit for the temperature of the etching workpiece 11 in the plasma reaction chamber 21 is preferably -20°C and is more preferably 0°C. The upper limit for the temperature of the etching workpiece 11 in the plasma reaction chamber 21 is preferably 150°C and more preferably 100°C.

The lower limit for the pressure in the plasma reaction chamber 21 is preferably 0.1 mTorr, more preferably 1 mTorr, and even more preferably 10 mTorr. The upper limit for the pressure in the plasma reaction chamber 21 is preferably 1,000 Torr, more preferably 100 Torr, and even more preferably 1 Torr.

The plasma reaction chamber 21 can be made of, for example, stainless steel or a surface-coated stainless steel, but there is no limitation to these.

The halogenated hydrocarbon-containing gas and the $C_4F_6O_3$ -containing gas are then introduced into the plasma reaction chamber 21. As illustrated in Fig. 1, gas
5 supplied through a flow rate-regulating mechanism 32 for the halogenated hydrocarbon-containing gas from a container 31 of the halogenated hydrocarbon-containing gas, and gas supplied through a flow rate-regulating mechanism 34 for the $C_4F_6O_3$ -containing gas from a container 33 of the $C_4F_6O_3$ -containing gas, can be further introduced into the plasma reaction chamber 21 after being merged upstream from the plasma reaction
10 chamber 21. The halogenated hydrocarbon-containing gas and the $C_4F_6O_3$ -containing gas may be further introduced into the plasma reaction chamber 21 from the respective flow rate-regulating mechanisms 32 and 34 and mixed within the plasma reaction chamber 21.

The flow rate ratio between the halogenated hydrocarbon-containing gas and
15 the $C_4F_6O_3$ -containing gas will vary depending on the type and characteristics of the halogenated hydrocarbon and depending on the characteristics of the etching target material. For the case of use of C_4F_6 as the halogenated hydrocarbon, the flow rate ratio between the halogenated hydrocarbon-containing gas and the $C_4F_6O_3$ -containing gas is, for example, 9 : 1 to 7 : 3 and is preferably 9 : 1 to 8 : 2. In this Description, the flow
20 rate ratio is the ratio of the volumetric flow rates per unit time.

At this point, the halogenated hydrocarbon-containing gas and/or the $C_4F_6O_3$ -containing gas can be introduced in a gaseous state or a liquid state into the plasma reaction chamber 21. The following are advantageously used in the case of introduction in the gaseous state, although there is no limitation to the following: a method in which
25 the vapor is directly withdrawn from the container 31 and/or the container 33; a direct injection method in which liquid droplets of the material from the container 31 and/or the container 33 are dripped onto a heater and the vapor thereby produced is introduced;

and a method in which the vapor of the halogenated hydrocarbon is introduced after being entrained by bubbling by introducing a carrier gas into the container 31. The carrier gas introduced to carry out bubbling can be exemplified by Ar, He, N₂, and their mixtures, but there is no limitation to these. When the halogenated hydrocarbon-containing gas and/or the C₄F₆O₃-containing gas is introduced in the liquid state, the method of inducing volatilization by dripping liquid droplets within the plasma reaction chamber 21 is preferably used. A mass flow controller, a variable leak valve, or a liquid flow meter can be used for the flow rate-regulating mechanism 32 in correspondence to, e.g., the properties and characteristics of the halogenated hydrocarbon-containing gas, and for the flow rate-regulating mechanism 34 in correspondence to, e.g., the properties and characteristics of the C₄F₆O₃-containing gas; however, there is no limitation to the preceding.

The flow rate of the halogenated hydrocarbon-containing gas introduced into the plasma reaction chamber 21 is brought to a liquid flow rate or gas flow rate in the range from, for example, 0.1 SCCM to 2,000 SCCM, by the flow rate-regulating mechanism 32. The flow rate of the C₄F₆O₃-containing gas introduced into the plasma reaction chamber 21 is brought to a liquid flow rate or gas flow rate in the range from, for example, 0.1 SCCM to 2,000 SCCM, by the flow rate-regulating mechanism 34. These flow rates can be modified in correspondence to, for example, the capacity of the plasma reaction chamber 21, the number of etching workpieces, and the properties of the halogenated hydrocarbon and/or the C₄F₆O₃-containing gas.

The time for which the halogenated hydrocarbon-containing gas and/or the C₄F₆O₃-containing gas is introduced into the plasma reaction chamber 21 can be varied in correspondence to the capacity of the plasma reaction chamber 21, the number of etching workpieces, the properties of the gases, and so forth, and, for example, can be in the range from 5 seconds to 60 minutes.

The halogenated hydrocarbon preferably is a compound represented by the following general formula (1)



(In general formula (1), a is a number from 1 to 5; b is a number from 1 to 9; c is a number from 0 to 4; and X is a halogen atom selected from the group consisting of a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. Preferably a is a number from 3 to 5; b is preferably a number from 1 to 9; c is preferably a number from 2 to 3; and X is preferably the fluorine atom and/or the iodine atom.).

Specific examples of the halogenated hydrocarbon are CF₄, CF₃I, C₂F₃I, C₃F₅I, C₃F₇I, C₂F₆, C₃F₆, C₃F₈, C₄F₈, C₄F₆, C₅F₈, C₆F₆, CH₃F, CHF₃, CH₂F₂, C₂HF₅, C₃HF₅, C₃H₂F₄, C₃H₂F₆, C₄HF₇, and C₄H₂F₆, and a single one of these or two or more of these may be used.

The execution of a more uniform etching is facilitated when the molecular weights and/or molecular diameters of the halogenated hydrocarbon and C₄F₆O₃ are close to one another, which is thus more preferred.

The Si-containing material is etched in the plasma reaction chamber 21 by inducing the formation of active species by a plasma. The mixed gas containing the halogenated hydrocarbon and C₄F₆O₃ that has been introduced into the plasma reaction chamber 21 forms active species by the plasma. The plasma can be generated by the application of RF power or DC power. The plasma can be generated by RF power in the range from 25 W to 20,000 W. The plasma is generated or is present within the plasma reaction chamber 21. The plasma may be generated in ICP mode or may be generated by dual CCP with the application of RF power to both electrodes. The RF frequency of the plasma can be in the range from 200 kHz to 1 GHz. Different RF sources having different frequencies can also be coupled and used at the same electrode. The plasma etching reactions can also be controlled using plasma RF pulsing.

1.2. Introduction of inert gas

An inert gas can be further introduced into the plasma reaction chamber 21 in order to sustain the plasma. The inert gas can be He, N₂, Ar, Xe, Kr, Ne, or a combination of the preceding. The halogenated hydrocarbon, C₄F₆O₃, and inert gas may be intermixed prior to introduction into the plasma reaction chamber 21. The halogenated hydrocarbon, C₄F₆O₃, and inert gas may be separately introduced into the plasma reaction chamber 21 and then intermixed within the plasma reaction chamber 21. The inert gas may be continuously introduced into the plasma reaction chamber 21 while intermittently introducing the halogenated hydrocarbon and C₄F₆O₃ gas into the plasma reaction chamber 21. The amount of inert gas introduction is preferably 0% v/v to 99.5% v/v, more preferably 10% v/v to 99% v/v, and even more preferably 50% v/v to 95% v/v of the total amount of the halogenated hydrocarbon, C₄F₆O₃, and inert gas. Ar gas is particularly advantageous for inducing a stable plasma generation and generating active species within the plasma reaction chamber 21.

1.3. Introduction of oxidizing gas

An oxidizing gas may be further introduced into the plasma reaction chamber 21. Due to the presence of three oxygen atoms in the C₄F₆O₃ molecule, etching can be performed in accordance with the invention without the introduction of an oxidizing gas. However, an oxidizing gas may be introduced in order to control etching more precisely. At least one gas selected from the group consisting of O₂, O₃, CO, CO₂, NO, N₂O, NOF, SO₂, and COS and combinations of the preceding can be used for the oxidizing gas. The halogenated hydrocarbon, C₄F₆O₃, and oxidizing gas may be intermixed prior to introduction into the plasma reaction chamber 21. The oxidizing gas may be further introduced into the plasma reaction chamber 21 separately from the halogenated hydrocarbon and the C₄F₆O₃. The oxidizing gas may also be continuously introduced into the plasma reaction chamber 21 while intermittently introducing the halogenated hydrocarbon and the C₄F₆O₃ gas into the plasma reaction chamber 21.

The amount of oxidizing gas introduction can be 0% v/v to 100% v/v of the total amount of the halogenated hydrocarbon, $C_4F_6O_3$, and oxidizing gas (100% refers to the case in which the pure oxidizing gas is not introduced continuously, but rather is introduced in alternation with gas other than the oxidizing gas. An example is the case in which the following process is repeated: a mixture of halogenated hydrocarbon and $C_4F_6O_3$ is introduced for a certain period of time; supply of the halogenated hydrocarbon and $C_4F_6O_3$ is halted; and 100% v/v oxidizing gas is then introduced.).

In accordance with the etching method according to one embodiment of the invention, a gas containing a halogenated hydrocarbon, which has a protective function through the formation of a polymer film on the surface of silicon-containing material, is intermixed to uniformity in the plasma reaction chamber with a gas containing $C_4F_6O_3$, which has the ability to etch the surface of silicon-containing material, and as a consequence a highly precise etching can be performed at a fast etching rate. Moreover, in the case of etching a depression formed in Si-containing material that is the etching target, the bottom of this depression can be more selectively etched while the sidewalls of the depression are protected. Because this etching method can be carried out without the introduction of an oxidizing gas, e.g., oxygen, with regard to the etching of a depression in Si-containing material, active species having a uniform composition ratio can be supplied to the location where etching is performed. Etching presenting a high degree of uniformity can therefore be carried out. An even more precisely controlled etching can also be carried out when an oxidizing gas is introduced.

1.4. $C_4F_6O_3$ purity

$C_4F_6O_3$ may contain trifluoroacetic acid as an impurity originating with its production process. $C_4F_6O_3$ is also readily degraded by oxygen-containing impurities and trifluoroacetic acid may be produced as a degradation product. Moreover, the oxygen-containing impurities, which are oxidizers therefor, are also excited under plasma conditions with the production of hydrogen· hydroxylated radicals, and the

problem arises that redox reactions unnecessary for the process occur. Thus, the $C_4F_6O_3$ purity preferably is at least 99.9 wt% and less than 100 wt%.

In particular, because oxygen-containing impurities have a large influence in terms of reducing the etching performance, the oxygen-containing impurity content ranges preferably from 0 weight-ppm to 100 weight-ppm. The upper limit on the oxygen-containing impurity content is preferably 100 weight-ppm, more preferably 50 weight-ppm, and even more preferably 5 weight-ppm.

Among the oxygen-containing impurities, H_2O has a particularly high reactivity and in addition can be admixed during the $C_4F_6O_3$ fill process from the fill container and supply conduits, and control of the H_2O content is essential with regard to control of the etching capacity. Thus, the H_2O content in the $C_4F_6O_3$ ranges preferably from 0.1 weight-ppb to 20 weight-ppm. The upper limit for the H_2O content in the $C_4F_6O_3$ is preferably 20 weight-ppm, but 1 weight-ppm is more preferred and 100 weight-ppb is particularly preferred.

In addition, the production of trifluoroacetic acid is facilitated when H_2O is contained in the $C_4F_6O_3$. Trifluoroacetic acid can also lower the etching capacity just like H_2O . Moreover, the etching selectivity is lowered since trifluoroacetic acid etches SiN. As a consequence, the trifluoroacetic acid in the $C_4F_6O_3$ ranges preferably from 0.1 weight-ppb to 20 weight-ppm. The upper limit on the trifluoroacetic acid content in the $C_4F_6O_3$ is preferably 20 weight-ppm, while 1 weight-ppm is more preferred and 100 weight-ppb is particularly preferred.

A high-performance, high-selectivity etching can be carried out when a $C_4F_6O_3$ is used that has the high purity indicated above and that contains little oxygen-containing impurity (particularly with regard to the H_2O content and trifluoroacetic acid).

1.5. The $C_4F_6O_3$ supply container and treatment of the container inner surface

In order to reduce the impurities in the $C_4F_6O_3$, in the etching method according to one embodiment of the invention, prior to being introduced into the plasma reaction chamber, the $C_4F_6O_3$ is preferably stored in a metal container having an inner surface with a surface roughness of 0 to 6 μm . With a metal container having an inner surface that has a surface roughness of 0 to 6 μm , the moisture remaining on the inner surface is easily eliminated in the drying step after container cleaning. Accordingly, the $C_4F_6O_3$ can be filled under conditions in which the moisture concentration in the container is low and a $C_4F_6O_3$ having a low moisture content can then be supplied into the plasma reaction chamber.

In order to fabricate a metal container having an inner surface with a surface roughness of 0 to 6 μm , the interior of the metal container, for example, is wet polished using an abrasive that contains an anticorrosion agent. There is no particular limitation on the metal container, and it may be made of stainless steel, manganese steel, or chromium molybdenum steel. The wet polishing preferably provides a surface roughness for the inner surface of the metal container of 6 μm or less. There are no particular limitations on the abrasive, and a ceramic-based abrasive, alumina-containing ceramic-based abrasive, silica-alumina abrasive, or combination of the preceding may be used. While only a single species of abrasive may be used, it is more effective to carry out polishing using a first abrasive followed by polishing using a second abrasive having a different composition. Polishing with the second abrasive may be carried out a plural number of times. A suspension of approximately 1 to 50 g in 1 liter of water can be used for the abrasive.

For example, approximately 5 to 10 g per 1 liter of water can be used for the first abrasive and 10 to 20 g per 1 liter of water can be used for the second abrasive, but there is no limitation to this. The use of a ceramic-based abrasive for the first abrasive and the use of an alumina-containing ceramic-based abrasive for the second abrasive is

preferred, but there is no limitation to this and the abrasive used may be freely selected.

After polishing, the metal container is washed and dried. The wash may be only a water wash (particularly a pure water wash), but the execution of an acid wash followed by a water wash is more effective. Water in which a spherical alumina-silica is suspended may also be used for the water wash. For the acid wash, at least one type selected from diammonium citrate, sodium dihydrogen phosphate, and sodium hydrogen diphosphate is preferred, and among them, diammonium citrate is particularly preferred. The use of at least one type selected from diammonium citrate, sodium dihydrogen phosphate, and sodium hydrogen diphosphate reduces the generation of ill effects on the anticorrosion film on the inner surface of the metal container, establishes a mild environment for the wash process, and also facilitates neutralization during disposal of the acid wash solution. Diammonium citrate is preferred in particular because it does not contain metal atoms, the phosphorus atom, or the sulfur atom, and as a consequence there is then little risk of contamination of the material filled into the metal container and the generation of ill effects on the film-forming operation using this material is thus also reduced. The drying step can be executed by blowing, e.g., nitrogen gas, dry air, and so forth, into the container; however, there is no particular limitation to these although an inert gas should be used. The residual amount of moisture can also be further lowered by heating the metal container using a heater.

A metal container having a low surface roughness, i.e., a surface roughness for the inner surface of 0 to 6 μm , can be obtained by going through the above-described wet polishing step, wash step, and drying step. Moisture adsorption to a metal surface having a low surface roughness is inhibited. Thus, there is little residual moisture in a metal container having a low surface roughness. Due to this, a high purity $\text{C}_4\text{F}_6\text{O}_3$ with a low moisture content can be stored by filling the $\text{C}_4\text{F}_6\text{O}_3$ into a metal container having a low surface roughness. A high-performance plasma etching can be performed when a high purity $\text{C}_4\text{F}_6\text{O}_3$ is used.

1.6. Functional effects

In accordance with the etching method according to one embodiment of the invention, a halogenated hydrocarbon and $C_4F_6O_3$ -containing gas are introduced into a plasma reaction chamber and active species can be produced by a plasma. The thusly produced active species perform the plasma etching of Si-containing material. In particular, a silicon atom- and oxygen atom-containing film, as typified by SiO , $SiON$, $SiOC$, $SiOH$, and $SiOCH$, can be etched at a high etching rate. As a consequence, the second film can be selectively removed at a high etching rate when etching is carried out on Si-containing material having a first film made of at least one material selected from the group consisting of SiN , amorphous carbon, doped amorphous carbon, Si, metal nitrides, metal oxides, organic photoresists, and metals, and having a second, silicon atom- and oxygen atom-containing film. When a depression formed in Si-containing material is to be etched with the etching method according to one embodiment of the invention, etching of only the bottom of the depression can proceed at a high rate while the sidewalls are protected by a polymer deposited on the sidewalls of the depression. In addition, a uniform etching can be carried out because the composition ratio for the active species supplied to the bottom of the depression is stable. Based on the preceding, the etching method is advantageous for the etching of depressions having a high aspect ratio and for the etching of depressions having a low aspect ratio.

In another embodiment of the invention, the plasma is stabilized by the addition of an inert gas and the etching efficiency can then be further improved. In yet another embodiment, the etching can also be even more precisely controlled through the addition of an oxidizing gas.

2. Examples

The invention is specifically described below based on examples, but the invention is not limited to these examples.

2.1. Treatment of the container inner surface

A metal container for the storage of $C_4F_6O_3$ -containing gas was subjected to treatment of the inner surface of the container. A wet polishing step, wash step, and drying step were carried out in the indicated sequence for the container inner surface treatment.

In the wet polishing step, a plurality of metal containers were supported horizontally with an abrasive and an anticorrosive being held in the interior. The containers were then installed in a wet polishing machine that caused them to revolve counterclockwise around a horizontal shaft while causing each container to rotate clockwise around its central axis. With such a wet polishing machine, the abrasive is concentrated on the outer side of the revolution trajectory by centrifugal force, and the metal container inner surface rotates and moves relative to this abrasive. When this is done, the metal container inner surface is polished by contact with the abrasive. While only one species of abrasive may be used, it is more effective when polishing is performed using a first abrasive followed by polishing using a second abrasive having a different composition. Polishing with the second abrasive may be performed a plurality of times. In the present example, the surface roughness of the inner surface of the metal container was approximately 3 to 5 μm after polishing with the first abrasive. The surface roughness of the inner surface of the metal container was approximately 1 μm when polishing with a second abrasive was carried out after polishing with the first abrasive.

In the wash step that follows the wet polishing step, upon completion of the polishing step the metal container is filled with spherical alumina-silica (particle diameter = 5 μm) and pure water and is rotated around its central axis. After this rotation, the abrasive and anticorrosive remaining in the metal container are removed. The inside of the metal container was then washed with pure water and dust attached to the anticorrosion film produced on the metal container inner surface was removed. The

dust that could not be removed by the pure water was then also removed using an acid wash solution. Washing with pure water was subsequently carried out again in order to remove the acid wash solution that remained in the metal container.

5 The metal container was baked at 120°C in the drying step that followed the wash step. This baking may be carried out in the air, but the residual amount of moisture can be further reduced by execution while purging with dry nitrogen gas.

According to the results of measurement with an atomic force microscope (AFM), the surface roughness of the inner surface of the metal container yielded by the preceding treatment was a surface roughness maximum value (Rmax) of 3 µm.

10 Conditions for treatment of the container inner surface

- Metal container used: Stainless steel, 1 L capacity, cylindrical
- Initial surface roughness of the metal container used: 15 µm
- First abrasive used: Spherical ceramic-based abrasive having a particle diameter of 5 mm, 5 g per 1 liter of water
- 15 • Second abrasive used: Spherical alumina-containing ceramic-based abrasive having a particle diameter of 5 mm, 15 g per 1 liter of water
- Acid wash solution used: 0.1% aqueous diammonium citrate solution
- Baking conditions: 12 hours, 120°C, under a nitrogen gas current

2.2. C₄F₆O₃ purity

20 The purity of the C₄F₆O₃ used in the following examples and comparative examples was as indicated in Table 1 below. The results of measurements of the purity and impurity contents on the C₄F₆O₃ are given in Table 1. A high etching performance was obtained by the use in the following Example 1 to Example 3 of the high-purity C₄F₆O₃ having a low moisture content and a low trifluoroacetic acid content.

TABLE 1

Item	Measured value	Measurement method
Purity	99.95 wt%	Gas chromatography (model name: “GC-2014”, Shimadzu Corporation)
Moisture content	30 weight-ppm	Cavity ring-down spectrophotometer (model name: “MTO-LP-H2O”, Tiger Optics, LLC)
Oxygen-containing impurities other than water	50 weight-ppm	Gas chromatography (model name: “GC-2014”, Shimadzu Corporation)
Trifluoroacetic acid content	20 weight-ppm	Gas chromatography (model name: “GC-2014”, Shimadzu Corporation)

2.3. Measurement of the etching rate

5 Ellipsometry (model name: SE-2000, SemiLab Inc.) and SEM (model name: S-5200, Hitachi, Ltd.) were used to measure the etching rate under the predetermined conditions of the silicon oxide film, silicon nitride film, polysilicon film, and amorphous carbon film.

2.4. Measurement of the etching selectivity ratio

10 The etching rates under the predetermined conditions of the silicon oxide film, silicon nitride film, polysilicon film, and amorphous carbon film were measured using the methods indicated above, and the value obtained by dividing the etching rate for the silicon oxide film by the etching rate for the silicon nitride film, the polysilicon, or the amorphous carbon film was used as the selectivity ratio.

15 2.5. Example 1

Table 2 and Table 3 give the results of the etching of a silicon oxide film, silicon nitride film, polysilicon, and amorphous carbon film using the apparatus illustrated in Fig. 1. The halogenated hydrocarbon, $C_4F_6O_3$, and an inert gas were supplied at flow rates controlled by respective mass flow controllers and were mixed
20 prior to introduction into the plasma reaction chamber followed by introduction into the

plasma reaction chamber 21. The total flow rate for the halogenated hydrocarbon and $C_4F_6O_3$ was 10 SCCM, and the inert gas flow rate was 90 SCCM. The gas introduced into the plasma reaction chamber 21 was excited by a plasma. The temperature within the plasma reaction chamber 21 was adjusted to 25°C by the temperature-regulating mechanism. The pressure within the plasma reaction chamber 21 was adjusted to 30 mTorr by the pressure-regulating mechanism.

An etching workpiece having any one of a silicon oxide film, silicon nitride film, amorphous carbon film, and polysilicon film was placed in the plasma reaction chamber 21, and each film was etched for a certain period of time. After the execution of etching, the interior of the plasma reaction chamber 21 was purged with inert gas. The interior of the plasma reaction chamber 21 was then returned to atmospheric pressure and the etching workpiece was removed. The etching rate was measured on the recovered etching workpiece.

With regard to the etching rate measurement, the thickness of the etched film was measured by ellipsometry for the silicon oxide film, silicon nitride film, and polysilicon film and the etching rate was calculated per the time for which the etching was performed. For the amorphous carbon film, the thickness of the etched film was measured using a scanning electron microscope (also referred to as “SEM” in this Description) and the etching rate was calculated per the time for which etching was performed.

Experimental conditions in Example 1

- Plasma reaction chamber: A 4520XLE from LAM Research Corporation was used.

- Temperature: 25°C

- Etching workpieces: Silicon oxide film, silicon nitride film, amorphous carbon film, polysilicon film

- Pressure in the processing chamber: 30 mTorr

- Inert gas: Argon (flow rate = 90 SCCM)
- Halogenated hydrocarbon: C_4F_6
- Total flow rate for the halogenated hydrocarbon (C_4F_6) and $C_4F_6O_3$: 10

SCCM (the individual flow rates are given in Table 2 and Table 3)

- 5
- Etching time: 60 seconds
 - High-frequency power: 27 MHz, 750 W
 - High-frequency bias power: 2 MHz, 1,500 W

Table 2 gives the results of measurement of the etching rate for the individual etching workpieces at different flow rate ratios between the halogenated hydrocarbon (hexafluoro-1,3-butadiene, C_4F_6) and $C_4F_6O_3$. Table 3 gives the etching selectivities calculated from the measurement results given in Table 2. The etching selectivity is given by the value provided by dividing the etching rate for the silicon oxide film by the etching rate for the particular film other than the silicon oxide film. The etching performance is evaluated based on the etching rate and the selectivity. Etching is preferably carried out at a fast etching rate and a high selectivity.

10

15

TABLE 2

Flow rate (SCCM)		Etching rate (nm/min)			
$C_4F_6O_3$	C_4F_6	Silicon oxide film	Silicon nitride film	Amorphous carbon film	Polysilicon film
9.0	1.0	703	61	71	50
8.5	1.5	706	58	46	41
8.0	2.0	700	47	44	39
7.5	2.5	575	40	37	25
7.0	3.0	460	36	29	22
6.5	3.5	180	22	20	13
6.0	4.0	105	13	0	8

TABLE 3

Flow rate (SCCM)		Etching selectivity		
C ₄ F ₆ O ₃	C ₄ F ₆	Silicon nitride film	Amorphous carbon film	Polysilicon film
9.0	1.0	11.5	9.9	14.1
8.5	1.5	12.2	15.3	17.2
8.0	2.0	14.9	15.9	17.9
7.5	2.5	14.4	15.5	23.0
7.0	3.0	12.8	15.9	20.9
6.5	3.5	8.2	9.0	13.8
6.0	4.0	8.1	-	13.1

In Example 1, even without the introduction of an oxidizing gas, the silicon oxide film could be selectively etched in comparison with the silicon nitride film, amorphous carbon film, and polysilicon film. At a flow rate ratio between the halogenated hydrocarbon (C₄F₆) and C₄F₆O₃ of 9 : 1 to 7 : 3 in particular, the etching rate was fast and the etching selectivity was high and thus a high etching performance was obtained as a result. The etching rate was faster when the flow rate ratio between the halogenated hydrocarbon (C₄F₆) and C₄F₆O₃ was 9 : 1 to 8 : 2 and an even higher etching performance was obtained as a result.

2.6. Example 2

Proceeding as in Example 1, a silicon oxide film, silicon nitride film, polysilicon, and amorphous carbon film were etched using the apparatus illustrated in Fig. 1, and the results are given in Table 4 and Table 5. The total flow rate for the halogenated hydrocarbon and C₄F₆O₃ was 6.0 SCCM, and the inert gas flow rate was 94 SCCM.

Experimental conditions in Example 2

• Plasma reaction chamber: A 4520XLE from LAM Research Corporation was used.

• Temperature: 25°C

5 • Etching workpieces: Silicon oxide film, silicon nitride film, amorphous carbon film, polysilicon film

• Pressure in the processing chamber: 30 mTorr

• Inert gas: Argon (flow rate = 94 SCCM)

• Halogenated hydrocarbon: C₄F₆

10 • Total flow rate for the halogenated hydrocarbon (C₄F₆) and C₄F₆O₃: 6.0 SCCM (the individual flow rates are given in Table 4 and Table 5)

• Etching time: 60 seconds

• High-frequency power: 27 MHz, 750 W

• High-frequency bias power: 2 MHz, 1,500 W

15 Table 4 gives the results of measurement of the etching rate for the individual etching workpieces at different flow rate ratios between the halogenated hydrocarbon (C₄F₆) and C₄F₆O₃. Table 5 gives the etching selectivities calculated from the measurement results given in Table 4. The etching selectivity is indicated by the value provided by dividing the etching rate for the silicon oxide film by the etching rate for

20 the particular film other than the silicon oxide film. When the etching rate is less than 0 nm/min, this indicates that film formation occurred without the occurrence of etching. The etching selectivity is not calculated when the etching rate is equal to or less than 0 nm/min, which is indicated by “-” in Table 5.

TABLE 4

Flow rate (SCCM)		Etching rate (nm/min)			
C ₄ F ₆ O ₃	C ₄ F ₆	Silicon oxide film	Silicon nitride film	Amorphous carbon film	Polysilicon film
5.0	1.0	535	35	31	23
4.5	1.5	569	27	26	18
4.0	2.0	461	18	17	10
3.5	2.5	59	0	8	4
2.0	3.0	51	-14	-15	-2

5 TABLE 5

Flow rate (SCCM)		Etching selectivity		
C ₄ F ₆ O ₃	C ₄ F ₆	Silicon nitride film	Amorphous carbon film	Polysilicon film
5.0	1.0	15.3	17.3	23.3
4.5	1.5	21.1	21.9	31.6
4.0	2.0	25.6	27.1	46.1
3.5	2.5	-	7.4	14.8
2.0	3.0	-	-	-

In Example 2, using conditions in which the flow rate of the halogenated hydrocarbon (C₄F₆) and C₄F₆O₃ made up less of the total gas flow rate than in Example 1, the silicon oxide film could be even more selectively etched in comparison with the silicon nitride film, amorphous carbon film, and polysilicon film—even without the introduction of an oxidizing gas.

2.7. Example 3

A low-k film was etched proceeding as in Example 1 and using the apparatus illustrated in Fig. 1. The total flow rate of the halogenated hydrocarbon and $C_4F_6O_3$ was 6.0 SCCM, and the inert gas flow rate was 94 SCCM.

5 Experimental conditions in Example 3

- Plasma reaction chamber: A 4520XLE from LAM Research Corporation was used.

- Temperature: 25°C

- Etching workpiece: Low-k film (Black Diamond II (registered trademark)

10 film acquired from SKW Associates, Inc.)

- Pressure in the processing chamber: 30 mTorr

- Inert gas: Argon (flow rate = 94 SCCM)

- Halogenated hydrocarbon: C_4F_6 (flow rate = 1.5 SCCM)

- $C_4F_6O_3$ flow rate: 4.5 SCCM

15 • Etching time: 60 seconds

- High-frequency power: 27 MHz, 750 W

- High-frequency bias power: 2 MHz, 1,500 W

Using an x-ray photoelectron spectrometer (XPS, K-Alpha, Thermo Fisher Scientific Inc.), the depth of damage was measured on the low-k film etched under the conditions described above, and the result was a low value of 30 nm for the depth of damage. In this Description, the “depth of damage for the low-k film” refers to the depth at which the carbon composition ratio in the low-k film post-etching returns to 95% of the carbon composition ratio in the low-k film pre-etching. The carbon composition ratio in a low-k film declines when the low-k film is damaged by etching.

25 As a consequence, the depth in a low-k film to which etching-induced damage extends can be observed by measurement by XPS of the carbon composition ratio in the low-k film in the depth direction.

Analysis of the low-k film with a Fourier-transform infrared spectrophotometer (FTIR) is another method for evaluating the damage to a low-k film caused by etching. This is a method in which the ratio is determined by FTIR between the intensity in the vicinity of the wavenumber $1,060\text{ cm}^{-1}$ originating with the Si-O-Si bond and the intensity in the vicinity of the wavenumber $1,270\text{ cm}^{-1}$ originating with the Si-CH₃ bond. When there is damage to a low-k film, the intensity in the vicinity of the wavenumber $1,270\text{ cm}^{-1}$ originating with the Si-CH₃ bond declines relative to the intensity in the vicinity of the wavenumber $1,060\text{ cm}^{-1}$ originating with the Si-O-Si bond. It was confirmed in this example that the intensity in the vicinity of the wavenumber $1,270\text{ cm}^{-1}$ originating with the Si-CH₃ bond was kept to a decline of 12.9% post-etching versus pre-etching and there was thus little damage.

Measurement of the etching rate of the low-k film by the same method as in Example 1 gave a result of 143 nm/min for the etching rate, and a satisfactorily fast etching rate could thus be obtained.

Based on the preceding, it was confirmed that in Example 3 there was little damage to the low-k film and etching could be performed at a satisfactorily fast etching rate.

2.8. Example 4

A silicon oxide film, silicon nitride film, polysilicon, and amorphous carbon film were etched under the same conditions as in Example 1, but using C₄F₈ as the halogenated hydrocarbon. As a result, almost the same results were obtained as in Example 1 and it was thus found that, even without the introduction of an oxidizing gas, the silicon oxide film could be selectively etched in comparison with the silicon nitride film, amorphous carbon film, and polysilicon film.

In addition, the low-k film was etched under the same conditions as in Example 3, but using C₄F₈ as the halogenated hydrocarbon. As a result, almost the same results were obtained as in Example 3 and it was thus confirmed that etching could be

performed at a satisfactorily fast etching rate with little damage to the low-k film.

2.9. Comparative Example 1

Etching was carried out as in Example 1, but using C_4F_6 , which is widely used as a halogenated hydrocarbon, in place of the $C_4F_6O_3$. The silicon oxide film, silicon nitride film, polysilicon, and amorphous carbon film were etched using the apparatus illustrated in Fig. 1, and the results are given in Table 6 and Table 7.

The flow rate for the halogenated hydrocarbon (C_4F_6) was 10 SCCM, and the total flow rate for the inert gas and an oxidizing gas (O_2) was 90 SCCM.

Experimental conditions in Comparative Example 1

• Plasma reaction chamber: A 4520XLE from LAM Research Corporation was used.

• Temperature: 25°C

• Etching workpieces: Silicon oxide film, silicon nitride film, amorphous carbon film, polysilicon film

• Pressure in the processing chamber: 30 mTorr

• Inert gas: Argon

• Oxidizing gas: Oxygen

• Total flow rate for the inert gas and oxidizing gas: 90 SCCM (the individual flow rates are indicated in Table 6 and Table 7)

• Halogenated hydrocarbon: C_4F_6 (flow rate = 10 SCCM)

• Etching time: 60 seconds

• High-frequency power: 27 MHz, 750 W

• High-frequency bias power: 2 MHz, 1,500 W

Table 6 gives the results of measurement of the etching rate for the individual etching workpieces at different flow rate ratios between the inert gas and the oxidizing gas. Table 7 gives the etching selectivities calculated from the measurement results given in Table 6.

The etching selectivity is indicated by the value provided by dividing the etching rate for the silicon oxide film by the etching rate for the particular film other than the silicon oxide film.

5 TABLE 6

Flow rate (SCCM)		Etching rate (nm/min)			
Ar	O ₂	Silicon oxide film	Silicon nitride film	Amorphous carbon film	Polysilicon film
90	0	-302	-178	-268	no data
87	3	-210	-110	-223	no data
84	6	-125	-70	-111	-13
81	9	81	13	6	16
79	11	152	23	-7	21
78	12	479	34	21	28
77	13	653	43	35	37
76	14	664	56	46	47
75	15	668	66	58	54
74	16	645	71	66	59
73	17	649	81	85	63
72	18	555	85	88	66
71	19	538	99	120	72
69	21	424	107	100	79
66	24	80	108	136	182

TABLE 7

Flow rate (SCCM)		Etching selectivity		
Ar	O ₂	Silicon nitride film	Amorphous carbon film	Polysilicon film
81	9	6.2	13.5	5.1
79	11	6.6	-	7.2
78	12	14.1	22.8	17.1
77	13	15.2	18.7	17.6
76	14	11.9	14.4	14.1
75	15	10.1	11.5	12.4
74	16	9.1	9.8	10.9
73	17	8.0	7.6	10.3
72	18	6.5	6.3	8.4
71	19	5.4	4.5	7.5
69	21	4.0	4.2	5.4
66	24	0.7	0.6	0.4

In Comparative Example 1, both for no introduction of oxidizing gas (oxygen) and for the introduction of a small amount (an oxygen flow rate of 6 or less SCCM in this comparative example), the occurrence of etching was completely absent and, conversely, a film was deposited on the film that was the etching target. When the amount of oxidizing gas introduction is increased, etching does occur, but the range in which both the etching rate and selectivity are satisfactory is narrow. For example, in the range of etching rates of at least 600 nm/min and etching selectivities for the silicon oxide film of at least 10, the amount of oxidizing gas introduction is limited to the range of 13 SCCM to 14 SCCM. This shows that, in order to obtain a high etching performance, the amount of oxidizing gas introduction must be regulated and controlling etching is problematic.

2.10. Comparative Example 2

The results for the use of perfluorohydrofuran (C_4F_8O), an oxyfluorocarbon, in place of $C_4F_6O_3$ are given in Table 8 and Table 9. An oxidizing gas was not used and C_4F_6 was used as the halogenated hydrocarbon. Proceeding as in Example 1, the silicon oxide film, silicon nitride film, polysilicon, and amorphous carbon film were etched using the apparatus illustrated in Fig. 1. The total flow rate for the halogenated hydrocarbon and C_4F_8O was 10 SCCM, and the inert gas flow rate was 90 SCCM.

Experimental conditions in Comparative Example 2

- Plasma reaction chamber: A 4520XLE from LAM Research Corporation was used.

- Temperature: 25°C

- Etching workpieces: Silicon oxide film, silicon nitride film, amorphous carbon film, polysilicon film

- Pressure in the processing chamber: 30 mTorr

- Inert gas: Argon (flow rate = 90 SCCM)

- Halogenated hydrocarbon: C_4F_6

- Total flow rate for the halogenated hydrocarbon (C_4F_6) and the C_4F_8O : 10 SCCM (the individual flow rates are indicated in Table 8 and Table 9)

- Etching time: 60 seconds

- High-frequency power: 27 MHz, 750 W

- High-frequency bias power: 2 MHz, 1,500 W

Table 8 gives the results of measurement of the etching rate for the individual etching workpieces at different flow rate ratios between the halogenated hydrocarbon (C_4F_6) and the C_4F_8O . Table 9 gives the etching selectivities calculated from the measurement results given in Table 8. The etching selectivity is indicated by the value provided by dividing the etching rate for the silicon oxide film by the etching rate for the particular film other than the silicon oxide film.

TABLE 8

Flow rate (SCCM)		Etching rate (nm/min)			
C ₄ F ₈ O	C ₄ F ₆	Silicon oxide film	Silicon nitride film	Amorphous carbon film	Polysilicon film
10.0	0	184	21	31	28
9.0	1.0	294	25	34	26
8.5	1.5	178	10	27	14
8.0	2.0	120	-5	-9	8
7.5	2.5	64	-17	-14	-1
7.0	3.0	130	-5	51	18

TABLE 9

Flow rate (SCCM)		Etching selectivity		
C ₄ F ₈ O	C ₄ F ₆	Silicon nitride film	Amorphous carbon film	Polysilicon film
10.0	0	8.8	5.9	6.6
9.0	1.0	11.8	8.6	11.3
8.5	1.5	17.8	6.6	12.7
8.0	2.0	-	-	15.0
7.5	2.5	-	-	-
7.0	3.0	-	2.5	7.2

5 Notwithstanding the use of C₄F₈O, which has oxygen atoms in the molecule, the etching rate was observed to be very slow in Comparative Example 2, which did not employ the introduction of an oxidizing gas (oxygen). The cause is thought to be the small number of oxygen atoms present in the molecule of the introduced oxyfluorocarbon.

2.11. Comparative Example 3

The results of etching by introducing $C_4F_6O_3$ and the halogenated hydrocarbon C_4F_6 are given in the aforementioned Example 1, while this comparative example provides the results for carrying out the same etching, but without the introduction of the C_4F_6 . The flow rate for the halogenated hydrocarbon was 0 SCCM; the flow rate for the $C_4F_6O_3$ was 6 to 10 SCCM; and the flow rate for the inert gas was 90 to 94 SCCM. The flow rates for each are indicated in Table 10 and Table 11.

Experimental conditions in Comparative Example 3

- Plasma reaction chamber: A 4520XLE from LAM Research Corporation was used.

- Temperature: 25°C

- Etching workpieces: Silicon oxide film, silicon nitride film, amorphous carbon film, polysilicon film

- Pressure in the processing chamber: 30 mTorr

- Inert gas: Argon (flow rate = 90 to 94 SCCM)

- Halogenated hydrocarbon: None

- Etching time: 60 seconds

- High-frequency power: 27 MHz, 750 W

- High-frequency bias power: 2 MHz, 1,500 W

Table 10 gives the results of measurement of the etching rate for the individual etching workpieces in Comparative Example 3. Table 11 gives the etching selectivities calculated from the measurement results given in Table 10. The etching selectivity is indicated by the value provided by dividing the etching rate for the silicon oxide film by the etching rate for the particular film other than the silicon oxide film.

TABLE 10

Flow rate (SCCM)		Etching rate (nm/min)			
C ₄ F ₆ O ₃	Ar	Silicon oxide film	Silicon nitride film	Amorphous carbon film	Polysilicon film
10.0	90.0	691	80	80	53
7.5	92.5	595	59	88	43
6.0	94.0	512	47	55	33

TABLE 11

Flow rate (SCCM)		Etching selectivity		
C ₄ F ₆ O ₃	Ar	Silicon nitride film	Amorphous carbon film	Polysilicon film
10.0	90.0	8.6	8.6	13.0
7.5	92.5	10.1	6.8	13.8
6.0	94.0	10.9	9.3	15.5

5

With Comparative Example 3, which used only C₄F₆O₃ and omitted the introduction of halogenated hydrocarbon, it was confirmed that the etching rate was slower than for the introduction of halogenated hydrocarbon and the selectivity was also lower. Upon the admixture of halogenated hydrocarbon (C₄F₆), a fluorocarbon polymer film is formed in a suitable thickness on the surface of the silicon oxide film and a high etching rate is assumed. Moreover, it is thought that the selectivity is improved by the protection against ion bombardment provided by the deposition of a thicker polymer on the silicon nitride film, amorphous carbon film, and polysilicon film.

2.12. Comparative Example 4

The low-k film was etched proceeding as in Example 3 using the apparatus illustrated in Fig. 1. The halogenated hydrocarbon C₄F₆ (flow rate = 10 SCCM), oxygen

(flow rate = 13 SCCM), and inert gas (Ar, flow rate = 77 SCCM) were used.

Experimental conditions in Comparative Example 4

• Plasma reaction chamber: A 4520XLE from LAM Research Corporation was used.

5 • Temperature: 25°C

• Etching workpiece: Low-k film (Black Diamond II (registered trademark) film acquired from SKW Associates, Inc.)

• Pressure in the processing chamber: 30 mTorr

• Inert gas: Argon (flow rate = 77 SCCM)

10 • Halogenated hydrocarbon: C₄F₆ (flow rate = 10 SCCM)

• Oxygen: Flow rate = 13 SCCM

• Etching time: 60 seconds

• High-frequency power: 27 MHz, 750 W

• High-frequency bias power: 2 MHz, 1,500 W

15 Using XPS as in Example 4, the depth of damage was measured on the low-k film etched under the conditions indicated above, and the result, at 57.3 nm, was a depth of damage having a larger value than in Example 4.

FTIR analysis as in Example 4 was carried out on the low-k film etched under the conditions indicated above. The result in Comparative Example 4 was a 24.9%
20 decline, post-etching versus pre-etching, in the intensity in the vicinity of the wavenumber 1,270 cm⁻¹ originating with the Si-CH₃ bond. It could thus be confirmed that the damage in this Comparative Example 4 was larger than the 12.9% in Example 4.

The result of measurement of the etching rate of the low-k film by the same method as in Example 4 was an etching rate of 11 nm/min, and the etching was thus
25 very slow.

It was confirmed in Comparative Example 4, which did not use C₄F₆O₃, that the damage to the low-k film was large and the etching rate was slow.

The invention is not limited to the embodiments described above, and various modifications are possible. For example, the invention includes various other configurations that are substantially the same as the configurations described in connection with the above embodiments (for example, configurations having the same function, method, and results, or a configuration having the same objective and effects). The invention also includes a configuration in which an unsubstantial section (element) described in connection with the above embodiments is replaced by another section (element). The invention also includes a configuration having the same effects as those of the constructions described in connection with the above embodiments, or a configuration capable of achieving the same objective as that of the configurations described in connection with the above embodiments. The invention further includes a configuration in which a known technique is added to the configurations described in connection with the above embodiments.

Reference Signs List

- 11: Etching workpiece, 12: Etching workpiece holder, 21: Plasma reaction chamber, 22: Pressure-regulating mechanism, 23: Temperature-regulating mechanism, 31: Halogenated hydrocarbon container, 32: Halogenated hydrocarbon flow rate-regulating mechanism, 33: $C_4F_6O_3$ container, 34: $C_4F_6O_3$ flow rate-regulating mechanism, 35: Inert gas container, 36: Inert gas flow rate-regulating mechanism, 37: Oxidizing gas container, 38: Oxidizing gas flow rate-regulating mechanism, 41: Matching box, 42: Electrode, 43: Matching box, 44: Bias power source, 45: Vacuum pump, 47: Plasma generation power source

CLAIMS

- 5 1. An etching method comprising etching a Si-containing material by introducing a gas containing a halogenated hydrocarbon and a gas containing $C_4F_6O_3$ into a plasma reaction chamber and by forming active species in the plasma reaction chamber by a plasma.
- 10 2. The etching method according to claim 1,
wherein the Si-containing material has a first film made of at least one material selected from the group consisting of silicon, silicon nitride, amorphous carbon, doped amorphous carbon, metal nitrides, metal oxides, organic photoresists, and metals, and has a second film made of at least one material selected from the group consisting of
15 SiO , $SiON$, $SiOC$, $SiOH$, and $SiOCH$; and
wherein the second film is selectively removed from the Si-containing material.
3. The etching method according to claim 1 or claim 2, wherein the halogenated hydrocarbon is a compound represented by the general formula (1):
20
$$C_aX_bH_c \quad (1)$$

(in general formula (1), a is a number from 1 to 5; b is a number from 1 to 9; c is a number from 0 to 4; and X is a halogen atom selected from the group consisting of a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom).
- 25 4. The etching method according to any one of claim 1 to claim 3, wherein the halogenated hydrocarbon contains at least one compound selected from the group consisting of CF_4 , CF_3I , C_2F_3I , C_3F_5I , C_3F_7I , C_2F_6 , C_3F_6 , C_3F_8 , C_4F_8 , C_4F_6 , C_5F_8 , C_6F_6 ,

CH₃F, CHF₃, CH₂F₂, C₂HF₅, C₃HF₅, C₃H₂F₄, C₃H₂F₆, C₄HF₇, and C₄H₂F₆.

5. The etching method according to any one of claim 1 to claim 4, wherein the halogenated hydrocarbon contains at least one compound selected from the group consisting of C₄F₆ and C₄F₈.

6. The etching method according to any one of claim 1 to claim 5, wherein an inert gas is further introduced into the plasma reaction chamber.

7. The etching method according to claim 6, wherein the inert gas contains at least one gas selected from the group consisting of N₂, He, Ar, Ne, Kr, and Xe.

8. The etching method according to any one of claim 1 to claim 7, wherein an oxidizing gas is further introduced into the plasma reaction chamber.

9. The etching method according to claim 8, wherein the oxidizing gas contains at least one gas selected from the group consisting of O₂, O₃, CO, CO₂, NO, N₂O, NOF, SO₂, and COS.

10. The etching method according to any one of claim 1 to claim 9, wherein the Si-containing material has a depression with a depth-to-width aspect ratio of from 0.5 : 1 to 20 : 1.

11. The etching method according to any one of claim 1 to claim 9, wherein the Si-containing material has a depression with a depth-to-width aspect ratio of from 21 : 1 to 300 : 1.

12. The etching method according to any one of claim 1 to claim 11, wherein the $C_4F_6O_3$ has a purity of at least 99.9 wt% and less than 100 wt%, and has a content of an oxygen-containing impurity of from 0 weight-ppm to 100 weight-ppm.

5 13. The etching method according to claim 12, wherein the oxygen-containing impurity contains H_2O , and the content of the H_2O ranges from 0.1 weight-ppb to 20 weight-ppm.

14. The etching method according to claim 12 or claim 13, wherein the oxygen-
10 containing impurity contains trifluoroacetic acid, and the content of the trifluoroacetic acid ranges from 0.1 weight-ppb to 20 weight-ppm.

15. The etching method according to any one of claim 1 to claim 14, wherein, prior to being introduced into the plasma reaction chamber, the $C_4F_6O_3$ is stored in a metal
15 container having an inner surface with a surface roughness of 0 to 6 μm .

16. A plasma etching material comprising $C_4F_6O_3$ and a halogenated hydrocarbon, the halogenated hydrocarbon containing at least one compound selected from the group consisting of CF_4 , CF_3I , C_2F_3I , C_3F_5I , C_3F_7I , C_2F_6 , C_3F_6 , C_3F_8 , C_4F_8 , C_4F_6 , C_5F_8 , C_6F_6 ,
20 CH_3F , CHF_3 , CH_2F_2 , C_2HF_5 , C_3HF_5 , $C_3H_2F_4$, $C_3H_2F_6$, C_4HF_7 , and $C_4H_2F_6$.