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METHOD FOR REMOVING INORGANIC HALOGENATED GAS

BACKGROUND OF THE INVENTION

The present invention relates to a method for removing an inorganic halogenated gas. The inorganic halogenated gas
5 may be present in an exhaust gas produced by dry cleaning an apparatus for producing a semiconductor device using ClF_3 .

An apparatus for forming a thin film such as a CVD apparatus is used to produce a semiconductor device, and a component for the thin film is attached to inner surfaces of
10 a housing and pipes of the apparatus. Such component for the thin film is automatically cleaned by a cleaning gas such as ClF_3 . As a diameter of a wafer to be worked increases, an amount of a cleaning gas such as ClF_3 and a period for cleaning tend to increase. An exhaust gas of the
15 cleaning gas contains ClF_3 , which is highly toxic and which has TLV as low as 0.1 ppm. Moreover, the exhaust gas contains harmful gases such as SiF_4 , SiCl_4 , BF_3 , BCl_3 , PF_3 , PCl_3 , Cl_2 , F_2 and so on, which are byproducts in cleaning the components for the thin film. Therefore, it is desirable to
20 establish a method for removing these harmful gases.

JP-B-177/1994 proposes a method for purifying an exhaust gas containing ClF_3 by combination of iron oxides and an alkaline agent such as calcium hydroxide. In addition, a wet scrubber by an alkaline aqueous solution and
25 dry removal by soda lime, activated alumina are generally conducted.

In the latter method, the sole use of soda lime and activated alumina as a treating agent cannot remove ClF_3 .



blow a value of TLV. Moreover, the reaction of the treating agent with ClF_3 may produce byproducts of Cl_2 . Furthermore, the treating agent has limited capacity to remove SiF_4 , SiCl_4 , BF_3 , BCl_3 , PF_3 , PCl_3 , Cl_2 and F_2 , which may be discharged with
5 ClF_3 .

The method in accordance with JP-B-177/1994 may solve the problem of the aforementioned problem. The method with the combination of iron oxides and an alkaline agent has still limited capacity to remove a large amount of ClF_3 ,
10 which is associated with an increased use of ClF_3 along with an increased diameter of the semiconductor wafer. Moreover, as an exhaust gas has an increased concentration, the treating agent may react with the exhaust gas to produce heat, thereby increasing temperatures. The increased
15 temperatures may lead to decreased performance for removing the harmful gases.

SUMMARY OF THE INVENTION

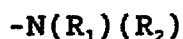
According to one aspect of the present invention, there is provided a method for removing an inorganic
20 halogenated gas, said method comprising the sequential steps of: exposing a gas containing an inorganic halogenated gas to at least one of iron oxide and a synthetic zeolite; and then exposing the gas to an anion exchange resin.

In the present invention, preferably, the inorganic
25 halogenated gas is at least one species selected from the group consisting of ClF_3 , SiX_4 , BX_3 , PX_3 and X_2 where X is a halogen atom. Further preferably, X is a fluorine atom or a chlorine atom.



Preferably, the inorganic halogenated gas comprises ClF_3 , SiF_4 , SiCl_4 , BF_3 , BCl_3 , PF_3 , PCl_3 , Cl_2 or F_2 . Further preferably, the inorganic halogenated gas comprises ClF_3 .

Preferably, the anion exchange resin comprises an
5 amino group represented by a following formula:



wherein R_1 and R_2 are same or different and are
10 hydrogen or C_1 to C_6 alkyl, which may be substituted by amino or hydroxy group.

According to another aspect of the present invention, there is provided an apparatus for removing an inorganic halogenated gas, comprising: a first packed bed containing
15 iron oxide or a synthetic zeolite; and a second packed bed being disposed in a downstream of the first bed and containing an anion exchange resin.

Preferably, an apparatus further comprises a column; and a perforated partition for defining a first compartment
20 and a second compartment in the column, the first compartment containing the first packed bed, and the second compartment containing the second packed bed. Preferably, the apparatus further comprises: a first packed column containing the first packed bed; and a second packed column
25 containing the second packed bed.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross section of an apparatus of one embodiment in accordance with the present invention.

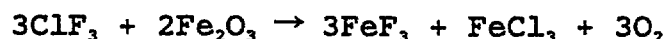


Fig. 2 is a cross section of an apparatus of another embodiment in accordance with the present invention.

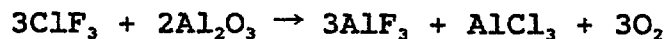
DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with a method of the present invention,
5 firstly, a gas containing an inorganic halogenated gas is exposed to at least one of iron oxide and a synthetic zeolite, thereby fixing the inorganic halogenated gas with the treating agent by forming, for example, a fluoride compound.

10 For example, ClF_3 reacts with iron oxide such as Fe_2O_3 as follows.



15 Similarly, ClF_3 reacts with an Al_2O_3 moiety in the synthetic zeolite as follows.



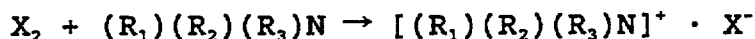
20 In accordance with these chemical reactions, fluorine atoms in trifluorochloride are fixed as iron fluorides or aluminum fluorides. However, chlorine atoms in trifluorochloride are converted into gaseous Cl_2 in addition to FeCl_3 and AlCl_3 . Although a portion of Cl_2 is removed by
25 iron oxides or the synthetic zeolite, most of Cl_2 passes through the adsorbent much earlier than the other inorganic halogenated gases since the iron oxide and the synthetic zeolite have limited capacity to remove Cl_2 .



Similarly, BX_x is removed by the iron oxides or the synthetic zeolite wherein X is a halogen atom. However, most of the dihalogen gas X_2 pass through the iron oxides or the synthetic zeolite.

5 In accordance with the method of the present invention, subsequently, the gas that passed through the iron oxide or the synthetic zeolite is further exposed to an anion exchange resin for removing the dihalogen gas X_2 such as Cl_2 . The dihalogen gas therein reacts with the anion exchange
10 resin so that the dihalogen gas is absorbed by the anion exchange resin.

For example, the reaction may be shown as follows:



15 wherein R_1 , R_2 and R_3 are same or different and are hydrogen; C_1 to C_6 alkyl, which may be substituted by amino or hydroxy group; or C_6 to C_{14} aryl, which may be a part of a repeating unit of a polymer chain; and

20 X is a halogen atom.

The present invention is explained in further details.

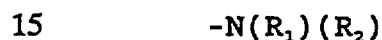
Iron oxide used in the present invention preferably consists essentially of Fe_2O_3 .

Zeolite used in the present invention preferably has a
25 large aluminum content, and the zeolite may contain 1 part by mole of Al_2O_3 and 0.5 to 10 part by mole of SiO_2 , preferably contain 1 part by mole of Al_2O_3 and 1 to 5 part by mole of SiO_2 , and further preferably contain 1 part by mole



of Al_2O_3 and about 2.5 part by mole of SiO_2 . For example, the zeolite having a formula of $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{SiO}_2$ may be used. The sodium oxide in the zeolite may be replaced by another alkali metal such as potassium and an alkali earth metal such as calcium, and so on. The zeolite may have an average pore diameter of 10 angstrom and a specific surface area of 650 square meter per gram.

An anion exchange resin used in the present invention may have a framework consisting essentially of a copolymer of styrene and divinylbenzene and a plurality of anion exchange groups bonded to benzene rings of the styrene and divinylbenzene. The anion exchange group may be an amino group represented by a following formula:



wherein R_1 and R_2 are same or different and are hydrogen or C_1 to C_6 alkyl, which may be substituted by amino or hydroxy group. Both R_1 and R_2 may be C_1 to C_3 alkyl and preferably methyl.

Preferably, the anion exchange resin has a water content up to 5 percent by weight for increasing its capacity to trap the dihalogen gas such as Cl_2 . For example, the anion exchange resin is dried at 100°C for 8 to 12 hours in advance.

In referring to Fig. 1, an apparatus 10 has a column 12 defining a bore extending therethrough. Perforated partitions 14, 16, and 18 are disposed in the bore of the



column 12. The partitions are perforated to pass through an inorganic halogenated gas. The perforated partition 16 along with the perforated partition 14 defines a first compartment 22, and the perforated partition 16 along with
5 the perforated partition 18 defines a second compartment 24 in the bore of the column 12.

The first compartment 22 containing a packed bed 23 containing iron oxide or a synthetic zeolite. The second compartment 24 containing a packed bed 25 is disposed in a
10 downstream of the packed bed 23 and contains an anion exchange resin 25.

The iron oxide, the zeolite, and the anion exchange resin may have any configuration such as particle, bar, and plate configurations. Preferably, the agent is finely
15 divided for increasing a surface area thereof. The iron oxide may have a size of 6 to 12 mesh. The synthetic zeolite may have a size of 14 to 20 mesh. The anion exchange resin may have a size of 20 to 50 mesh.

An inorganic halogenated gas or an exhaust gas
20 containing the inorganic halogenated gas is introduced to the apparatus 10 through an inlet 26, and the gas is exposed to the packed bed 23 containing the iron oxide or the synthetic zeolite. Subsequently, the gas is exposed to the packed bed 25 containing the anion exchange resin and
25 discharged from the apparatus 10 through an outlet 28.

It is unnecessary to heat the packed beds 23, 25. Even though the gas at room temperature is introduced to the apparatus 10 at room temperature, typically chemical



reactions in the packed bed 23 generate heat and warm up the apparatus 10. For example, the packed bed 23 may reach to about 200°C.

In this embodiment, a gas moves up through the apparatus 10 from the bottom to the top. Alternatively, a gas may move down through the apparatus of Fig. 1 from the top to the bottom. In the latter embodiment, the packed bed is reversed also.

Fig. 2 shows another embodiment of the present invention. An apparatus 30 has a packed column 32 containing a packed bed 34; another packed column 34 containing a packed bed 44; and a connection 36 connecting the packed column 32 and the packed column 40. The packed bed 34 contains iron oxide or the synthetic zeolite, and the packed bed 44 contains the anion exchange resin.

A CVD apparatus 50 generates an exhaust gas containing an inorganic halogenated gas, and the exhaust gas passes through a connection 56 and is introduced to the packed column 32, and the exhaust gas is exposed to the packed bed 34 containing iron oxide or the synthetic zeolite. Subsequently, the exhaust gas passes through the connection 36 and introduced to the packed column 40. The exhaust gas is exposed to the packed bed 44 containing the anion exchange resin, and discharged from the apparatus 30 through an outlet 46.

EXAMPLE

The present invention is illustrated by way of Examples hereinafter. However, the present invention is not



limited by the following Examples.

Reference Example

A column made of poly(tetrafluoroethylene) and having a cylindrical configuration with a diameter of 40 mm was
5 packed by a packing agent to form a packed bed having a height of 50 mm. Each of the packing agent was commercially available and had a particle configuration. A synthetic zeolite having a formula of $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{SiO}_2$ had a particle diameter corresponding to 14 to 20 mesh, the anion exchange
10 resin, which was dried to have a water content up to 5 percent by weight, had a particle diameter of 20 to 50 mesh. Iron oxides and calcium hydroxide had particle diameters corresponding to 7 to 16 mesh and 6 to 10 mesh, respectively. The anion exchange resin had a framework consisting
15 essentially of a copolymer of styrene and divinylbenzene and a plurality of a species represented by a formula $-\text{N}(\text{CH}_3)_2$ bonded to benzene rings of the styrene and divinylbenzene.

A sample gas was introduced into the packed column at room temperature with a flow rate of 300 ml per minute and
20 LV of 24 cm per minute. A sample gas has one percent by weight of one of ClF_3 , Cl_2 , SiF_4 , and BCl_3 and the remainder being a carrier gas of dinitrogen. Concentrations of the inorganic halogenated gas was determined at the inlet and outlet of the packed column. With regard to analysis of a
25 gas at the outlet, the outlet gas was introduced into an alkaline solution for absorbing the gas, and the amounts of Cl and F in the solution were analyzed by ion exchange chromatography and a detecting tube process.



The sample gas was kept introduced to the packed column until the gas at the outlet contained one of ClF_3 , Cl_2 , SiF_4 , and BCl_3 beyond its permissible concentration. The permissible concentrations of ClF_3 , Cl_2 , SiF_4 , and BCl_3 are 0.1 ppm, 0.5 ppm, 3 ppm and 5 ppm, respectively.

The results are shown in Table 1.

Table 1

packing agent	Amount of Removed Gases(l/l)			
	ClF_3	Cl_2	SiF_4	BCl_3
synthetic zeolite	12	10	20	10
anion exchange resin	40	30	2	2
15 Fe_2O_3	10	2	20	35
Ca(OH)_2	0	10	15	20

An amount of a removed gas refers to an amount of a removed gas in liter per one liter of a packing agent.

Table 1 shows that the synthetic zeolite has relatively high capacity for removing ClF_3 , Cl_2 , SiF_4 , and BCl_3 gases. On the other hand, the anion exchange resin has high capacity to remove ClF_3 and Cl_2 and low capacity to remove SiF_4 and BCl_3 . Fe_2O_3 has reduced capacity to remove ClF_3 and Cl_2 , comparable capacity to remove SiF_4 , and improved capacity to remove BCl_3 , compared to the synthetic zeolite. Ca(OH)_2 has limited capacity to remove Cl_2 , which is as little as 10 liter per liter and about one third of



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the anion exchange resin.

Examples 1 and 2

An apparatus 10 of Fig. 1 was used in Examples 1 and 2. Column 12 had a cylindrical configuration with a diameter of 40 mm and was made of poly(tetrafluoroethylene). The first compartment 22 was packed with a packed bed 23 having a height of 72 mm. In Examples 1 and 2, Fe_2O_3 and the synthetic zeolite were used as the packed bed 23, respectively. The second compartment 24 was packed with a packed bed 25 having a height of 72 mm. In Examples 1 and 2, the anion exchange resin was used as the packed bed 25. Fe_2O_3 , the synthetic zeolite and the anion exchange resin were the same as those in Reference Example.

A sample gas was introduced into the packed column through an outlet 26 at room temperature with a flow rate of 1,300 ml per minute and LV of 104 cm per minute. A sample gas had 0.21 percent by weight of ClF_3 , 0.38 percent by weight of Cl_2 , and 0.25 percent by weight of SiF_4 , and the remainder being a carrier gas of dinitrogen. Concentrations of the inorganic halogenated gas was determined at the outlet of the packed column. The sample gas was kept introduced to the packed column until the gas at the outlet contained one of ClF_3 , Cl_2 , SiF_4 , and BCl_3 beyond its permissible concentration.

The result is shown at Table 2.

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Table 2

	Treating Time (min.)	Passed Gas
5 Example 1	240	Cl ₂
Example 2	360	Cl ₂

10 In both Examples, Cl₂ leaked first above the permissible level. The treating time up to the leakage is longer in the combination of the synthetic zeolite and the anion exchange resin than the combination of Fe₂O₃ and the anion exchange resin.

Comparative Example 1

15 In Comparative Example 1, the apparatus of Example 1 was used except that the anion exchange resin of Example 1 is replaced by Ca(OH)₂. The packed bed 23 of Ca(OH)₂ had the same height of 72 mm. The same sample gas was introduced to the apparatus in the same conditions as Example 1.

20 The result is shown at Table 3.

Table 3

	Treating Time (min.)	Passed Gas
25 Comparative Example 1	120	Cl ₂

30 Cl₂ leaked first beyond the permissible level. The treating time up to the leakage is half of the treating time



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in the combination of the synthetic zeolite and the anion exchange resin and one third of the treating time in the combination of Fe_2O_3 and the anion exchange resin.

The present invention allows to remove an inorganic
5 halogenated gas and to remove even a large amount of inorganic halogenated gas, thereby increasing a service life of the packed agent.

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WHAT IS CLAIMED IS:

1. A method for removing an inorganic halogenated gas, said method comprising the sequential steps of:

5 exposing a gas containing an inorganic halogenated gas to at least one of iron oxide and a synthetic zeolite; and then

exposing the gas to an anion exchange resin.

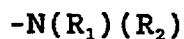
2. A method of claim 1 wherein the inorganic halogenated gas comprises at least one species selected from the group
10 consisting of ClF_3 , SiX_4 , BX_3 , PX_3 and X_2 where X is a halogen atom.

3. A method of claim 2 wherein X is a fluorine atom or a chlorine atom.

4. A method of claim 1 wherein the inorganic halogenated
15 gas comprises ClF_3 , SiF_4 , SiCl_4 , BF_3 , BCl_3 , PF_3 , PCl_3 , Cl_2 or F_2 .

5. A method of claim 1 wherein the inorganic halogenated gas comprises ClF_3 .

6. A method of claim 1 wherein the anion exchange resin
20 comprises an amino group represented by a following formula:



wherein R_1 and R_2 are same or different and are
25 hydrogen or C_1 to C_6 alkyl, which may be substituted by amino or hydroxy group.

7. An apparatus for removing an inorganic halogenated gas, comprising:

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a first packed bed containing iron oxide or a synthetic zeolite; and

a second packed bed being disposed in a downstream of the first bed and containing an anion exchange resin.

5 8. An apparatus of claim 7, further comprising:

a column; and

a perforated partition for defining a first compartment and a second compartment in the column, the first compartment containing the first packed bed, and the
10 second compartment containing the second packed bed.

9. An apparatus of claim 7, further comprising:

a first packed column containing the first packed bed;
and

a second packed column containing the second packed
15 bed.

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