

SPECIFICATION

TITLE OF INVENTION: METHOD OF PROCESSING SUBSTRATE AND METHOD OF
MANUFACTURING SUBSTRATE

5

TECHNICAL FIELD

[0001]

The present invention relates to a method of processing a
substrate and a method of manufacturing a substrate.

10

BACKGROUND ART

[0002]

In the related art, fine patterning has been carried out by
a plurality of lithography treatments or etching treatments in
15 order to obtain a semiconductor device. However, in recent
years, there has been a tendency for semiconductor devices to be
more highly integrated and miniaturized, and there has been such
a problem that, in a case where an attempt is made to satisfy
these requirements, the lithography treatment tends to be
20 complicated and costly. Therefore, there is a demand for an
alternative technique for the lithography technique.

[0003]

As an alternative technique for the lithography technique,
a technique using a self-assembled monolayer (SAM) has been
25 studied. Specifically, it is a technique of selectively
depositing a self-assembled monolayer (hereinafter, simply
referred to as a "monolayer") as a mask material or a protective

material in a substrate region that is not subjected to treatment, and subjecting a desired film material to a film formation or deposition in a remaining region (that is, a region that is subjected to treatment) of the substrate or carrying out an etching treatment.

[0004]

A method of selectively performing an etching treatment or the like on only an oxide silicon surface in a wafer having a silicon nitride surface and an oxide silicon surface using the monolayer has been studied. As this type of technique, the technique described in Patent Document 1 is known.

[0005]

Patent Document 1 describes a dry treatment of exposing a substrate containing a silicon oxide film and a silicon nitride film to a plasma-excited passivation gas containing carbon, sulfur, or both of carbon and sulfur to form a passivation layer thicker on the silicon nitride film than on the silicon oxide film.

20 RELATED DOCUMENT

PATENT DOCUMENT

[0006]

Patent Document 1: PCT Japanese Translation Patent
Publication No. 2022-527552

25

SUMMARY OF THE INVENTION

TECHNICAL PROBLEM

[0007]

However, as a result of the investigation by the present inventor, it has been found that a dry treatment technology of forming a protective film on a surface having silicon nitride
5 using a gas containing a surface modifier has not yet been sufficiently studied.

SOLUTION TO PROBLEM

[0008]

As a result of intensive studies, the present inventor has
10 found that, in a case of performing a dry treatment in order to form a protective film, the protective property of a surface having silicon nitride can be improved by heating the surface to a heated state and further using a silyl ester of a carboxylic acid, which is a specific silicon compound, as a surface
15 modifier, and has completed the present invention.

Although the detailed mechanism is not clear, it is presumed that the reactivity on the surface is improved by heating the surface to a heated state, the basic site derived from the N element of the silicon nitride contained in the
20 surface acts as a reaction catalyst, the reactivity with the silyl ester of the carboxylic acid is improved, and the protective property is improved.

[0009]

According to one aspect of the present invention, there are
25 provided a method of processing a substrate and a method of manufacturing a substrate.

[0010]

Hereinafter, examples of the reference forms will be added.

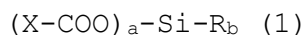
1. A method of processing a substrate, the method including:

a preparation step of preparing a substrate having a first surface including silicon nitride; and

a surface modification step of forming a protective film that protects the first surface,

in which the surface modification step includes a gas exposure treatment in which the first surface in a heated state is brought into contact with a modification gas containing gas of a surface modifier in a substrate holding space, and

the surface modifier includes at least one silicon compound represented by the following general formula (1):



in the general formula (1),

X each independently represents a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms, in which part or all of hydrogen atoms may be substituted by halogen atoms;

R each independently represents a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms, in which part or all of hydrogen atoms may be substituted by halogen atoms; and

a and b each independently represent an integer of 1 to 3, provided that $a + b = 4$.

2. The method of processing a substrate according to 1,

in which in the preparation step, the substrate having the first surface and a second surface having silicon oxide is prepared, and

in the surface modification step, the protective film for selectively protecting the first surface with respect to the second surface is formed at least over the first surface by the gas exposure treatment of bringing the modification gas into contact with the first surface and the second surface in the heated state in the substrate holding space.

3. The method of processing a substrate according to 1 or 2,

in which in the surface modification step, a water contact angle of the first surface at 25°C after the gas exposure treatment is equal to or more than 55°.

4. The method of processing a substrate according to 2,

in which in the surface modification step, in a case where a water contact angle of the first surface at 25°C after the gas exposure treatment is denoted by CA_1 , and a water contact angle of the second surface at 25°C is denoted by CA_2 , the CA_1 and the CA_2 satisfy $1 < CA_1/CA_2 \leq 5$.

5. The method of processing a substrate according to any one of 1 to 4,

in which a surface temperature of the substrate during the gas exposure treatment is equal to or higher than 50°C and equal to or lower than 400°C.

6. The method of processing a substrate according to any one of 1 to 5,

in which a temperature of the modification gas to be introduced into the substrate holding space is equal to or higher than 0°C and equal to or lower than 400°C.

7. The method of processing a substrate according to any one of 1 to 6,

in which a concentration of the silicon compound in the modification gas is equal to or more than 1% by volume and equal
5 to or less than 100% by volume.

8. The method of processing a substrate according to any one of 1 to 7,

in which a boiling point of the silicon compound in the modification gas is equal to or higher than 40°C and equal to or
10 lower than 400°C.

9. The method of processing a substrate according to any one of 1 to 8,

in which the modification gas contains equal to or more than 0% by volume and equal to or less than 99% by volume of an
15 inert gas.

10. The method of processing a substrate according to any one of 1 to 9,

in which a pressure of the substrate holding space during the gas exposure treatment is equal to or higher than 1 Pa and
20 equal to or lower than 10^6 Pa.

11. The method of processing a substrate according to any one of 1 to 10,

in which the surface modification step includes a gas substitution treatment of introducing an inert gas into the
25 substrate holding space in at least one of before and after the gas exposure treatment.

12. The method of processing a substrate according to any

one of 1 to 11,

in which the surface modification step includes a pretreatment of removing a natural oxide film of the first surface before the gas exposure treatment.

5 13. The method of processing a substrate according to any one of 1 to 12, further including a processing step including one or two or more selected from the group consisting of an etching treatment and a film forming treatment after the surface modification step.

10 14. The method of processing a substrate according to any one of 1 to 13,

in which the silicon compound is trimethylsilyl trifluoroacetate and/or trimethylsilyl acetate.

15 15. A method of manufacturing a substrate, the method comprising:

a step of obtaining a substrate on which each step in the method of processing a substrate according to any one of 1. to 14. is performed.

20 ADVANTAGEOUS EFFECTS OF INVENTION

[0011]

According to the present invention, a method of processing a substrate and a method of manufacturing a substrate, in which a good protective film can be formed on a surface having silicon
25 nitride using a dry treatment technology, are provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

FIG. 1(A) to Fig. 1(C) are schematic process sectional views showing each process of a method of processing a substrate according to the present embodiment.

5

DESCRIPTION OF EMBODIMENTS

[0013]

Hereinafter, a description will be made for an embodiment of the present invention using the drawings. It is noted that in all the drawings, the same constitutional elements are denoted as the same reference numerals and explanations thereof will not be repeated, as appropriate. In addition, the figures are schematic views and do not correspond to the actual dimensional ratios.

15 [0014]

An outline of the method of processing a substrate according to the present embodiment will be described.

[0015]

A method of processing a substrate according to a first embodiment includes a preparation step of preparing a substrate having a first surface having silicon nitride, and

a surface modification step of forming a protective film for protecting the first surface, in which the surface modification step includes a gas exposure treatment of bringing a modification gas containing gas of a surface modifier into contact with the first surface in a heated state in a substrate holding space.

[0016]

A method of processing a substrate according to a second embodiment includes a preparation step of preparing a substrate having a first surface having silicon nitride and a second surface having silicon oxide, and a surface modification step of forming a protective film for selectively protecting the first surface with respect to the second surface at least on the first surface by a gas exposure treatment of bringing a modification gas containing gas of a surface modifier into contact with the first surface and the second surface in a heated state in a substrate holding space.

[0017]

In both the first embodiment and the second embodiment, the surface modifier has at least one kind of silicon compound represented by General Formula (1) (hereinafter, also referred to as a silyl ester of a carboxylic acid).

[0018]

According to the findings of the present inventors, in the first embodiment, it has been found that the protective property with respect to the first surface having silicon nitride is improved because the frequency of contact with the surface modifier is increased by the dry treatment, the diffusibility of the surface modifier is increased by heating the first surface to a heated state, and the reactivity is increased because the basic site derived from the N element is likely to act as a reaction catalyst by using the silyl ester of the carboxylic acid as the surface modifier.

[0019]

In addition, since the frequency of contact between the first surface and the second surface and the surface modifier is increased by the dry treatment, the selective protection property of selectively protecting the first surface acts in a direction of being decreased. However, in the second embodiment, in a case where the second surface having silicon oxide is in a heated state, even in a case where the silyl ester of the carboxylic acid used as the surface modifier is brought into contact with or adsorbed on the second surface, it is difficult to maintain the adsorbed state, and since the basic site derived from the N element, which can act as a reaction catalyst of the silyl ester of the carboxylic acid, is hardly present unlike the first surface, the protective property on the second surface is suppressed as compared with the first surface. That is, it has been found that the selective protection property of the first surface with respect to the second surface can be improved.

[0020]

In a wet treatment using a chemical liquid containing a surface modifier and a solvent, the detailed mechanism is not clear, but it is presumed that the surface modifier and the solvent compete with each other when brought into contact with the surface, and the adsorption of the surface modifier is likely to be hindered by the solvent. In addition, in the wet treatment, the reaction catalytic action of the silyl ester of the carboxylic acid is not observed. According to the results

of the preliminary experiment of the present inventors, it has been found that in the wet treatment using a chemical liquid containing a silyl ester of a carboxylic acid and a solvent, the oxide silicon surface is preferentially protected with respect to the silicon nitride surface. It is considered that the reaction catalytic action in the dry treatment is a relatively weak action exhibited to the extent that it is not hindered by the solvation and the like.

[0021]

Hereinafter, each configuration of the method of processing a substrate according to the embodiment of the present disclosure will be described in detail.

An example of the method of processing a substrate will be described with reference to FIG. 1(A) to Fig. 1(C). FIGS. 1(A) to 1(C) are schematic process sectional views showing each process of the method of processing a substrate. FIG. 1(A) shows a preparation step, and FIGS. 1(B) and 1(C) show a surface treatment step. In addition, the present embodiment is not limited to the following.

[0022]

(Preparation Step)

In the preparation step, a substrate 1 having at least a first surface 11 containing silicon nitride is prepared. The substrate 1 of FIG. 1(A) has a first surface 11 and a second surface 12 containing silicon oxide.

[0023]

A material of the substrate 1 is not particularly limited

as long as it is a substrate that is used in a semiconductor manufacturing process. The material of the substrate 1 may be composed of, for example, silicon, silicon carbide, a plurality of components containing a silicon element, sapphire, various compound semiconductors, or the like. In addition, the substrate 1 may be, for example, a wafer.

[0024]

The substrate 1 may include an uneven structure (not shown in the drawing) formed on the substrate surface.

The uneven structure may be composed of a three-dimensional structure having, for example, one or two or more structural bodies disposed along a vertical direction of a substrate surface 1a and/or one or two or more structural bodies disposed along a horizontal direction orthogonal to the vertical direction. As an example, such a three-dimensional structure may constitute at least a part of a logic device, a memory device, a gate electrode, or the like, and examples thereof include a FinFET, a nanowire FET, a nanosheet FET, or another multi-gate type FET, and a three-dimensional memory cell.

[0025]

Each of the first surface 11 and the second surface 12 may be disposed along the plane direction of the substrate surface, or may alternatively be disposed along a vertical direction with respect to the substrate surface. According to the present embodiment, it is possible to carry out not only a two-dimensional selective processing treatment on a plane but also a three-dimensional selective processing treatment on a three-

dimensional structure (three-dimensional film formation, three-dimensional etching, or the like).

[0026]

The first surface 11 and the second surface 12 may be
5 formed to be adjacent to each other; however, they may be formed
to be spaced from each other. Each of the first surface 11 and
the second surface 12 may be composed of one region or a
plurality of two or more regions. In each surface, the
plurality of regions may be formed to be spaced apart from each
10 other, and the materials of the surfaces constituting the
plurality of regions may be the same as or different from each
other.

[0027]

The first surface 11 is a surface containing silicon
15 nitride. The surface containing silicon nitride is not
particularly limited as long as it is a surface containing a Si
element and an N element. A stoichiometric ratio of the Si
element and the N element in the silicon nitride is not limited
to 1:1, and may not be an integer ratio. For example, the
20 stoichiometric ratio is 1:1.33 as in Si_3N_4 . In addition, in the
present specification, in a case where a compound is described
as "SiN" or the like, the stoichiometric ratio is not limited to
1:1, and may not be an integer ratio. Specific examples of the
surface containing silicon nitride include SiN, SiON, SiCN, and
25 SiOCN, and among these, SiN is preferable.

The total amount of Si atoms and N atoms in the first
surface 11 may be equal to or more than 80% by mole. In

addition, the first surface 11 may contain other elements (H, P, B, and the like) in addition to Si and N as long as the water repellency is not significantly impaired.

In addition, the Si element of the first surface 11 may be naturally oxidized and form a natural oxide film by being left in the air, but such a natural oxide film can be removed by a pretreatment of removing a natural oxide film described later, and thus even in a case of having a natural oxide film in a preparation stage, the first surface 11 may be a surface containing silicon nitride. However, in a case of being oxidized for a reason other than natural oxidation, the first surface 11 does not include a surface that is prepared as the above-described SiON, SiOCN, or the like, unless the surface is originally prepared as the above-described SiON, SiOCN, or the like.

[0028]

The second surface 12 is a surface containing silicon oxide. The surface containing silicon oxide is not particularly limited as long as it is a surface containing a Si element and an O element. In addition, in the second surface, a content of N atoms is preferably equal to or less than 1 mol%. A stoichiometric ratio of the Si element and the O element in the silicon oxide is not limited to 1:1 as in the above-described silicon nitride, and may not be an integer ratio. For example, the stoichiometric ratio is 1:2 as in SiO₂. Specific examples of the surface containing silicon oxide include SiO, SiCO, and SiCOH, and among these, SiO is preferable.

The total amount of Si atoms and O atoms in the second surface 12 may be equal to or more than 80% by mole. In addition, the second surface 12 may contain other elements (O, C, H, P, B, and the like) as long as the other elements do not adversely affect each step after the surface treatment step.

[0029]

The first surface 11 and the second surface 12 may be surfaces of members formed of the above-described materials, or may be configured as the surfaces of films formed of the above-described materials. In addition, both a surface of a member formed of the above-described material and a surface of a film formed of the above-described material may be present.

[0030]

(Surface Modification Step)

As shown in FIG. 1(B), the surface modification step includes a gas exposure treatment of bringing a modification gas into contact with the first surface 11 in a heated state or the first surface 11 and the second surface 12 in a heated state in a substrate holding space 30.

[0031]

As an example of the surface modification step, the following procedure may be performed.

First, the substrate 1 is installed in the substrate holding space 30 such as a chamber. In the substrate holding space 30, the substrate 1 may be held by a substrate holding unit (not shown).

[0032]

As an example of the configuration of the chamber, a sealed space constituting the substrate holding space 30, a substrate holding unit that holds the substrate in the substrate holding space 30, a gas supply pipe that connects the gas supply device
5 and the chamber for each gas type to be supplied, a gas discharge pipe that discharges a gas in the substrate holding space 30, and the like may be provided. In addition, a heater that can heat each gas to be supplied to the substrate 1 or the substrate holding space 30 may be set inside and/or outside the
10 chamber. A valve or a mechanism for adjusting a temperature inside each pipe may be provided.

In addition, the chamber may have various instruments such as a thermometer that measures an internal temperature and/or a surface temperature of the substrate 1 and a pressure measuring
15 device that measures a pressure of the substrate holding space 30, and may have a control device (computer) that controls these temperatures and pressures.

[0033]

Subsequently, the inside of the substrate holding space 30
20 is filled with an inert gas such as nitrogen gas (gas purging) to be replaced with a gas. The inert gas may be introduced into the substrate holding space 30 from the gas supply device of the inert gas through the supply pipe (gas substitution treatment).

[0034]

25 Subsequently, the first surface 11 and the second surface 12 are brought into a heated state. A heating method for bringing the first surface 11 and the second surface 12 into the

heated state can adopt a known means, but for example, the entire chamber or a part thereof may be heated by a heater to indirectly heat the substrate 1, or the substrate 1 may be directly heated by a heater installed in the substrate holding unit. In addition, the first surface 11 may be heated by using the modification gas or by blowing any inert gas or the like as long as the first surface 11 can be modified.

During the gas exposure treatment, the first surface 11 and the second surface 12 may be in the heated state, and a timing of heating and a timing of stopping the heating are not particularly limited. For example, the heating may be started before the gas exposure treatment or may be started at the same time as the gas exposure treatment. In addition, the heating may be stopped before the gas exposure treatment is completed as long as the heated state can be maintained. It is suitable to start heating the substrate 1 before the gas exposure treatment because the surface can be efficiently modified.

In the present specification, the "heated state" refers to a state in which the above-described surface is at a temperature higher than room temperature (5°C to 35°C).

[0035]

The lower limit of the surface temperature of the substrate 1 is preferably equal to or higher than 50°C, more preferably equal to or higher than 75°C, and still more preferably equal to or higher than 100°C.

The upper limit of the surface temperature of the substrate 1 is, for example, equal to or lower than 400°C and preferably

equal to or lower than 250°C.

In a case of directly heating the substrate 1, a value measured by a non-contact method for the surface of the substrate 1 may be adopted as the surface temperature of the substrate 1, but in a case of indirectly heating the substrate 1, a value measured by a contact method for the inside space of the substrate holding space 30 may be adopted.

[0036]

Subsequently, the surface modifier that has been gasified by the gas supply device of the modification gas is introduced into the substrate holding space 30 through the supply pipe. As a result, the modification gas is brought into contact with the first surface 11 and the second surface 12 in the heated state. Then, the substrate 1 is subjected to a surface treatment with the modification gas at a predetermined temperature, time, and pressure (gas exposure treatment).

Thereafter, the modification gas is discharged to the outside of the substrate holding space 30, and the surface treatment step is ended.

[0037]

As a result of the above-described gas exposure treatment, as shown in FIG. 1(C), a protective film 21 can be formed on the first surface 11. In addition, depending on the conditions of the gas exposure treatment and the type of the surface modifier to be used, a protective film (not shown) having low protective property may be formed on the second surface 12.

[0038]

In the present specification, the "protective film" refers to both a compound having a protective group derived from a surface modifier chemically bonded to the first surface and a group of the compound, and whether or not there is an

5 interaction between the compounds or whether or not there is a bond is not limited. It is noted that the above-described binding is not required to be a direct bonding and includes a case of bonding through another element, a substituent, or the like.

10 In addition, even in a case where the protective film is formed, there is a case where the protective property is high to the extent that desired performance can be exhibited depending on the amount or density of the compound having the protective group, and there is a case where the protective property is low
15 to the extent that desired performance is not exhibited, but in the present specification, even a protective film having low protective property is described as a "protective film".

[0039]

(Protective Property)

20 The protective property in the present specification can be shown by water repellency described later. Specifically, in a case where the water repellency of the surface after the gas exposure treatment is higher than the water repellency of the surface before the gas exposure treatment and the water
25 repellency of the surface after the gas exposure treatment is higher than a predetermined value, the surface is regarded as having high protective property, and in a case where the water

repellency of the surface after the gas exposure treatment is lower than the predetermined value, the surface is regarded as having low protective property. In addition, in a case where the improvement amount of the water repellency after the gas exposure treatment is small or there is no change, it is considered that the protective property is not exhibited or the protective film is not formed.

In addition, the selective protection property in the second embodiment refers to a case where the protective film is provided on the first surface and the water repellency of the first surface is higher than the water repellency of the second surface.

[0040]

(Water Repellency)

The water repellency in the present specification will be described using a water contact angle obtained by the following measurement. It is noted that details of the cleaning, drying, or the like before each measurement will be described later.

First, the substrate is placed horizontally such that each smooth surface of the substrate faces upward, and a water droplet of 2 μ l of pure water is placed on the surface. Next, in accordance with JIS R 3257:1999 "Testing method of wettability of surface of substrate glass", an angle formed by a water droplet and the substrate is measured with a contact angle meter (manufactured by Kyowa Interface Science Co., Ltd.: CA-X type), and the obtained value is defined as a water contact angle.

[0041]

The water contact angle of the first surface 11 at 25°C after the gas exposure treatment is, for example, equal to or more than 50°, preferably equal to or more than 55°, and more
 5 preferably equal to or more than 60°. In a case where the water contact angle of the first surface is equal to or higher than the lower limit value, and preferably equal to or more than 55°, for example, in a case where an etching treatment is performed after forming the protective film, it is suitable because the
 10 first surface can be protected.

[0042]

A water contact angle of the first surface 11 at 25°C after the gas exposure treatment is denoted by CA_1 , and a water contact angle of the second surface 12 at 25°C is denoted by
 15 CA_2 .

CA_1 and CA_2 may satisfy, for example, $1 < CA_1/CA_2 \leq 5$.

The lower limit of CA_1/CA_2 is, for example, more than 1, preferably equal to or more than 1.2, more preferably equal to or more than 1.5, and still more preferably equal to or more
 20 than 1.9. On the other hand, the upper limit of CA_1/CA_2 is not particularly limited, but may be equal to or less than 5. In a case where $1 < CA_1/CA_2$, the first surface 11 is selectively protected with the protective film with respect to the second surface 12, and for example, in a case where an etching
 25 treatment is performed after forming the protective film, it is suitable because the second surface 12 can be selectively etched.

[0043]

The lower limit of the surface treatment time with the modification gas is, for example, equal to or more than 0.1 minutes, preferably equal to or more than 0.2 minutes, and more
5 preferably equal to or more than 0.5 minutes.

The upper limit of the surface treatment time with the modification gas is, for example, equal to or less than 100 minutes, preferably equal to or less than 10 minutes, and more preferably equal to or less than 5 minutes.

10 [0044]

In a case where the modification gas is introduced into the substrate holding space 30, the inert gas filled in the substrate holding space 30 may be discharged to the outside through the gas discharge pipe as necessary.

15 [0045]

The lower limit of the pressure of the substrate holding space 30 during the surface treatment is, for example, equal to or more than 1 Pa, preferably equal to or more than 10^2 Pa, and more preferably equal to or more than 10^3 Pa.

20 The upper limit of the pressure is, for example, equal to or less than 10^6 Pa, preferably equal to or less than 5.0×10^4 Pa, and more preferably equal to or less than 2.0×10^4 Pa.

[0046]

The lower limit of the temperature of the modification gas
25 to be introduced into the substrate holding space 30 is, for example, equal to or higher than 0°C , preferably equal to or higher than 10°C , and more preferably equal to or higher than

15°C.

The upper limit of the temperature of the modification gas is, for example, equal to or lower than 400°C, preferably equal to or lower than 300°C, and more preferably equal to or lower
5 than 250°C.

[0047]

After the gas exposure treatment, the substrate holding space 30 may be purged with an inert gas, and the subsequent treatment of the substrate 1 may be performed in the substrate
10 holding space 30, but the subsequent treatment may be performed on the substrate 1 taken out from the substrate holding space 30.

[0048]

(Modification Gas)

15 Here, the modification gas used for the gas exposure treatment will be described.

The modification gas contains at least gas of a surface modifier.

[0049]

20 The surface modifier is at least a modifier that modifies the surface of the first surface, and has at least one kind of silicon compound represented by General Formula (1). In a suitable embodiment of the present disclosure, by using the following silicon compound, the surface modifier can improve at
25 least the water repellency of the first surface. In addition, the surface modifier may consist of only one or more kinds of the following silicon compounds, or may further include another

compound that imparts a performance other than water repellency to the first surface.

[0050]

The lower limit of the concentration of the silicon
5 compound in the modification gas is, for example, equal to or more than 1% by volume, preferably equal to or more than 5% by volume, and more preferably equal to or more than 10% by volume.

The upper limit of the concentration of the silicon
compound is not particularly limited, but may be, for example,
10 equal to or less than 100% by volume.

In a case where two or more kinds of silicon compounds are contained, the total value thereof is defined as the concentration of the silicon compound.

[0051]

15 The lower limit of the boiling point of the silicon compound used as the surface modifier is, for example, equal to or higher than 40°C, preferably equal to or higher than 50°C, and more preferably equal to or higher than 60°C.

The upper limit of the boiling point of the silicon
20 compound is, for example, equal to or lower than 400°C, preferably equal to or lower than 300°C, and more preferably equal to or lower than 250°C.

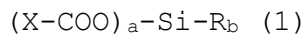
By setting the boiling point to be equal to or less than the upper limit value, the thermal stability of the silicon
25 compound in the modification gas can be improved. In addition, by setting the boiling point to be equal to or more than the lower limit value, the silicon compound is liquid at room

temperature (25°C), so that the handleability is good in storage, transport, and the like, which is preferable.

[0052]

(Silicon Compound)

5 As the silicon compound, a silyl ester of a carboxylic acid represented by Formula (1) is used.



In General Formula (1),

X each independently represent a hydrogen atom or a
10 hydrocarbon group having 1 to 8 carbon atoms, in which some or all of hydrogen atoms may be substituted with a halogen atom,

R each independently represent a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms, in which some or all of hydrogen atoms may be substituted with a halogen atom,
15 and

a and b each represent an integer of 1 to 3. In the formula (1), $a + b = 4$.

[0053]

The group represented by (X-COO) in General Formula (1) is
20 a leaving group that is dissociated in a case where the protective film is formed, and is not particularly limited as long as it can be removed from the substrate. In addition, it is more preferable that the leaving group is volatilizable in the gas exposure treatment.

25 X may be a hydrogen atom, but from the viewpoint of chemical stability and high volatility, it is preferable that X is a hydrocarbon group having 1 to 8 carbon atoms, in which some

or all of hydrogen atoms may be substituted with a halogen atom. In addition, in a case where the above-described group is a hydrocarbon group, it is more preferable that the number of carbon atoms is small.

5 In addition, the halogen atom that substitutes the hydrogen atom may be the same atom or two or more kinds of atoms. The number of hydrogen atoms substituted with a halogen atom is not particularly limited as long as it is possible to exhibit desired protective properties. In addition, the kind of the
10 halogen atom is not particularly limited as long as it does not hinder the protective property, and examples thereof include chlorine and fluorine.

[0054]

 The group represented by (Si-R_b) in General Formula (1) is a
15 group that remains on the substrate as a protective group.

 R may be a hydrogen atom. In addition, in a case where R is a hydrocarbon group having 1 to 8 carbon atoms, in which some or all of hydrogen atoms may be substituted with a halogen atom, the smaller the number of carbon atoms, the higher the tendency
20 for the reactivity with the substrate surface to increase. In addition, as the number of carbon atoms increases, the value of the water contact angle tends to increase. Therefore, the number of carbon atoms may be appropriately selected in order to obtain desired protective properties. In addition, in a case
25 where R is a hydrocarbon group, a branched structure or a ring structure may be included.

 In addition, the halogen atom that substitutes the hydrogen

atom may be the same atom or two or more kinds of atoms. The number of hydrogen atoms substituted with a halogen atom is not particularly limited as long as it is possible to exhibit desired protective properties. In addition, as the kind of the
5 halogen atom, fluorine or chlorine is preferably used in order to improve the water repellency.

[0055]

Examples of the above-described silicon compound include trimethylsilyl trifluoroacetate, trimethylsilyl acetate,
10 hydroxydimethylsilyl trifluoroacetate, hydroxydimethylsilyl acetate, butyldimethylsilyl trifluoroacetate, butyldimethylsilyl acetate, octyldimethylsilyl trifluoroacetate, octyldimethylsilyl acetate, tert-butyldimethylsilyl trifluoroacetate, and tert-butyldimethylsilyl acetate.

15 Among the above, as the silicon compound, trimethylsilyl trifluoroacetate and/or trimethylsilyl acetate is preferably used.

[0056]

The modification gas may or may not contain an inert gas.
20 The content of the inert gas in the modification gas is, for example, equal to or more than 0% by volume and equal to or less than 99% by volume, preferably equal to or more than 0% by volume and equal to or less than 80% by volume, and more preferably equal to or more than 0% by volume and equal to or
25 less than 50% by volume.

By containing the inert gas, it is easy to suppress a temperature change in a supply path of the gasified silicon

compound. In a case where two or more kinds of inert gases are contained, the total amount thereof is defined as the content of the inert gas.

[0057]

5 As the inert gas, for example, one or two or more selected from the group consisting of nitrogen gas, and rare gases such as helium gas, argon gas, and xenon gas may be contained.

[0058]

Here, a modification example of the surface modification
10 step of the present embodiment will be described.

[0059]

The surface modification step may include a gas substitution treatment of introducing an inert gas into the substrate holding space 30 in at least one of before or after
15 the gas exposure treatment.

[0060]

The surface modification step may include a pretreatment of removing a natural oxide film of the first surface 11 before the gas exposure treatment. The pretreatment may be performed in a
20 chamber or may be performed outside the chamber.

[0061]

Specific examples of the pretreatment include a method in which hydrogen fluoride (HF) is brought into contact with the first surface 11 and the second surface 12, and a method in
25 which a diluted aqueous solution of hydrogen fluoride, that is, hydrofluoric acid (DHF), is brought into contact with the first surface 11 and the second surface 12. A specific method of

bringing into contact can adopt a known method, but in a case of being supplied with a gas or vapor and brought into contact with the first surface 11 and the second surface 12 and then being liquid, a known vapor jet method can be used. In addition, a
5 mixed gas of hydrogen fluoride and ammonia may be brought into contact with the first surface 11 and the second surface 12.

After the pretreatment, a washing treatment with a washing agent described later may be performed before the gas exposure treatment.

10 [0062]

A washing treatment of cleaning at least a part of the substrate surface using a washing agent may be performed once or twice or more between the surface modification step and the processing step described later.

15 [0063]

The washing agent may be any washing agent as long as it does not oxidize at least the first surface 11, and is not particularly limited. Examples thereof include an aqueous washing solution such as water and alcohol. These may be used
20 alone, or two or more thereof may be used in combination.

[0064]

In addition, a rinsing solution may be used as the washing agent. The rinsing solution may be any rinsing solution as long as it does not oxidize at least the first surface 11, and is not particularly limited as in the above-described aqueous washing
25 solution. As the rinsing solution, it is possible to use a washing agent different from the aqueous washing solution and

examples thereof include water, an organic solvent, a mixture thereof, or a mixture containing at least one of an acid, an alkali, and a surfactant.

Examples of the organic solvent used in the rinsing solution include hydrocarbons, esters, ethers, ketones, halogen element-containing solvents, sulfoxide-based solvents, alcohols, polyhydric alcohol derivatives, and nitrogen element-containing solvents. Among the above, it is preferable to use, as an organic solvent, at least one selected from alcohols having the number of equal to or less than 3 carbon atoms, such as methanol, 1-propanol, and 2-propanol (isopropanol).

[0065]

In the present embodiment, the method of bringing the washing agent into contact is not particularly limited, and examples thereof include an immersion method, a coating method such as spin coating or spray coating, and vapor contacting.

[0066]

A drying treatment of drying at least a part of the substrate surface may be performed once or twice or more between the surface modification step and the processing step described later. The drying treatment and the washing treatment may be alternately repeated.

[0067]

As a drying treatment, for example, a known unit may be used, such as a spin drying method, IPA (2-propanol) vapor drying, Marangoni drying, heat drying, air blowing drying, hot air drying, and vacuum drying.

[0068]

(Processing Step)

The method of processing a substrate according to the present embodiment may include, after the surface modification

5 step, a processing step of including one or two or more selected from the group consisting of an etching treatment and a film forming treatment, as necessary.

[0069]

In a case where the processing step is an etching
10 treatment, the etching treatment is not particularly limited as long as the second surface 12 can be etched, and a known dry etching method or wet etching method can be selected.

In addition, it is preferable that various etching treatments are carried out using an etching agent. In a case of
15 a gas, examples thereof include HF gas, HCl gas, Cl₂ gas, F₂ gas, interhalogen gas (for example, ClF₃ gas, IF₇ gas, and the like), and a mixed gas of these various gases. In a case of a liquid, examples thereof include at least one of HF, NH₄F, NH₄HF₂, H₃PO₄, or H₂SO₄ diluted with a solvent. In addition, as the etching
20 agent, such as one that is heated or is made into a plasma state or a radical state may be used.

[0070]

After the etching step, in a case where the protective film
21 remaining on the first surface 11 is not necessary, a removal
25 treatment of removing at least a part of the protective film 21 may be performed. The removal method is not particularly limited as long as it is a method of removing a known protective

film.

Examples thereof include light (ultraviolet rays) irradiation, heat treatment, ozone exposure, plasma irradiation, and corona discharge. In addition, the removal by a wet process is also possible, and examples thereof include contacting with an aqueous ammonium hydroxide solution, an aqueous tetramethylammonium solution, an aqueous hydrochloric acid solution, an aqueous sulfuric acid solution, or the like. In addition, by appropriately controlling the etching conditions, the etching agent used in the etching step may be used in the above-described removal treatment. As a result, the process can be simplified.

In addition, by selecting a non-plasma method as the above-described removal method, defects on the substrate surface can be suppressed.

[0071]

In a case where the processing step is a film forming treatment, as the film forming method, a known CVD method, an atomic layer deposition method, or the like can be used, and particularly, the atomic layer deposition method is preferable because the film thickness control, the uniformity, the conformality to surface shape of the film forming target, and the like are favorable.

As the film forming method according to the atomic layer deposition method, a publicly known ALD device can be used. For example, it is preferable to use a thin film forming method (thermal ALD method) by adsorption using a first gas phase

reactant as a film material and a desired second gas phase reactant, a thin film forming method (plasma ALD method) in which the first gas phase reactant as a film material is adsorbed on the surface and then reacted with a plasma of oxygen or the like, as described above, or the like. The film forming temperature and the film forming time can be appropriately selected depending on the film thickness and the film material.

[0072]

The method of manufacturing a substrate according to the present embodiment includes a step of obtaining a substrate that has been subjected to each step in the above-described method of processing a substrate. A desired semiconductor wafer or a desired semiconductor device can be obtained by the method of manufacturing a substrate.

[0073]

Although the embodiments of the present invention have been described above, these are examples of the present invention, and various configurations other than the above can be adopted. In addition, the present invention is not limited to the embodiments described above and modifications, improvements, and the like are included in the present invention in a range in which it is possible to achieve the object of the present invention.

Examples

[0074]

A detailed description will be given below of the present invention with reference to Examples, but the present invention

is not limited to the descriptions of these Examples.

[0075]

(1). Preparation Step for Substrate

As the substrate, a silicon substrate having a size of 30
5 mm × 40 mm × 1 mm and a smooth surface was used. A silicon
oxide film or a silicon nitride film was formed on a surface of
the substrate, the substrate on which the silicon nitride film
was formed was regarded as the first surface, and the substrate
on which the silicon oxide film was formed was regarded as the
10 second surface. The following test is a simulation test using
the substrate described above.

[0076]

(2) Step of Removing Natural Oxide Film of Substrate
(Pretreatment)

15 Each prepared substrate was immersed in 1% by weight
hydrofluoric acid at room temperature for 1 minute, and then
immersed in a rinsing solution (ultrapure water) for 1 minute.

In addition, in the etching treatment described later, the
thickness of the silicon oxide or silicon nitride film was
20 measured with an ellipsometer after the immersion in order to
calculate the etching amount after the treatment.

[0077]

3 Surface Modification Step

A tubular furnace was used as a chamber, the substrate
25 after the pretreatment described above was set in the chamber,
and the gas inside was replaced with nitrogen gas. Next, the
temperature of the tubular furnace was raised to heat the

substrate, and the substrate was raised to a predetermined temperature to be in a heated state. At this time, the substrate temperature was measured with a thermometer (thermocouple) disposed in contact with the substrate in advance. The substrate temperature was set to each temperature shown in Table 1.

[0078]

Next, the surface modifier was supplied to a vaporization chamber connected to the chamber through a pipe, and was gasified to form a modification gas. The composition of the surface modifier used was 100% by mass of the silicon compound shown in Table 1, and the modification gas supplied to the inside of the chamber also contained substantially the same silicon compound at 100% by volume. Each reference example is an example (blank) in which the surface modifier was not used, and the modification gas was not prepared in each reference example.

[0079]

Next, the inside of the chamber was evacuated, and the pressure in the was lowered to be lower than the pressure in the vaporization chamber, so that the modification gas was introduced into the chamber, and the modification gas was brought into contact with the substrate surface (gas exposure treatment). At this time, the pressure in the chamber was 6.7 kPa, and the treatment time was 10 minutes. In each reference example, the modification gas was not supplied, the inside of the chamber was filled with nitrogen gas, the pressure was set

to 6.7 kPa, and the state was maintained for 10 minutes.

Next, the heating was stopped, the gas in the chamber was discharged, the inside of the chamber was replaced with air, and the substrate was taken out after the temperature of the substrate was lowered to room temperature or lower, thereby obtaining a measurement sample.

[0080]

(4) Various Evaluations

(Evaluation of Water Repellency of Substrate)

The water contact angle of the substrate surface in the obtained measurement sample was measured by the following method, and the results are shown in Table 1. A water contact angle of the first surface was denoted by CA_1 , and a water contact angle of the second surface was denoted by CA_2 .

First, the substrate was placed horizontally such that the surface to be treated of the measurement sample was on the upper side, and a water droplet of 2 μ l of pure water was placed on the surface. Next, in accordance with JIS R 3257:1999 "Testing method of wettability of surface of substrate glass", an angle formed by a water droplet and the substrate was measured with a contact angle meter (manufactured by Kyowa Interface Science Co., Ltd.: CA-X type), and the obtained value was defined as a water contact angle.

[0081]

[Table 1]

Table 1

	Substrate Temperature (°C)	Surface Modifier	Water Contact Angle (°)		
			CA ₁	CA ₂	CA ₁ /CA ₂
Example 1-1	100	trimethylsilyl trifluoroacetate (CH ₃) ₃ -Si-OC(O)CF ₃	60	45	1.33
Example 1-2	150		64	32	2.00
Example 2-1	100	trimethylsilyl acetate (CH ₃) ₃ -Si-OC(O)CH ₃	55	27	2.04
Example 2-2	150		61	28	2.18
Comparative Example 1	25	trimethylsilyl trifluoroacetate	54	74	0.73
Comparative Example 2	25	trimethylsilyl acetate	33	34	0.97
Comparative Example 3-1	25	trimethylsilyl methyl ether (CH ₃) ₃ -Si-OCH ₃	43	24	1.79
Comparative Example 3-2	100		46	32	1.44
Comparative Example 3-3	150		49	29	1.69
Reference Example 1-1	25	none (blank)	10	19	0.53
Reference Example 1-2	100		14	28	0.50
Reference Example 1-3	150		15	34	0.44

[0082]

(Evaluation of Protective Property of Protective Film)

5 Among the obtained measurement samples, the substrates of Examples 1-1, Comparative Example 3-2, and Reference Example 1-2 were immersed in hydrofluoric acid (HF) for 60 seconds, and then immersed in ultrapure water as a rinsing solution to be sufficiently washed. The concentration of the hydrofluoric acid

10 was set to 0.1% by mass and 0.5% by mass as shown in Table 2.

Next, the film thickness of the silicon oxide or silicon nitride after the etching was measured with an ellipsometer, and the amount of decrease from the thickness measured in the procedure (2) was calculated as the etching amount.

15 [0083]

[Table 2]

Table 2

	Etching Amount (nm)			
	0.1% by mass HF		0.5% by mass HF	
	SiN	SiO	SiN	SiO
Example 1-1	0	0.6	0	2.7
Comparative Example 3-2	1.0	0.6	0.7	3.1
Reference Example 1-2	1.0	0.6	0.7	3.2

[0084]

It was found that in the surface treatment method of the substrates of Examples 1 and 2, the water contact angle of the first surface (silicon nitride film surface) in the heated state could be set to be equal to or more than 55° by performing a dry treatment of the first surface with the silyl ester of the carboxylic acid. In addition, it was shown that the substrate of Example 1-1 in which the water contact angle was actually 60° had protective properties against the etching treatment.

On the other hand, in Comparative Examples 1 and 2 in which the surface was not in the heated state, both water contact angles were lower than those of Examples.

In addition, it was found that in Comparative Example 3 in which a silicon compound other than the silyl ester of the carboxylic acid was used as the surface modifier, the water contact angle was less than 50°, and protective properties against the etching treatment were not obtained.

As described above, it was shown that the protective property of the first surface having silicon nitride could be improved by using the silyl ester of the carboxylic acid as the surface modifier and performing the dry treatment with the

surface in the heated state.

[0085]

In addition, it was shown that in each of Examples, the protective property of the silicon nitride film, which is the first surface, could be selectively improved as compared with Comparative Examples 1 and 2 by performing the dry treatment of the first surface and the second surface (silicon oxide film surface) in the heated state with the silyl ester of the carboxylic acid.

On the other hand, in Comparative Example 1 in which the surface was not in the heated state, the water contact angle of the second surface was higher than the water contact angle of the first surface, and it could not be said that the first surface was selectively protected. In addition, it was shown that in Comparative Example 2, the water contact angles were the same, and the first surface was not selectively protected as in Comparative Example 1.

In addition, in each of Comparative Examples 3, the water contact angle of the first surface was higher than that of the second surface, but as described above, since the water contact angle of the first surface was low, only a protective film having low protective properties could be formed.

[0086]

This application claims priority based on Japanese Patent Application No. 2023-145315 filed on September 7, 2023, the entire disclosure of which is incorporated herein by reference.

REFERENCE SIGNS LIST

[0087]

- 1 substrate
- 11 first surface
- 5 12 second surface
- 20 modification gas
- 21 protective film
- 30 substrate holding space

CLAIMS

[Claim 1]

A method of processing a substrate, the method comprising:

5 a preparation step of preparing a substrate having a first surface including silicon nitride; and

a surface modification step of forming a protective film that protects the first surface,

wherein the surface modification step includes a gas
10 exposure treatment in which the first surface in a heated state is brought into contact with a modification gas containing gas of a surface modifier in a substrate holding space, and

the surface modifier includes at least one silicon compound represented by the following general formula (1):

15 $(X-COO)_a-Si-R_b$ (1)

in the general formula (1),

X each independently represents a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms, in which part or all of hydrogen atoms may be substituted by halogen atoms;

20 R each independently represents a hydrogen atom or a hydrocarbon group having 1 to 8 carbon atoms, in which part or all of hydrogen atoms may be substituted by halogen atoms; and

a and b each independently represent an integer of 1 to 3, provided that $a + b = 4$.

25

[Claim 2]

The method of processing a substrate according to Claim 1,

wherein in the preparation step, the substrate having the first surface and a second surface having silicon oxide is prepared, and

in the surface modification step, the protective film for selectively protecting the first surface with respect to the second surface is formed at least over the first surface by the gas exposure treatment of bringing the modification gas into contact with the first surface and the second surface in the heated state in the substrate holding space.

10

[Claim 3]

The method of processing a substrate according to Claim 1, wherein in the surface modification step, a water contact angle of the first surface at 25°C after the gas exposure treatment is equal to or more than 55°.

15

[Claim 4]

The method of processing a substrate according to Claim 2, wherein in the surface modification step, in a case where the water contact angle of the first surface at 25°C after the gas exposure treatment is denoted by CA_1 , and a water contact angle of the second surface at 25°C is denoted by CA_2 , the CA_1 and the CA_2 satisfy $1 < CA_1/CA_2 \leq 5$.

20

25 [Claim 5]

The method of processing a substrate according to Claim 1 or 2,

wherein a surface temperature of the substrate during the gas exposure treatment is equal to or higher than 50°C and equal to or lower than 400°C.

5 [Claim 6]

The method of processing a substrate according to Claim 1 or 2,

wherein a temperature of the modification gas to be introduced into the substrate holding space is equal to or
10 higher than 0°C and equal to or lower than 400°C.

[Claim 7]

The method of processing a substrate according to Claim 1 or 2,

15 wherein a concentration of the silicon compound in the modification gas is equal to or more than 1% by volume and equal to or less than 100% by volume.

[Claim 8]

20 The method of processing a substrate according to Claim 1 or 2,

wherein a boiling point of the silicon compound in the modification gas is equal to or higher than 40°C and equal to or lower than 400°C.

25

[Claim 9]

The method of processing a substrate according to Claim 1

or 2,

wherein the modification gas contains equal to or more than 0% by volume and equal to or less than 99% by volume of an inert gas.

5

[Claim 10]

The method of processing a substrate according to Claim 1 or 2,

wherein a pressure of the substrate holding space during the gas exposure treatment is equal to or higher than 1 Pa and equal to or lower than 10^6 Pa.

[Claim 11]

The method of processing a substrate according to Claim 1 or 2,

wherein the surface modification step includes a gas substitution treatment of introducing an inert gas into the substrate holding space in at least one of before and after the gas exposure treatment.

20

[Claim 12]

The method of processing a substrate according to Claim 1 or 2,

wherein the surface modification step includes a pretreatment of removing a natural oxide film of the first surface before the gas exposure treatment.

25

[Claim 13]

The method of processing a substrate according to Claim 1 or 2, further comprising:

5 a processing step including one or two or more selected from the group consisting of an etching treatment and a film forming treatment after the surface modification step.

[Claim 14]

The method of processing a substrate according to Claim 1
10 or 2,

wherein the silicon compound is trimethylsilyl trifluoroacetate and/or trimethylsilyl acetate.

[Claim 15]

15 A method of manufacturing a substrate, the method comprising:

a step of obtaining a substrate on which each step in the method of processing a substrate according to Claim 1 or 2 is performed.