

DESCRIPTION

Title of Invention: GAS-FILLED CONTAINER AND METHOD FOR
STORING (E)-1,1,1,4,4,4-HEXAFLUORO-2-BUTENE

5

Technical Field

[0001]

The present invention relates to a gas-filled
container and a method for storing (E)-1,1,1,4,4,4-
10 hexafluoro-2-butene.

Background Art

[0002]

To stably perform fine processing in dry etching, a
15 dry etching gas is demanded to have a high purity (e.g.,
99.9% by volume or more). Further, the dry etching gas
is stored in a state of being filled in a filled
container until use, and therefore the high purity needs
to be maintained over a long term in the filled
20 container.

PTL 1 discloses a technology of storing 2-
fluorobutane, 2-fluoro-2-methylpropane, and 2-
fluoropentane usable as a dry etching gas while
maintaining the high purity over a long term. The
25 technology disclosed in PTL 1 suppresses a decrease in
purity by filling 2-fluorobutane, 2-fluoro-2-
methylpropane, or 2-fluoropentane into a manganese steel
container having a small amount of aluminum adhering to

the inner surface.

Citation List

Patent Literature

5 [0003]

PTL 1: WO 2016/117464

Summary of Invention

Technical Problem

10 [0004]

It has been examined to utilize (E)-1,1,1,4,4,4-hexafluoro-2-butene as a dry etching gas for manufacturing semiconductors. However, (E)-1,1,1,4,4,4-hexafluoro-2-butene has a double bond in the molecule, and thus has stability lower than that of 2-fluorobutane, 2-fluoro-2-methylpropane, and 2-fluoropentane, so that (E)-1,1,1,4,4,4-hexafluoro-2-butene has easily caused reactions, such as isomerization, polymerization, and decomposition, during storage.

20 Therefore, when the technology disclosed in PTL 1 is applied to (E)-1,1,1,4,4,4-hexafluoro-2-butene, the reactions, such as isomerization, polymerization, and decomposition, have progressed during long-term storage, so that the purity has decreased in some cases.

25 It is an object of the present invention to provide a gas-filled container in which the purity of the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene is less likely to decrease over a long term and a method for storing (E)-

1,1,1,4,4,4-hexafluoro-2-butene.

Solution to Problem

[0005]

5 To solve the above-described problems, one aspect of the present invention is as described in [1] to [13] below.

 [1] A gas-filled container includes: a filled container filled with (E)-1,1,1,4,4,4-hexafluoro-2-
10 butene, in which

 a part in contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene of the filled container is formed of a metal having a copper concentration of less than 0.5% by mass.

15 [0006] [2] The gas-filled container according to [1], in which the part in contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene of the filled container is formed of a metal having a copper concentration of less than 0.4% by mass.

20 [3] The gas-filled container according to [1] or [2], in which the metal is steel.

 [4] The gas-filled container according to [1] or [2], in which the metal is at least one of manganese steel and chromium molybdenum steel.

25 [5] The gas-filled container according to any one of [1] to [4], in which the copper concentration is measured by X-ray photoelectron spectroscopy.

[0007] [6] The gas-filled container according to any one

of [1] to [5], in which the filled container includes: a cylinder containing the (E)-1,1,1,4,4,4-hexafluoro-2-butene; and a valve configured to open and close a flow passage for causing the (E)-1,1,1,4,4,4-hexafluoro-2-butene inside the cylinder to flow to the outside.

[7] The gas-filled container according to any one of [1] to [6], in which the purity of the (E)-1,1,1,4,4,4-hexafluoro-2-butene to be filled is 99.90% by volume or more.

[0008] [8] A method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene includes: filling (E)-1,1,1,4,4,4-hexafluoro-2-butene into a container for storage, in which

a part in contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene of the filled container is formed of a metal having a copper concentration of less than 0.5% by mass.

[0009] [9] The method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to [8], in which the part in contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene of the filled container is formed of a metal having a copper concentration of less than 0.4% by mass.

[10] The method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to [8] or [9], in which the metal is steel.

[11] The method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to [8] or [9], in which the metal is at least one of manganese steel and chromium

molybdenum steel.

[0010] [12] The method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to any one of [8] to [11], in which the copper concentration is measured by X-ray photoelectron spectroscopy.

[13] The method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to any one of [8] to [12], in which the purity of the (E)-1,1,1,4,4,4-hexafluoro-2-butene to be filled is 99.90% by volume or more.

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Advantageous Effects of Invention

[0011]

According to the present invention, the purity of the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene is less likely to decrease over a long term.

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Description of Embodiments

[0012]

One embodiment of the present invention will be described below. This embodiment describes one example of the present invention, and the present invention is not limited to this embodiment. Further, this embodiment can be variously altered or modified and embodiments obtained by such alternations or modifications may also be included in the present invention.

25

[0013]

(E)-1,1,1,4,4,4-hexafluoro-2-butene is considered for utilization as a dry etching gas for manufacturing

semiconductors, but is not widely used industrially.
Therefore, the physical properties thereof have not been
sufficiently elucidated, and there have been almost no
reports on the long-term storage stability and compounds
5 serving as decomposition catalysts.

[0014]

As a result of intensive studies, the present
inventors have found that (E)-1,1,1,4,4,4-hexafluoro-2-
butene causes reactions, such as isomerization,
10 polymerization, and decomposition, upon contact with
metallic copper, copper alloys, or copper compounds,
leading to a decrease in purity, and thus have completed
the present invention. The present invention defines the
material of a filled container filled with (E)-
15 1,1,1,4,4,4-hexafluoro-2-butene to suppress the
reactions, such as isomerization, polymerization, and
decomposition, of (E)-1,1,1,4,4,4-hexafluoro-2-butene.

[0015]

More specifically, a gas-filled container according
20 to this embodiment is a filled container filled with (E)-
1,1,1,4,4,4-hexafluoro-2-butene, in which a part in
contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-
butene of the filled container is formed of a metal
having a copper concentration of less than 0.5% by mass.

25 [0016]

A method for storing (E)-1,1,1,4,4,4-hexafluoro-2-
butene according to this embodiment includes filling (E)-
1,1,1,4,4,4-hexafluoro-2-butene into a container for

storage, in which a part in contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene of the filled container is formed of a metal having a copper concentration of less than 0.5% by mass.

5 [0017]

The part in contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene of the filled container is formed of a metal having a copper concentration of less than 0.5% by mass, and therefore the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene is less likely to cause the reactions, such as isomerization, polymerization and decomposition. Therefore, even when the gas-filled container according to this embodiment is stored over a long term, the purity of the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene is less likely to decrease. Accordingly, in the case of the gas-filled container filled with high-purity (E)-1,1,1,4,4,4-hexafluoro-2-butene, the high purity is likely to be maintained even after the long-term storage.

20 [0018]

The copper refers to a copper element. When the metal forming the part in contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene of the filled container contains copper, the copper may be metallic copper, copper alloys, or copper compounds, such as copper salts.

[0019]

The concentration of copper contained in the metal is required to be less than 0.5% by mass and preferably

0.4% by mass or less. To further suppress the reactions, such as isomerization, polymerization, and decomposition, of (E)-1,1,1,4,4,4-hexafluoro-2-butene, the concentration is more preferably 0.1% by mass or less and still more preferably 0.01% by mass or less. There is particular no lower limit for the copper concentration, but the concentration may be 0.001% by mass or more.

A method for measuring the copper concentration is not particularly limited, and the copper concentration can be measured by X-ray photoelectron spectroscopy.

[0020] [Filled container]

The filled container in the gas-filled container according to this embodiment and the filled container in the method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to this embodiment preferably include a cylinder and a valve. The cylinder is a member containing (E)-1,1,1,4,4,4-hexafluoro-2-butene. The cylinder is preferably an integrally-molded seamless container.

The valve is a member opening and closing a flow passage for causing (E)-1,1,1,4,4,4-hexafluoro-2-butene inside the cylinder to flow to the outside and controlling the flow of (E)-1,1,1,4,4,4-hexafluoro-2-butene flowing through the flow passage.

[0021]

The parts in contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene of the filled container, such as the cylinder (particularly the inner surface of

the cylinder) and the valve, are preferably formed of steel. Steel includes at least one of stainless steel, manganese steel, and chromium molybdenum steel.

[0022]

5 Cylinders formed of manganese steel and chromium molybdenum steel include, for example, cylinders manufactured from steel tubes specified in JIS standard JIS G3429 (seamless steel tubes for high-pressure gas cylinders), such as STH11, STH12 (manganese steel tubes)
10 and STH21, STH22 (chromium molybdenum steel tubes).

[0023]

 However, these standards do not include items for copper, and thus the concentration of copper contained in manganese steel and chromium molybdenum steel is unknown,
15 and therefore it is not enough to simply satisfy these standards. As a result of analyzing the inner surface of a plurality of cylinders actually on the market and satisfying the STH12 standard, some having a copper concentration of 1.0% by mass and some having a copper
20 concentration of less than 0.005% by mass were mixed. Therefore, the use of common manganese steel and chromium molybdenum steel in the present invention requires the selection of those having a copper concentration of less than 0.5% by mass.

25 [0024]

 The valve is preferably formed of steel as with the cylinder. However, when plated with nickel plating or the like and prevented from directly contacting (E)-

1,1,1,4,4,4-hexafluoro-2-butene, even valves formed of copper alloys, such as brass and Monel (registered trademark), are usable.

[0025] [(E)-1,1,1,4,4,4-hexafluoro-2-butene]

5 The purity of (E)-1,1,1,4,4,4-hexafluoro-2-butene to be filled into the container (purity before being filled into the container) is preferably 99.90% by volume or more, more preferably 99.95% by volume or more, and still more preferably 99.99% by volume or more.

10 When the high-purity (E)-1,1,1,4,4,4-hexafluoro-2-butene described above is filled into the container, the purity hardly decreases during storage, and therefore the high purity is likely to be maintained even after the long-term storage.

15 [0026]

For example, when the purity of (E)-1,1,1,4,4,4-hexafluoro-2-butene before being filled into the container is defined as X and the purity of (E)-1,1,1,4,4,4-hexafluoro-2-butene after being stored in the
20 filled container at 23°C for 30 days is defined as Y, the purity Y can be set to 99.90% by volume or more. Further, a difference between the purity X and the purity Y (purity X - purity Y) can be set to less than 0.02 percentage point.

25 [0027]

When dry etching is performed using (E)-1,1,1,4,4,4-hexafluoro-2-butene having a purity of 99.90% by volume or more as a dry etching gas, the behavior of plasma and

the reproducibility of the etching performance are likely to be improved.

A method for measuring the purity of (E)-1,1,1,4,4,4-hexafluoro-2-butene is not particularly limited, and the purity can be measured by gas chromatography or Fourier transform infrared spectroscopy (FT-IR spectroscopy).

[0028]

A method for filling (E)-1,1,1,4,4,4-hexafluoro-2-butene into the container is not particularly limited. For example, a method is mentioned which includes filling (E)-1,1,1,4,4,4-hexafluoro-2-butene into an evacuated filled container through a filling line purged with an inert gas selected from a nitrogen gas (N₂), argon (Ar), and helium (He).

[0029]

The purge may be either cycle purge in which the filling line is filled with an inert gas, and then evacuated or flow purge in which the inert gas is continuously caused to flow through the filling line.

The filling line is preferably constituted by a tube the inner surface of which is passivated or electropolished.

[0030]

Examples of products generated by reactions resulting from the contact of (E)-1,1,1,4,4,4-hexafluoro-2-butene with copper include, for example, (Z)-1,1,1,4,4,4-hexafluoro-2-butene generated by cis-

trans isomerization, 1,2,3,4-tetrakis
(trifluoromethyl)cyclobutane, generated by dimerization,
and polymers of (E)-1,1,1,4,4,4-hexafluoro-2-butene
generated by polymerization.

5

EXAMPLES

[0031]

The present invention is more specifically described
with reference to Examples and Comparative Examples
10 below.

[Example 1]

A 10 L capacity seamless manganese steel container
having a copper concentration of 0.4% by mass was
prepared as a cylinder. The inner surface of the
15 cylinder was shot blasted, acid cleaned, and washed with
water, and further dried. Thereafter, a SUS316L valve
having a copper concentration of less than 0.005% by mass
was attached to the cylinder, thereby obtaining a
container. Then, the inside of the container was
20 evacuated in a heated state.

[0032]

The container was connected to a gas filling line
connected to a SUS316 tank containing (E)-1,1,1,4,4,4-
hexafluoro-2-butene. The purity X of (E)-1,1,1,4,4,4-
25 hexafluoro-2-butene in the tank analyzed by gas
chromatography is 99.95% by volume. The inner surface of
this tank was electropolished.

[0033]

Next, the gas filling line was subjected to the cycle purge of filling the gas filling line with a nitrogen gas, and then repeating evacuation, and then 1 kg of (E)-1,1,1,4,4,4-hexafluoro-2-butene was transferred from the tank to the container through the gas filling line, thereby obtaining a gas-filled container in which the filled container was filled with (E)-1,1,1,4,4,4-hexafluoro-2-butene. The internal pressure (gauge pressure) of the obtained gas-filled container was 0.06 MPaG.

[0034]

The gas-filled container thus obtained was filled with (E)-1,1,1,4,4,4-hexafluoro-2-butene and allowed to stand still at 23°C for 30 days. Thereafter, the purity Y of (E)-1,1,1,4,4,4-hexafluoro-2-butene in the filled container was measured. As a result, the purity did not decrease from the purity X before being filled into the container and was 99.95% by volume. More specifically, the difference between the purity X and the purity Y (purity X - purity Y) was 0.00 percentage point. Table 1 shows the results.

[0035]

[Table 1]

	Cylinder		Valve		Purity X before filling (% by volume)	Purity Y after filling (% by volume)	Purity X – Purity Y
	Material	Copper concentration (% by mass)	Material	Copper concentration (% by mass)			
Ex. 1	Manganese steel	0.4	SUS316L	Less than 0.005	99.95	99.95	0.00
Ex. 2	Manganese steel	0.05	SUS316L	Less than 0.005	99.95	99.95	0.00
Ex. 3	Manganese steel	Less than 0.005	SUS316L	Less than 0.005	99.95	99.95	0.00
Ex. 4	Chromium molybdenum steel	0.4	SUS316L	Less than 0.005	99.95	99.95	0.00
Ex. 5	Chromium molybdenum steel	0.05	SUS316L	Less than 0.005	99.95	99.95	0.00
Ex. 6	Chromium molybdenum steel	Less than 0.005	SUS316L	Less than 0.005	99.95	99.95	0.00
Ex. 7	Manganese steel + nickel alloy coating	Less than 0.005	SUS316L	Less than 0.005	99.95	99.95	0.00
Comp. Ex. 1	Manganese steel	0.5	SUS316L	Less than 0.005	99.95	99.89	0.06
Comp. Ex. 2	Manganese steel	1.0	SUS316L	Less than 0.005	99.95	99.10	0.85
Comp. Ex. 3	Manganese steel	Less than 0.005	Brass	70	99.95	98.84	1.11
Comp. Ex. 4	Chromium molybdenum steel	0.5	SUS316L	Less than 0.005	99.95	99.88	0.07
Comp. Ex. 5	Chromium molybdenum steel	1.0	SUS316L	Less than 0.005	99.95	99.12	0.83
Comp. Ex. 6	Chromium molybdenum steel	Less than 0.005	Brass	70	99.95	98.89	1.06
Comp. Ex. 7	Manganese steel + nickel alloy coating	Less than 0.005	Brass	70	99.95	98.88	1.07

[0036]

After the measurement of the purity Y of (E)-
1,1,1,4,4,4-hexafluoro-2-butene, the filled container was
subjected to the cycle purge of extracting (E)-
5 1,1,1,4,4,4-hexafluoro-2-butene and charging a nitrogen
gas, and then repeating evacuation. Then, the filled
container was cut into 2 cm squares using a laser cutting

machine, and then the inner surface of the filled container was subjected to XPS analysis using the resultants as measurement samples, thereby measuring the copper concentration. As a result, the copper
5 concentration did not change from the initial 0.4% by mass.

[0037]

An analyzer and analysis conditions used for the gas chromatography are as follows.

10 Analyzer: Gas Chromatograph GC-2014s manufactured by Shimadzu Corporation

Column: CarboPak B 60/80 SP-1000

Column temperature: 150°C/200°C

Injection temperature: 200°C

15 Carrier gas: Helium

Detector: Flame ionization detector (FID)

[0038]

An analyzer, analysis conditions, and sputtering conditions used for the XPS analysis are as follows.

20 Analyzer: X-ray photoelectron spectrometer PHI5000VersaProbeII manufactured by ULVAC-Phi, Inc.

Atmosphere: Vacuum (less than 1.0×10^6 Pa)

X-ray source: Monochromatic Al Ka (1486.6 eV)

Spectrometer: Electrostatic concentric hemispherical
25 spectrometer

[0039]

X-ray beam diameter: 100 μ m (25 W, 15 kV)

Signal capture angle: 45.0°

Pass energy: 23.5 eV

Measurement energy range: Cr2p 570-584 eV

Mn2p 632-648 eV

Fe2p 704-720 eV

5 Cu2p 930-945 eV

[0040]

Sputtering ion source: Ar2, 500+

Sputtering acceleration voltage: 10 kV

Sputtering region: 2 mm × 2 mm

10 Sputtering time: 10 minutes

[0041] [Examples 2 to 6 and Comparative Examples 1, 2, 4,
5]

The purity Y of (E)-1,1,1,4,4,4-hexafluoro-2-butene
in each gas-filled container after allowed to stand still
15 at 23°C for 30 days was measured by performing the same
operation as the operation in Example 1, except that
steel forming the seamless container used as the cylinder
(steel grade and copper concentration are shown in Table
1) was different. Table 1 shows the results.

20 [0042] [Example 7]

The purity Y of (E)-1,1,1,4,4,4-hexafluoro-2-butene
in a gas-filled container after allowed to stand still at
23°C for 30 days was measured by performing the same
operation as the operation in Example 1, except that a
25 nickel alloy coating was formed on the inner surface of a
cylinder by an electroless plating method. Table 1 shows
the results. The copper concentration of the surface of

the nickel alloy coating was confirmed to be less than 0.05% by mass by XPS analysis.

[0043] [Comparative Example 3]

The purity Y of (E)-1,1,1,4,4,4-hexafluoro-2-butene
5 in a gas-filled container after allowed to stand still at 23°C for 30 days was measured by performing the same operation as the operation in Example 3, except for using a brass valve. Table 1 shows the results. The copper concentration of brass is 70% by mass.

10 [0044] [Comparative Example 6]

The purity Y of (E)-1,1,1,4,4,4-hexafluoro-2-butene
in a gas-filled container after allowed to stand still at 23°C for 30 days was measured by performing the same operation as the operation in Example 6, except for using
15 a brass valve. Table 1 shows the results. The copper concentration of brass is 70% by mass.

[0045] [Comparative Example 7]

The purity Y of (E)-1,1,1,4,4,4-hexafluoro-2-butene
in a gas-filled container after allowed to stand still at
20 23°C for 30 days was measured by performing the same operation as the operation in Example 7, except for using a brass valve. Table 1 shows the results. The copper concentration of brass is 70% by mass.

[0046]

25 As is understood from the results shown in Table 1, Examples 1 to 7 did not exhibit a decrease in purity due to the storage at 23°C for 30 days and had the difference between the purity X and the purity Y of 0.00 percentage

point. In contrast thereto, a decrease in purity due to the storage at 23°C for 30 days was observed in Comparative Examples 1 to 7. It is considered in Comparative Examples 1 to 7 that the reactions, such as
5 isomerization, polymerization, and decomposition, of (E)-1,1,1,4,4,4-hexafluoro-2-butene by copper occurred.

CLAIMS

1. A gas-filled container comprising:
a filled container filled with (E)-1,1,1,4,4,4-
5 hexafluoro-2-butene, wherein
a part in contact with the filled (E)-1,1,1,4,4,4-
hexafluoro-2-butene of the filled container is formed of
a metal having a copper concentration of less than 0.5%
by mass.
10
2. The gas-filled container according to claim
1, wherein the part in contact with the filled (E)-
1,1,1,4,4,4-hexafluoro-2-butene of the filled container
is formed of a metal having a copper concentration of
15 less than 0.4% by mass.
3. The gas-filled container according to claim 1
or 2, wherein the metal is steel.
- 20 4. The gas-filled container according to claim 1
or 2, wherein the metal is at least one of manganese
steel and chromium molybdenum steel.
5. The gas-filled container according to any one
25 of claims 1 to 4, wherein the copper concentration is
measured by X-ray photoelectron spectroscopy.
6. The gas-filled container according to any one

of claims 1 to 5, wherein the filled container includes:

a cylinder containing the (E)-1,1,1,4,4,4-hexafluoro-2-butene; and

a valve configured to open and close a flow passage
5 for causing the (E)-1,1,1,4,4,4-hexafluoro-2-butene
inside the cylinder to flow to an outside.

7. The gas-filled container according to any one
of claims 1 to 6, wherein a purity of the (E)-
10 1,1,1,4,4,4-hexafluoro-2-butene to be filled is 99.90% by
volume or more.

8. A method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene comprising:
15 filling (E)-1,1,1,4,4,4-hexafluoro-2-butene into a
container for storage, wherein

a part in contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene of the filled container is formed of
a metal having a copper concentration of less than 0.5%
20 by mass.

9. The method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to claim 8, wherein the
part in contact with the filled (E)-1,1,1,4,4,4-hexafluoro-2-butene of the filled container is formed of
25 a metal having a copper concentration of less than 0.4%
by mass.

10. The method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to claim 8 or 9, wherein the metal is steel.

5 11. The method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to claim 8 or 9, wherein the metal is at least one of manganese steel and chromium molybdenum steel.

10 12. The method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to any one of claims 8 to 11, wherein the copper concentration is measured by X-ray photoelectron spectroscopy.

15 13. The method for storing (E)-1,1,1,4,4,4-hexafluoro-2-butene according to any one of claims 8 to 12, wherein a purity of the (E)-1,1,1,4,4,4-hexafluoro-2-butene to be filled is 99.90% by volume or more.