

Description

The present invention relates to a method for removing halogens or halogen compounds from a waste gas. With this method halogen-containing waste gases resulting from the dry etching step of the process of fabricating semiconductor devices are rendered harmless by removing the halogen compounds concomitant with said waste gases.

Many kinds of deleterious gases are employed in the process of fabricating semiconductor devices and they are potential pollutants of the environment. Halogen-containing gases that are present in the waste gases from the dry etching step are very toxic to the human body and it is strongly desired to establish a method by which those gases can be removed effectively.

While several methods for removing halogen-containing gases have so far been described, "dry systems" employ the following treating agents: (1) metal oxides; (2) activated carbon or a chemical supported on activated carbon; (3) an alkali agent; and (4) an oxidizing agent. Included within the class of (1) are oxides of various metals; included within the class of (2) are absorbents having chlorides or hydroxides of alkaline earth metals supported on activated carbon; known examples of alkali agents (3) include Ca(OH)_2 , Mg(OH)_2 , CaO and MgO ; and a known example of oxidizers (4) is KMnO_4 .

The halogen-containing gases that are discharged from the dry etching step are classified as the following three types; (1) oxidizing gases (e.g. Cl_2 and Br_2); (2) acidic gases (e.g. HCl and SiF_4); and (3) organic chlorine-containing gases (e.g. CCl_4 and CHCl_3). In practice, these gases are rarely discharged individually and a plurality of gases having different properties are discharged simultaneously.

In the prior art, there is no single treating agent that is effective in treating all of those halogen-containing gases. For example, metal oxides, alkali agents and oxidizing agents are not capable of removing all oxidizing and organic chlorine-containing gases, whereas activated carbon is not capable of removing all acidic gases. In the absence of a single agent that is capable of treating all halogen-containing gases, it is necessary to select an appropriate agent for each waste gas to be treated, but this is not only a difficult and cumbersome task; the throughput of the treatment is also small.

The document US-A-4 594 231 describes a method for removing halogens and/or hydrogen halides from a waste gas by contacting the gas with an adsorbent of activated carbon supporting copper oxide and/or zinc oxide and, in addition, one or more components selected from alkali metal oxides, alkaline earth metal oxides, and oxides of Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cd and Pb. The efficiency of the adsorbent for removing HCl and Cl_2 is shown to decrease more rapidly with the time of use when no copper oxide or zinc oxide are present. The mechanism of the adsorption is not described, but the small amounts of copper oxide, zinc oxide and other components used suggest that it is catalytic.

The Patent Abstracts of Japan, Vol. 10, No. 349 (C-456)[2796] of November 14, 1987, page 83 C 456, reporting on the document JP-A-62-121621, describe a gas adsorbing and trapping device for a waste gas containing a component gas such as BCl_3 that generates HCl when contacting water contained in the gas. The waste gas is passed through an adsorbent layer and then through an HCl trap containing soda lime. When the temperature of the HCl trap rises, the temperature rise of the outflowing gas is detected by a sensor as an indication that the break-through point has been reached.

The use of soda lime as an alkaline agent for treating halogen containing gases has the following problems.

If wafers are contaminated with Na, the electrical properties of semiconductors become very unstable to lower the yield of acceptable products. Under these circumstances, utmost care is taken in semiconductor shops to prevent wafer contamination by requiring that the operating personnel wash their hands and wear masks, gloves and other protectors. Equipment for removing deleterious gases is not an exception. If Na-based treating agents are used, a Na-containing waste gas may flow back in an accident to potentially contaminate wafers. Hence, the use of Na-based treating agents is avoided as much as possible in semiconductor shops.

Furthermore, When a strong alkali agent such as soda lime is used, it reacts with a halogen gas and the resulting heat will cause water to be formed in a large amount, whereupon the individual particles of the agent will cohere together. If this occurs, the resistance to gas flow will increase and, in an extreme case, clogging occurs and the gas will no longer flow. For these reasons, the use of soda, lime as an alkali agent is not preferred.

It is the object of the present invention to provide a method for simultaneously removing a plurality of halogens or halogen compounds having different properties from waste gases in an effective way using treating agents that need not be replaced for a prolonged period of time.

The achievement of this object is shown by the features of patent claim 1.

Other objects and advantages of the present invention will become apparent to those skilled in the art from the following description and disclosure.

Fig. 1 is a graph showing the relationship between volume ratios of activated carbon to Ca(OH)_2 and time ratios for treatment for Cl_2 and HCl , wherein the time for treatment for Cl_2 and HCl obtained when the volume ratio of activated carbon to Ca(OH)_2 is one, is expressed as one.

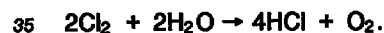
In the present invention halogen compound containing waste gases are brought into contact first with activated carbon in a granular form having particle sizes of about 6.73 to 0.55 mm (3 - 32 mesh) at a linear velocity of about 3 - 50 cm/min at ambient temperature, and then into contact with a member selected from the group consisting of an alkaline earth agent and ferric oxide (Fe_2O_3) in a granular form having particle sizes of about 6.73 to 0.55 mm (3 - 32 mesh) at a linear velocity of about 3 - 50 cm/min at ambient temperature, volume ratios of said activated carbon to the alkali agent or the ferric oxide in terms of a substantially dried base being about 2 - 4, and said alkali agent being selected from the group consisting of calcium hydroxide, calcium oxide, magnesium hydroxide and magnesium oxide.

In accordance with the present invention, a mixture of halogen containing waste gases (e.g. oxidizing gases, acidic gases and organic chlorine-containing gases) is first brought into contact with activated carbon so that the individual components are fixed by physical adsorption or reactive adsorption. Subsequently, acidic gases that are released as by-products as well as some acidic gases (e.g. HCl and SiF_4) that are difficult to remove with activated carbon are completely removed by contact with an alkaline earth agent or ferric oxide, whereby the waste gases are rendered harmless.

The activated carbon to be used in the present invention is preferably derived from coconut shells and it preferably has a specific surface area of 1000 - 1500 m^2/g . The alkaline earth agent to be used in the present invention is preferably at least one compound selected from among calcium hydroxide, calcium oxide, magnesium hydroxide and magnesium oxide. The compounds are substantially free from the problems associated with Na-based agents and hence can be used in practice with satisfactory results. Further, they undergo a mild reaction and will not generate as much heat as soda lime. Hence, the particles of such compounds will not cohere to a significant extent.

Halogen-containing gases that can be treated by the method of the present invention are those which contain at least one of the following halogen compounds: Cl_2 , F_2 , Br_2 , HCl , HBr , BCl_3 , SiF_4 , SiCl_4 , WF_6 , CCl_4 , CHCl_3 , etc.

When halogen-containing gases are brought into contact with activated carbon, organic chlorine-containing gases are fixed by physical adsorption whereas some of the oxidizing and acidic gases are fixed by reactive adsorption. At the same time, additional acidic gases are released as by-products. An example of the reaction between Cl_2 and activated carbon is expressed as follows:



As a result of reaction with activated carbon, HCl is released. Such a by-product gas and other acidic gases such as HCl and SiF_4 that are produced in the etching reaction cannot be treated with activated carbon but they can be completely fixed on fluorides or chlorides by subsequent contact with the alkaline earth agent or a ferric oxide.

In order that an undesirably high pressure loss does not occur in the passage of waste gases, the particles of those treating agents are as small as possible, desirably in the range of about 6.73 to 0.55 mm (3 - 32 mesh) and preferably about 2.83 to 1.19 mm (7 - 16 mesh), in order to ensure a large surface area.

In practice, a column may be packed with two stages of treating agents (activated carbon and ferric oxide) in about 2 - 4 volume ratios of the activated carbon to the ferric oxide; then, the waste gases are supplied into the column either downward or upward so that they are brought into contact first with the activated carbon, then with the ferric oxide.

The following examples and comparative examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

Example 1 and Comparative Examples 1 and 2

A polyacrylic vessel (40 mm ϕ) was packed with three different treating agents to a height of 50 mm and supplied with various N_2 diluted halogen-containing gases individually at a flow rate of 0.3 L/min (24 cm/min as linear velocity). The concentration of each gas at the inlet of the column was 1%. The treatment was continued until the concentration of each gas detected at the outlet exceeded its permissible level (TLV) and the throughput of treatment was determined from the cumulative volume of each gas and the amount of each treating agent packed.

The treating agents used were commercial products in a granular form having particle sizes of 2.83 to 1.19 mm (7 - 16 mesh).

The results are shown in Table 1. Activated carbon exhibited high throughputs in the treatment of oxidizing gases (e.g. Cl_2 and Br_2) and organic chlorine-containing gases (e.g. CCl_4 and CHCl_3) but it was not very effective in treating acidic gases (e.g. HCl and SiF_4). On the other hand, $\text{Ca}(\text{OH})_2$ and Fe_2O_3 exhibited high throughputs in the treatment of acidic gases but they were little effective in removing organic chlorine-containing gases. They also were not very effective in treating oxidizing gases.

When Cl_2 was treated with activated carbon, HCl was detected at the outlet before Cl_2 was detected and this indicated the release of HCl as the result of reaction with activated carbon.

Table 1

		Example 1 Activated carbon	Comparative Example 1 $\text{Ca}(\text{OH})_2$	Comparative Example 2 Fe_2O_3
Through-put (L/L)	Cl_2	48	38	2.0
	Br_2	70	1.6	3.7
	HCl	9.5	70	90
	SiF_4	8.7	24	35
	CCl_4	40	0	0
	CHCl_3	40	0	0

Examples 2 and 3 and Comparative Examples 3 - 5

A polyacrylic vessel (40 mm ϕ) was divided into two stages, one of which was packed with activated carbon to a height of 200 mm and the other being packed with Fe_2O_3 to a height of 100 mm (Example 2). Another polyacrylic vessel (40 mm ϕ) was divided into two stages, one of which was packed with activated carbon to a height of 200 mm and the other being packed with $\text{Ca}(\text{OH})_2$ to a height of 100 mm (Example 3). In Comparative Examples 3 - 5, polyacrylic vessels (40 mm ϕ) were packed with activated carbon, $\text{Ca}(\text{OH})_2$ and Fe_2O_3 , respectively, to a height of 300 mm. The treating agents, i.e., activated carbon, $\text{Ca}(\text{OH})_2$ and Fe_2O_3 , were of the same types as used in Example 1 and Comparative Examples 1 and 2.

A N_2 diluted gaseous mixture of Cl_2 and SiF_4 was supplied into each of the packed vessels at a flow rate of 0.3 l/min. In Examples 2 and 3, the feed gas was introduced in such a way that it would first pass through the layer of activated carbon. The concentrations of Cl_2 and SiF_4 were each 1% at the inlet of the vessel.

The time of treatment required for Cl_2 and acidic gases to be detected at the outlet of the vessel was measured and the results are shown in Table 2. Being packed in the same amount, the combination of activated carbon and Fe_2O_3 could be used for the longest time of treatment and the combination of activated carbon and $\text{Ca}(\text{OH})_2$ could be used for the second longest time. Hence, it was verified that the combination of activated carbon and Fe_2O_3 or $\text{Ca}(\text{OH})_2$ was more effective than using those treating agents individually.

Example 2

		Treating agent	Amount of packing (ml)	Time of treatment (min)
5	Example 2	First stage Second stage activated carbon Fe_2O_3	250 125	1500
10	Example 3	First stage Second stage activated carbon $\text{Ca}(\text{OH})_2$	250 125	1400
15	Comparative Example	3 Activated carbon	375	700
		4 $\text{Ca}(\text{OH})_2$	375	900
		5 Fe_2O_3	375	60

Example 4

20 In order to establish the optimum volume ratio of charging of activated carbon to an alkaline earth agent or ferric oxide, treating agents having various volume ratios of the activated carbon to $\text{Ca}(\text{OH})_2$ were tested on a waste gas containing halogen compounds.

25 A polyacrylic vessel (40 mmI, internal volume: 250 ml) was charged into two stages with the volume ratios of the activated carbon to $\text{Ca}(\text{OH})_2$ being 5 - 1. The treating agents, i.e., activated carbon and $\text{Ca}(\text{OH})_2$ were of the same type as used in Example 1.

30 A N_2 diluted gaseous mixture Cl_2 and HCl was supplied into each of the packed vessels at a flow rate of 0.3 l/min. The feed gas was introduced in such a way that it would first pass through the layer of activated carbon and then pass through the layer of $\text{Ca}(\text{OH})_2$ in that order. The concentrations of Cl_2 and HCl were each 1% at the inlet of the vessel. The time of treatment required for Cl_2 and HCl gases to be detected at the outlet of the vessel was measured and the results are shown in Fig. 1 wherein the time for treatment for Cl_2 and HCl , obtained when the volume ratio of activated carbon to $\text{Ca}(\text{OH})_2$ in terms of a substantially dried base is one, is expressed as one. From the Fig. 1, it was verified that volume ratios of the activated carbon to $\text{Ca}(\text{OH})_2$ of about 2 - 4 provide greater treating effects.

35 According to the present invention, a plurality of halogen-containing gases having different properties can be effectively treated even if they are discharged simultaneously as waste gases. Further, the treating agents used in the method of the present invention have such a high throughput that they need not be replaced for a prolonged period of time.

Claims

- 40 1. A method for removing halogens or halogen compounds from a waste gas, wherein said waste gas is first passed through activated carbon in a granular form having particle sizes of 6.73 to 0.55 mm (3 to 32 mesh) at a linear velocity of 3 - 50 cm/min at ambient temperature, and then through an alkaline earth agent selected from the group consisting of calcium hydroxide, calcium oxide, magnesium hydroxide and magnesium oxide or ferric oxide, said alkaline earth agent or said ferric oxide having granular form and particle sizes of 6.73 to 0.55 mm (3 to 32 mesh), at a linear velocity of 3 to 50 cm/min at ambient temperature, the volume ratio of said activated carbon to said alkaline earth agent or said ferric oxide on a dry basis being 2 to 4.
- 50 2. A method according to claim 1, wherein activated carbon, alkaline earth agent and ferric oxide having particle sizes of 2.83 to 1.19 mm (7 to 16 mesh) are used.
- 55 3. A method according to claim 1, wherein activated carbon having a surface area of 1000 to 1500 m^2/g is used.

Example 2

		Treating agent	Amount of packing (ml)	Time of treatment (min)
Example 2	First stage Second stage	activated carbon Fe_2O_3	250 125	1500
Example 3	First stage Second stage	activated carbon $\text{Ca}(\text{OH})_2$	250 125	1400
Comparative Example	3	Activated carbon	375	700
	4	$\text{Ca}(\text{OH})_2$	375	900
	5	Fe_2O_3	375	60

Example 4

In order to establish the optimum volume ratio of charging of activated carbon to an alkaline earth agent or ferric oxide, treating agents having various volume ratios of the activated carbon to $\text{Ca}(\text{OH})_2$ were tested on a waste gas containing halogen compounds.

A polyacrylic vessel (40 mm l, internal volume: 250 ml) was charged into two stages with the volume ratios of the activated carbon to $\text{Ca}(\text{OH})_2$ being 5 - 1. The treating agents, i.e., activated carbon and $\text{Ca}(\text{OH})_2$ were of the same type as used in Example 1.

A N_2 diluted gaseous mixture Cl_2 and HCl was supplied into each of the packed vessels at a flow rate of 0.3 l/min. The feed gas was introduced in such a way that it would first pass through the layer of activated carbon and then pass through the layer of $\text{Ca}(\text{OH})_2$ in that order. The concentrations of Cl_2 and HCl were each 1% at the inlet of the vessel. The time of treatment required for Cl_2 and HCl gases to be detected at the outlet of the vessel was measured and the results are shown in Fig. 1 wherein the time for treatment for Cl_2 and HCl , obtained when the volume ratio of activated carbon to $\text{Ca}(\text{OH})_2$ in terms of a substantially dried base is one, is expressed as one. From the Fig. 1, it was verified that volume ratios of the activated carbon to $\text{Ca}(\text{OH})_2$ of about 2 - 4 provide greater treating effects.

According to the present invention, a plurality of halogen-containing gases having different properties can be effectively treated even if they are discharged simultaneously as waste gases. Further, the treating agents used in the method of the present invention have such a high throughput that they need not be replaced for a prolonged period of time.

Claims

1. A method for removing halogens or halogen compounds from a waste gas, wherein said waste gas is first passed through activated carbon in a granular form having particle sizes of 6.73 to 0.55 mm (3 to 32 mesh) at a linear velocity of 3 - 50 cm/min at ambient temperature, and then through an alkaline earth agent selected from the group consisting of calcium hydroxide, calcium oxide, magnesium hydroxide and magnesium oxide or ferric oxide, said alkaline earth agent or said ferric oxide having granular form and particle sizes of 6.73 to 0.55 mm (3 to 32 mesh), at a linear velocity of 3 to 50 cm/min at ambient temperature, the volume ratio of said activated carbon to said alkaline earth agent or said ferric oxide on a dry basis being 2 to 4.
2. A method according to claim 1, wherein activated carbon, alkaline earth agent and ferric oxide having particle sizes of 2.83 to 1.19 mm (7 to 16 mesh) are used.
3. A method according to claim 1, wherein activated carbon having a surface area of 1000 to 1500 m^2/g is used.



Patentansprüche

1. Verfahren zum Entfernen von Halogenen oder Halogenverbindungen aus einem Abgas, bei dem das Abgas zuerst mit einer Lineargeschwindigkeit von 3-50 cm/min bei Raumtemperatur durch aktivierte Kohle in körniger Form mit Teilchengrößen von 6,73 bis 0,55 mm (3 bis 32 mesh) und dann mit einer Lineargeschwindigkeit von 3 bis 50 cm/min bei Raumtemperatur durch ein Erdalkaliagens, das ausgewählt ist aus der Gruppe bestehend aus Calciumhydroxid, Calciumoxid, Magnesiumhydroxid und Magnesiumoxid, oder Eisen(III)-oxid hindurchgeführt wird, wobei das Erdalkaliagens oder das Eisen(III)-oxid eine körnige Form und Teilchengrößen von 6,73 bis 0,55 mm (3 bis 32 mesh) aufweist und das Volumenverhältnis von aktivierter Kohle zu Erdalkaliagens oder Eisen(III)-oxid auf Trockenbasis 2 bis 4 beträgt.
2. Verfahren nach Anspruch 1, bei dem aktivierte Kohle, Erdalkaliagens und Eisen(III)-oxid mit Teilchengrößen von 2,83 bis 1,19 mm (7 bis 16 mesh) eingesetzt werden.
3. Verfahren nach Anspruch 1, bei dem aktivierte Kohle mit einer Oberfläche von 1000 bis 1500 m²/g eingesetzt wird.

Revendications

1. Procédé pour éliminer des halogènes ou des composés halogénés d'un gaz résiduaire, dans lequel on fait passer ledit gaz résiduaire d'abord à travers du charbon actif sous une forme granulaire avec des tailles de particules de 6,73 à 0,55 mm (3 à 32 mesh), à une vitesse linéaire de 3 à 50 cm/min à température ambiante, puis à travers un agent alcalinoterreux sélectionné dans le groupe constitué de l'hydroxyde de calcium, de l'oxyde de calcium, de l'hydroxyde de magnésium et de l'oxyde de magnésium, ou de l'oxyde ferrique, ledit agent alcalino-terreux ou ledit oxyde ferrique ayant une forme granulaire et des tailles de particules de 6,73 à 0,55 mm (3 à 32 mesh), à une vitesse linéaire de 3 à 50 cm/min à température ambiante, le rapport volumique dudit charbon actif audit agent alcalinoterreux ou audit oxyde ferrique sur une base sèche étant compris entre 2 et 4.
2. Procédé selon la revendication 1, dans lequel on utilise du charbon actif, un agent alcalinoterreux et de l'oxyde ferrique ayant des tailles de particules de 2,83 à 1,19 mm (7 à 16 mesh).
3. Procédé selon la revendication 1, dans lequel on utilise du charbon actif présentant une surface spécifique de 1000 à 1500 m²/g.

