

SPECIFICATION

SUBSTRATE PROCESSING GAS, STORAGE CONTAINER, AND SUBSTRATE
PROCESSING METHOD

5

TECHNICAL FIELD

[0001]

The present invention relates to a substrate processing gas,
a storage container, and a substrate processing method.

10

BACKGROUND ART

[0002]

Various studies on a technique for producing IF₇ gas (iodine
heptafluoride) have been conducted. As this type of technique, for
example, a technique described in Patent Document 1 is known. In
Patent Document 1, while supplying a fluorine gas with circulation,
iodine pentafluoride which is another raw material is gasified, and
both gases are mixed and react in a gas state (claim 1, paragraph
0001, and the like in Patent Document 1). Thus, obtained gases are
an unreacted iodine pentafluoride gas, a product iodine heptafluoride
gas, and an unreacted fluorine gas, and are separated and recovered
as follows, by utilizing the fact that each gas is liquefied at
different temperatures. Specifically, it is described that the
iodine pentafluoride is cooled and collected by IF₅ cold trap 40,
iodine heptafluoride is cooled and collected by IF₇ cold trap 44,
and iodine heptafluoride collected in the IF₇ cold trap 44 is gasified
by switching the cooling to heating and transferred (recovered) to

IF₇ recovery cylinder 66 (paragraph 0020 in Patent Document 1).

RELATED DOCUMENT

PATENT DOCUMENT

5 [0003]

[Patent Document 1] Japanese Unexamined Patent Publication No.
2006-265057

SUMMARY OF THE INVENTION

10 [0004]

However, as a result of the study by the present inventor, it was found that IF₇ gas described in Patent Document 1 has room for improvement in terms of speed of an etching rate and variations.

[0005]

15 As a result of further study, the present inventor found that in a case where IF₇ single gas is used as a substrate processing gas, the maximum etching rate becomes good, but variation in the etching rate may increase. When the etching rate of the substrate processing gas changes, there is a concern that etching conditions such as the
20 etching rate and etching depth may be affected and variations in quality between products may occur.

Further intensive research based on such findings revealed that variations in etching rate may be suppressed by using a mixed gas in which IF₅ is added to IF₇. Although detailed mechanism is not clear,
25 it is considered that, since IF₅ may suppress decomposition of IF₇ generated in the IF₇ single gas, the variation in the etching rate may be suppressed.

On the other hand, it was found that, by appropriately selecting an upper limit of the amount of IF₅ to be added to IF₇, it is possible to suppress the etching rate from being lowered to be equal to or less than a predetermined value.

5 As described above, it was found that, by appropriately controlling a range of the amount of IF₅ to be added to IF₇, it is possible to increase the speed of the etching rate of a substrate processing gas and is also possible to suppress variation in the etching rate. Then, the present invention was completed.

10 [0006]

There is provided a substrate processing gas containing IF₅ and IF₇, in which a content of the IF₅ is equal to or more than 1 ppm and equal to or less than 2% on a volume basis with respect to a total amount of the IF₅ and the IF₇.

15 [0007]

According to the present invention, there is also provided a storage container filled with the substrate processing gas.

[0008]

According to the present invention, there is also provided a
20 substrate processing method including dry-etching silicon without plasma, using the substrate processing gas.

[0009]

According to the present invention, there are provided a substrate processing gas which is excellent in speed of an etching
25 rate and suppression of variation in the etching rate, a storage container for storing the same, and a substrate processing method.

DESCRIPTION OF EMBODIMENTS

[0010]

An outline of a substrate processing gas of the present embodiment will be described.

5 The substrate processing gas of the present embodiment contains IF₅ and IF₇. A content of the IF₅ in the substrate processing gas can be set to equal to or more than 1 ppm and equal to or less than 2% on a volume basis with respect to the total amount of the IF₅ and the IF₇.

10 [0011]

According to findings of the present inventor, it was found in a case where IF₇ single gas was used as a substrate processing gas, variation in an etching rate occurred. It was considered that decomposition of IF₇ causes the variation in the etching rate, and
15 as a result of proceeding with the study, it was found that the variation in the etching rate of the substrate processing gas can be suppressed by adding a trace amount of IF₅ to the IF₇. Although a detailed mechanism is not clear, it is considered that the decomposition of the IF₇ during storage ($\text{IF}_7 \rightarrow \text{IF}_5 + \text{F}_2$) can be
20 suppressed by the trace amount of IF₅.

[0012]

On the other hand, it was found that in a case where a mixed gas obtained by adding a large amount of IF₅ to the IF₇ was used, the etching rate decreased excessively. Although a detailed mechanism
25 is not clear, it is considered that an excessive amount of IF₅ has a boiling point lower than that of IF₇, and thus is condensed first and forms an IF₅ layer (functioning as an etching stop layer) on a

surface of a treatment surface to suppress a reaction between the IF₇ and the treatment surface. The reason was considered that the excessive amount of IF₅ interferes with an etching ability of IF₇, and as a result of proceeding with the study, it was found that it is possible to suppress a decrease in the speed of the etching rate of the substrate processing gas, by appropriately selecting an upper limit of the amount of IF₅ to be added to IF₇.

[0013]

As described above, in the substrate processing gas containing both components of IF₇ and IF₅, by adding the IF₅ to the IF₇ in the amount of equal to or less than the upper limit value, it is possible to increase the speed of the etching rate by the IF₇ and by adding the IF₅ to the IF₇ in the amount of equal to or more than the lower limit value, it is possible to suppress variation in the etching rate by the IF₇.

[0014]

The substrate processing gas of the present embodiment can be used as a cleaning gas in various fields such as a semiconductor field. The substrate processing gas can be used, for example, as a cleaning gas for etching a substrate, forming a thin film such as chemical vapor deposition (CVD), and cleaning an inside of a semiconductor producing apparatus, in a semiconductor production process for a micro electro mechanical systems (MEMS) device, a liquid crystal thin film transistor (TFT) panel, a solar cell, and the like. Among these, the substrate processing gas can be preferably used as an etching gas compatible with miniaturization in the semiconductor field.

[0015]

Hereinafter, components of the substrate processing gas of the present embodiment will be described in detail.

[0016]

The substrate processing gas of the present embodiment contains
5 IF₅ and IF₇.

[0017]

The upper limit value of the content of the IF₅ in the substrate processing gas is equal to or less than 2% (% by volume) on a volume basis with respect to the sum (100 volume%) of the amount of the IF₅
10 and the IF₇, preferably equal to or less than 1.5%, and more preferably equal to or less than 1%. Accordingly, it is possible to suppress a decrease in the speed of the etching rate in IF₇. For example, in a case where dry-etching of the silicon (a silicon substrate with a polysilicon film) is performed 10 times using the substrate
15 processing gas, an average value of the etching rates is preferably equal to or more than 100 nm/min, and more preferably equal to or more than 150 nm/min, and particularly preferably equal to or more than 200 nm/min.

[0018]

20 The lower limit value of the content of the IF₅ in the substrate processing gas is, for example, equal to or more than 1 ppm, preferably equal to or more than 5 ppm, and more preferably equal to or more than 10 ppm on a volume basis with respect to the sum of the amount of the IF₅ and the IF₇ (100% by volume). Accordingly, it is possible
25 to suppress a variation in the etching rate in IF₇. For example, in a case where the dry-etching of the silicon (a silicon substrate with a polysilicon film) is performed 10 times using the substrate

processing gas, a standard deviation of the etching rate is preferably equal to or less than 10, and more preferably equal to or less than 5.

[0019]

5 The lower limit value of the content of the IF_7 is, for example, equal to or more than 50% (% by volume), preferably equal to or more than 80%, more preferably equal to or more than 90%, and further preferably equal to or more than 95% on a volume basis with respect to the entirety of the substrate processing gas (100% by volume).
10 Accordingly, the speed of the etching rate in the IF_7 increases. On the other hand, the upper limit value of the content of the IF_7 may be, for example, equal to or less than 99.99%, equal to or less than 99.9%, equal to or less than 99%, or equal to or less than 98%, on a volume basis with respect to the entirety of the substrate processing
15 gas (100% by volume). Accordingly, it is possible to suppress a variation in the etching rate in the IF_7 .

[0020]

 The substrate processing gas may contain other components in addition to the IF_7 and the IF_5 . Examples of other components include
20 a metal component.

[0021]

 Examples of the metal component (metal impurity) of the substrate processing gas include one or more metals selected from the group consisting of Fe, Cr, Mn, Co, Ti, Mo, Cu, and Ni or an oxide
25 of the metal and a metal compound such as halides and acid halides.

[0022]

 The substrate processing gas contains one or more metals

selected from the group consisting of Fe, Cr, Mn, Co, Ti, Mo, Cu, and Ni. A content of each of the metal contained is equal to or less than 100 ppb (ppb by mass), preferably equal to or less than 80 ppb, more preferably equal to or less than 50 ppb, and further preferably equal to or less than 30 ppb on a mass basis, with respect to the entirety of the substrate processing gas (100% by mass). Accordingly, it is possible to realize a high-purity substrate processing gas that is excellent in production stability of a product. Each lower limit value of the content of the metal is not particularly limited, and may be, for example, equal to or more than 0.1 ppb on a mass basis. [0023]

In the substrate processing gas of the present embodiment, the content of the metal component or a gas component can be measured by, for example, an inductively coupled plasma mass spectrometer (ICP-MS). [0024]

The substrate processing gas of the present embodiment may be appropriately used in combination with an oxidizing gas and/or an inert gas, in order to adjust a performance as an etching gas, unless the effects of the present invention are impaired. A content rate of the substrate processing gas in the etching gas is appropriately adjusted to fall within a range of 1% by volume to 100% by volume, for example. [0025]

Examples of the oxidizing gas include an oxygen-containing gas such as O₂, O₃, CO₂, COCl₂, COF₂, N₂O, NO, and NO₂, and a halogen gas such as HF, F₂, NF₃, Cl₂, Br₂, I₂, YFn (Y = Cl, Br, or I, and 1 ≤ n

≤ 5). Among these, O₂, COF₂, F₂, NF₃, and Cl₂ are preferable.

The amount of the oxidizing gas added is appropriately adjusted depending on the performance and shape of the etching apparatus to be used and an etching condition.

5 Examples of the inert gas include N₂, Ar, Ne, He, and Kr.
[0026]

In a case where the substrate processing gas of the present embodiment is used as an etching gas, examples thereof may include those produced and recovered by a method of producing a substrate
10 processing gas to be described below, those stored in a storage container, those with which a storage tank in a gas supply system is filled, and those supplied in a reaction chamber in an etching apparatus.

[0027]

15 In the present embodiment, an object to be processed by the dry-etching method is not particularly limited as long as a structure such as a semiconductor element has a material such as silicon, which reacts with IF₇. The substrate processing gas can be applied to the object to be processed made of silicon alone, and can also be applied
20 to a structure such as a semiconductor element including a silicon layer and an etching resistant member that does not substantially react with IF₇. In addition, the substrate processing gas can be used for surface processing of a silicon substrate. Specifically, for example, the substrate processing gas can be used for forming a trench
25 or a hole in a silicon substrate.

[0028]

As the silicon layer, a silicon layer used for forming a

semiconductor element is suitable, and examples thereof include an amorphous silicon film, a polysilicon film, and a single crystal silicon film.

In addition, there may be a case where the etching resistant member is used as a mask for processing a silicon layer into a predetermined shape or a case where by removing the silicon layer of an object to be processed, the etching resistant member itself is formed into a predetermined shape such as a three-dimensional structure and the etching resistant member is used as a structure of a semiconductor element.

[0029]

In the case where the etching resistant member is used as the mask, a method of selectively etching a silicon layer by using a mask patterned on a surface of the silicon layer into a predetermined shape and using the substrate processing gas of the present embodiment as an etching gas without plasma may be applied. A material used for the mask is not particularly limited as long as the material does not substantially react with IF_7 , and examples thereof include SiO_2 , SiOC , SiON , SiN , TiN , TiO_2 , photoresist, a carbon-based material, and a metal material such as Ru, Cu, Ni, Co, Hf, Zr, and oxides thereof.

[0030]

Hereinafter, a method of producing the substrate processing gas of the present embodiment will be described in detail.

[0031]

As an example of the method of producing the substrate processing gas of the present embodiment, it is possible to include a reaction step of reacting two or more compounds to obtain an IF_7 -containing

gas, and a purification step of purifying the obtained IF₇-containing gas to obtain an IF₇-purified gas. Here, the IF₇ purified gas refers to a gas obtained by purifying the IF₇.

[0032]

5 The reaction step of obtaining the IF₇-containing gas is not particularly limited, and includes a step of reacting two or more compounds such as a first raw material and a second raw material to obtain the IF₇-containing gas. Specific examples of the method of obtaining the IF₇-containing gas include a first method of reacting
10 IF₅ as the first raw material with F₂ as the second raw material to obtain an IF₇ gas, and a second method of reacting F₂ as the first raw material with I₂ as the second raw material to obtain the IF₇ gas.

[0033]

 In the first method, a method of obtaining the IF₇-containing
15 gas by reacting the IF₅ gas with the F₂ gas after the IF₅ gas is obtained by reacting the IF₇ gas with I₂ (solid) dispersed in the IF₅ (liquid) may be adopted. Accordingly, it is possible to large-scale synthesis with a small facility. In addition, in the second method, a method of obtaining the IF₇-containing gas by gas-gas synthesis in which
20 the F₂ gas and the I₂ gas are directly reacted may be adopted. In both the first method and the second method, a fluorinating agent such as an NF₃ gas or a ClF₃ gas can be used instead of the F₂ gas.

[0034]

 In the step of purifying the IF₇-containing gas, various known
25 purification means can be used, for example, distillation means can be used. Accordingly, the IF₇ can be separated and recovered from the IF₇-containing gas by utilizing difference in boiling points.

[0035]

Here, in a case where a fluorinated interhalogen compound or a halogen molecule raw material having high oxidizing property or corrosive property contacts a metal material during the (synthesis) reaction step, storage, or transportation of the IF₇-containing gas, it is presumed that impurities (components other than the IF₇) are mixed in the obtained IF₇-containing gas. Examples of the metal material include members that configure an inside of a container, a valve, a pipe, and the like that make up appliances or equipment.

A content of the impurities in the IF₇-containing gas can be appropriately adjusted by a purification step such as distillation.

[0036]

As the distillation means, for example, a distillation process including one or more selected from the group consisting of batch distillation, continuous distillation, atmospheric distillation, reduced-pressure distillation (vacuum distillation), simple distillation, and precision distillation can be carried out. These may be used alone or two or more thereof may be used in combination. In addition, these may be carried out repeatedly. In addition, by using a distillation column and controlling a distillation condition appropriately, the separability between the IF₇ and the components other than the IF₇ in the IF₇-containing gas can be improved.

[0037]

In the present embodiment, for example, by appropriately selecting the IF₇ reaction step or the IF₇ purification step, in the substrate processing gas, it is possible to control a content of the IF₇, a content of the IF₅, and the content of other components. Among

these, for example, appropriate selection of the distillation condition or the distillation procedure, mixing the purified IF_7 with the purified IF_5 , and the like are exemplified as factors for controlling the content of IF_7 , the content of the IF_5 , and the content of other components in the substrate processing gas to be in a desired numerical range.

[0038]

In addition, in the reaction in which a fluorine-containing component is reacted with an iodine-containing component to obtain the IF_7 , by setting F/I to be equal to or more than 6.86 and less than 7, the IF_7 containing a trace amount of IF_5 can be obtained and the substrate processing gas of the present embodiment can be obtained.

[0039]

The storage container of the present embodiment is filled with the substrate processing gas. The IF_7 and the IF_5 (gas component) can be stored as liquid in the storage container. Accordingly, storability and transportability can be improved.

[0040]

The storage container may include a metal container having an internal space, an inlet or outlet port of a gas component, which is provided in the metal container, and a valve provided at the inlet or outlet port. The gas component introduced from the inlet or outlet port is stored in an internal space inside the metal container. Accordingly, it is possible to improve handleability of the gas components.

[0041]

It is preferable that, in the metal container of the storage container, at least an inside (an inner wall contacting with the IF₇) is made of corrosion-resistant metal or ceramics. Examples of the corrosion-resistant metal or ceramics include nickel, nickel-based alloys, stainless steel (SUS), manganese steel, aluminum, aluminum-based alloys, titanium, titanium-based alloys, platinum, and alumina. Among these, the metal container is more preferably made of nickel, such as nickel or nickel-based alloy, or SUS, from the viewpoint of being inexpensive and easy to handle. In a case where the SUS is used, it is preferable to perform a process such as flowing a fluorine compound gas or a fluorine gas to form a passivation film on a surface, before filling with the IF₇. Accordingly, it is possible to store and transport the IF₇ while maintaining high purity.

[Examples]

[0042]

Hereinafter, the present invention will be described in detail with reference to examples, but the present invention is not limited to the description of these examples.

[0043]

(Preparation of substrate processing gas)

<Examples 1 to 4 and Comparative Examples 1 and 2>

IF₇ was distilled to obtain high-purity IF₇ (purity of equal to or higher than 99.9%, IF₅ concentration of equal to or lower than 0.5 ppm by volume). In addition, IF₅ was distilled to obtain high-purity IF₅ (purity of equal to or higher than 99.9%, IF₇ concentration of equal to or lower than 0.5 ppm by volume).

As a substrate processing gas in Comparative Example 1, the obtained high-purity IF_7 was used as it was.

As a substrate processing gas of Examples 1 to 4 and Comparative Example 2, a mixed gas in which the high-purity IF_5 is mixed with the obtained high-purity IF_7 was obtained under conditions of IF_5 concentration shown in Table 1, and the obtained mixed gas was used. In Table 1, the IF_5 concentration (content of IF_5) is expressed on a volume basis, with respect to a total amount of IF_5 and IF_7 .

[0044]

The content of each metal component contained in the substrate processing gas of Examples 1 to 4 was measured by an inductively coupled plasma mass spectrometer (ICP-MS). As a result, the content of each metal component of Fe, Cr, Mn, Co, Ti, Mo, Cu, and Ni was equal to or less than 100 ppb by mass.

[0045]

(Evaluation of etching rate)

First, a configuration of an etching apparatus will be described. A reaction chamber is equipped with a stage for supporting a sample. As the sample, a 6-inch silicon substrate on which a silicon oxide film (20 nm) was formed and a polysilicon film (30 μm) was further formed thereon was used. The stage is equipped with a stage temperature adjuster capable of adjusting a temperature of the stage. A first gas pipe for introducing a gas and a second gas pipe for exhausting a gas are connected to the reaction chamber. An etching gas supply system is connected to the first gas pipe through a first valve and supplies the substrate processing gas to the reaction chamber. A vacuum pump is connected to the second gas pipe through

a second valve for exhausting gas.

A pressure inside the reaction chamber is controlled by the second valve based on an indicated value of a pressure gauge attached to the reaction chamber.

5 [0046]

Next, a method of operating the etching apparatus will be described. The sample is placed on the stage, the inside of the reaction chamber, the inside of the first gas pipe, and the inside of the second gas pipe are vacuum replaced to 1.5 kPa, and then the
10 temperature of the stage is set to a predetermined value (25°C). After confirming that the temperature of the stage has reached the predetermined value, the first valve and the second valve are opened, the pressure of the etching gas supply system is set to a predetermined pressure (100 Pa). Then, each substrate processing gas of Examples
15 1-4 and Comparative Examples 1 and 2 is introduced into the reaction chamber by the first gas pipe. A total flow rate of the substrate processing gas at this time was set to 100 sccm. No plasma was generated when the substrate processing gas was introduced into the reaction chamber.

20 [0047]

After a predetermined time (processing time for etching, 1 minute) has passed after introducing the substrate processing gas, the introduction of the substrate processing gas was stopped, the inside of the reaction chamber was vacuum replaced, and then the sample
25 was taken out to measure the etching rate.

[0048]

Using the silicon substrate with a polysilicon film (sample),

a film thickness of the polysilicon film before etching and a film thickness of the polysilicon film after etching were measured at five points respectively, and the etching amount at each measurement point (a difference in film thickness before and after the etching) was determined. An etching rate (nm/min) was calculated from an average etching amount at each measurement point and the etching time.

[0049]

Using the substrate processing gas of Examples 1 to 4 and Comparative Examples 1 and 2 as the etching gas, the etching rates were evaluated 10 times using different silicon substrates, and the average value and a standard deviation thereof were determined. Table 1 shows evaluation results.

[0050]

[Table 1]

	IF ₅ concentration	Pressure	Temperature	Processing time	Etching rate [nm/min]											Standard deviation
					First time	Second time	Third time	Fourth time	Fifth time	Sixth time	Seventh time	Eighth time	Ninth time	Tenth time	Average	
Example 1	1ppm	100Pa	25°C	1 min.	261	265	262	267	260	265	266	255	263	262	262.6	3.5
Example 2	10ppm	100Pa	25°C	1 min.	234	237	232	238	234	230	231	237	236	235	234.4	2.7
Example 3	800ppm	100Pa	25°C	1 min.	221	219	220	215	215	221	221	216	217	214	217.9	2.8
Example 4	1%	100Pa	25°C	1 min.	202	199	204	200	207	202	207	197	201	203	202.2	3.2
Comparative Example 1	<0.5ppm	100Pa	25°C	1 min.	258	298	167	287	224	233	202	273	271	217	243.0	41.5
Comparative Example 2	3%	100Pa	25°C	1 min.	22	21	30	40	43	24	20	17	35	33	28.5	9.0

[0051]

It was found that, as the etching gas, the substrate processing gases of Examples 1 to 4 have suppressed variation in the etching rate compared to Comparative Example 1, and were excellent in speed
5 of etching rate, compared to Comparative Example 2.

[0052]

Priority is claimed on Japanese Patent Application No. 2018-065433, filed March 29, 2018, the entire disclosure of which is incorporated herein.

CLAIMS

1. A substrate processing gas comprising:

IF₅; and

5 IF₇,

wherein a content of the IF₅ is equal to or more than 1 ppm or more and equal to or less than 2% on a volume basis with respect to a total amount of the IF₅ and the IF₇.

10 2. The substrate processing gas according to claim 1,

wherein the content of the IF₅ is equal to or less than 1% on a volume basis with respect to the total amount of IF₅ and IF₇.

3. The substrate processing gas according to claim 1 or 2,

15 wherein a content of the IF₇ is equal to or more than 50% on a volume basis with respect to an entirety of the substrate processing gas.

4. The substrate processing gas according to any one of claims 1

20 to 3, further comprising:

one or more metals selected from the group consisting of Fe, Cr, Mn, Co, Ti, Mo, Cu, and Ni,

wherein a content of each of the metals contained is equal to or less than 100 ppb on a mass basis, with respect to an entirety
25 of the substrate processing gas.

5. The substrate processing gas according to any one of claims 1

to 4,

wherein the substrate processing gas is used as an etching gas.

6. A storage container filled with the substrate processing gas
5 according to any one of claims 1 to 5.

7. A substrate processing method comprising: dry-etching silicon
without plasma, using the substrate processing gas according to any
one of claims 1 to 5.

10

8. The substrate processing method according to claim 7,

wherein in a case where the dry-etching of the silicon is
performed 10 times,

an average value of etching rates is equal to or more than 100
15 nm/min, and

a standard deviation of the etching rates is equal to or less
than 10.