

DESCRIPTION



159159

EXHAUST GAS TREATMENT PROCESS AND TREATMENT SYSTEM

5

Technical Field

The present invention relates to an exhaust gas treatment process and treatment apparatus. More particularly, the invention relates to a process and apparatus for treatment of an exhaust gas, containing fluorine gas or halogen fluoride gas, which is emitted from the etching or the cleaning steps of semiconductor fabrication processes, and to a semiconductor device fabrication process which employs the process and apparatus.

Background Art

The exhaust gas emitted from various steps in the fabrication of semiconductors contains gases such as semiconductor material gas, etching gas or cleaning gas, and these gases are often harmful. They sometimes include environmentally unfriendly gases and, therefore, exhaust gas containing such components cannot be directly emitted into the atmosphere.

Methods for exhaust gas treatment are widely known, and include:

(1) wet abatement methods whereby neutralizing agents such as caustic soda (sodium hydroxide) are used for oxidation reaction or neutralization reaction,

(2) reactive decomposition methods using catalyst beds,

(3) dry abatement methods based on adsorption onto oxides or the like,

(4) thermal decomposition methods incorporating electrical heaters, and

(5) combustion abatement methods, and such methods are employed depending on the desired



G00002

features.

Recent years have seen an increasing diversity of harmful components contained in exhaust gases emitted from semiconductor fabrication processes, as well as
5 markedly larger sizes of wafers and liquid crystal panels and correspondingly larger fabricating apparatuses, resulting in vastly greater volumes of gases used in the fabrication processes. In addition, with increasing use of multi-chambers for sheet-fed apparatuses and the
10 concomitant greater complexity of fabrication processes, it often becomes necessary to simultaneously treat large volumes of exhaust gases from different pathways, or to safely treat exhaust gases, streaming in the same pathway while changing the time cycle, with vastly differing
15 properties using the same abatement system. In recent years, therefore, various thermal treatment-type abatement methods, such as combustion-type or thermal decomposition-type methods, have been investigated as abatement methods whereby flammable fuel gases or the
20 like are burned at high temperature to convert toxic components in the exhaust gas or the environmentally-unfriendly exhaust gas components to harmless substances, or to convert them to substances that can be easily treated.

25 However, particularly in the case of combustion-type abatement systems, the exhaust gas emitted from the semiconductor fabrication process is subjected to combustion treatment at high temperature together with fuel gases such as utility gas, LPG, methane or the like
30 and with supporting gases such as air and oxygen, and this results in the generation of NO_x gases, as by-products, from the elemental nitrogen in the exhaust gas or the nitrogen gas in the air.

NO_x gases are often generated, in burned exhaust
35 gas, at very high concentrations of 1-30%, depending on the apparatus and combustion conditions employed, and several methods have been investigated to limit the

concentration to the TLV (25 ppm NO, 3 ppm NO₂). For example, Japanese Unexamined Patent Publication No. 2001-193918 describes studies of combustion chamber shapes and nozzle shapes to reduce generation of NO_x. However, when
5 burning exhaust gas containing NF₃ gas which is used in large quantities for etching and cleaning steps, the generation of NO_x is particularly high, creating a situation in need of improvement.

On the other hand, cleaning has also been used, in
10 semiconductor fabrication processes using fluorine gas or halogen fluoride gases, or mixtures thereof, as cleaning gases exhibiting higher performance. For example, J. Appl. Phys., p.2939, 56(10), No.15, 1984 reports on research indicating that the cleaning performance of
15 fluorine gas and halogen fluoride gases is superior to that of NF₃ gas.

Nevertheless, fluorine gas or halogen fluoride gases are highly active, strong oxidizers with high chemical reactivity and therefore often react with oxidizing
20 substances at ordinary temperature resulting in ignition, while they are also highly corrosive to apparatus materials. The apparatus materials must therefore be strictly selected from among specific highly corrosion-resistant metals, and be free from oils and water;
25 moreover, tetrafluoroethylene resins which are widely used as highly corrosion-resistant resins for semiconductor fabrication apparatuses are often unsuitable for the given conditions of use.

As abatement systems for fluorine gas or halogen
30 fluoride gases such as chlorine trifluoride there are used wet absorption systems which accomplish neutralizing absorption with scrubbers employing alkali aqueous solutions such as caustic soda or caustic potash, or dry abatement systems which accomplish adsorption removal
35 with a solid adsorbent such as active alumina or soda lime. All such methods, however, have a drawback in that they do not allow treatment of exhaust gas containing

high concentrations of fluorine gas or halogen fluoride gases. Additional problems encountered when employing a wet abatement system such as an alkali scrubber in cases of large volumes of fluorine gas or halogen fluoride gases, is that the absorption tower must be increased in size, waste treatment of the absorption solution becomes complicated, and running costs are higher. With dry decomposition abatement systems or adsorption removal abatement systems, not only is it difficult to set up large flow abatement systems, but the increased frequency of replacement of the solid decomposer and adsorbent results in drastically higher operating cost, while the added maintenance procedures tend to lead to safety management problems.

Disclosure of the Invention

In light of this background, it is an object of the present invention to provide an abatement process and system which allows treatment of exhaust gases emitted from semiconductor fabrication processes, containing fluorine gas or halogen fluoride gases at high concentrations or in large amounts, and which is safe and energy efficient and can accomplish abatement in a more efficient manner.

As mentioned above, when fluorine gas or halogen fluoride gas is used in a semiconductor fabrication process the exhaust gas is treated alone by a special abatement system, but the process of the invention overcomes the problems described above by allowing semiconductor devices to be increased in size and complexity and be provided with multiple functions, while reducing the installation space for the abatement system.

As a result of much diligent research directed toward solving the aforementioned problems, the present inventors have completed the present invention upon finding that the aforementioned problems can be solved by using a treatment process whereby exhaust gas containing

fluorine gas or halogen fluoride gases emitted from etching or cleaning steps is introduced into a combustion apparatus equipped with a combustion chamber having a fluoride passivation film formed on its surface.

5 In other words, the invention provides an exhaust gas treatment process which comprises burning exhaust gas containing fluorine gas or halogen fluoride gases emitted from etching or cleaning steps, in a combustion chamber having a fluoride passivation film formed on its surface.

10 The fluoride passivation film is preferably composed of nickel fluoride.

 The concentration of fluorine gas or halogen fluoride gases is preferably no greater than 5 vol%.

15 The content of nitrogen oxides in the exhaust gas after combustion is preferably less than 5 volppm.

 The invention further provides an exhaust gas treatment system equipped with an exhaust gas introduction port, a fuel introduction port, a precombustion chamber, a combustion chamber, an air
20 introduction port and an exhaust duct, and having a fluoride passivation film formed on at least the surface of the combustion chamber.

 According to a preferred embodiment, the combustion chamber is formed of at least one type of material
25 selected from the group consisting of nickel, nickel-rich alloys and Monel metal, and a fluoride passivation film is formed on the surface of the material.

 According to another preferred embodiment, the combustion chamber is formed of at least one type of
30 material selected from the group consisting of stainless steel and steel materials, with the surface of the material having a thin-film composed of nickel, nickel alloy electroplating, electrocast plating or nickel alloy electroless plating or a ceramic thin-film composed of
35 alumina or aluminum nitride, and a fluoride passivation film formed over the surface of the thin-film.

 The invention still further provides a semiconductor

device fabrication process comprising an etching or
cleaning step employing fluorine gas or halogen fluoride
gas as the etching gas or cleaning gas and an abatement
step wherein the gas containing fluorine gas or halogen
5 fluoride gas emitted from the previous step is burned,
the abatement step being carried out in a combustion
chamber having a fluoride passivation film formed on its
surface.

10 The fluoride passivation film is preferably composed
of nickel fluoride.

Brief Description of the Drawings

Fig. 1 is a schematic view showing an embodiment of
a treatment system for carrying out the exhaust gas
15 treatment process of the invention.

In this schematic drawing, 1 is process exhaust gas,
2 is diluting gas, 3 is supporting gas, 4 is flammable
gas for combustion, 5 is air, 6 is atmospheric discharge
gas, 7 is a precombustion chamber, 8 is a combustion
20 chamber, 9 is a combustion gas cooling apparatus, 10 is
an alkali scrubber and 11 is an exhaust blower.

Best Mode for Carrying Out the Invention

Preferred embodiments of the invention will now be
25 explained in detail.

In the exhaust gas treatment process of the
invention, exhaust gas containing fluorine gas or halogen
fluoride gases emitted from etching or cleaning steps is
burned in a combustion chamber having a fluoride
30 passivation film formed on its surface. That is, the
invention encompasses a treatment to render harmless
exhaust gas emitted from semiconductor fabrication
processes including fluorine gas or halogen fluoride
gases as well as gases such as SiH_4 used as film-forming
35 gases or other gases, at a prescribed temperature.

The treatment process of the invention can notably
reduce the amount of carbon dioxide and NO_x gases as

decomposition by-products emitted from abatement systems, by allowing an adequate harmless-rendering treatment to be carried out under conditions with reduced fuel feed and lower combustion temperature compared to the ordinary combustion conditions when no fluorine gas or halogen fluoride gases are present, or in other words, it permits treatment to be carried out on compounds which can be easily rendered harmless so that operation may be carried out under such suitable conditions.

According to the invention, a combustion-type abatement system is used for simultaneous abatement treatment of film-forming gases such as SiH_4 , SiH_2Cl_2 , NH_3 , PH_3 , WF_6 , $\text{Si}(\text{OC}_2\text{H}_5)_4$, NF_3 , H_2 , B_2H_6 , CH_4 , C_2H_2 and the like, cleaning gases or other gas components emitted in semiconductor fabrication processes, which are commonly used in steps of semiconductor fabrication, along with the fluorine gas and halogen fluoride gases. In such cases, the components to be treated in the exhaust gas may be fluorine gas or halogen fluoride gas alone. The concentration of the fluorine gas or halogen fluoride gas in the exhaust gas is preferably no greater than 5 vol%.

Operation of the combustion-type abatement system of the invention can accomplish harmless rendering of toxic gas components and conversion to substances which are easily removed by decomposition, under operating conditions with 10-30% lower fuel feed and a combustion temperature of more than 50°C below the combustion conditions employed when the introduced exhaust gas contains no fluorine gas or halogen fluoride gases (for example, combustion conditions necessary for decomposition of nitrogen trifluoride gas). By utilizing the treatment process of the invention, therefore, it is possible to reduce the amount of carbon dioxide, which is decomposition by-products emitted from the abatement system, in proportion to the amount of reduction in fuel gas used. The lower combustion temperature also notably reduces the generation of NO_x gases, making it possible

to achieve NO_x generation of less than 5 volppm.

Operation at a lower combustion temperature is an obvious major advantage in terms of safety in operation management and, as the surface temperature of the machinery materials at the sections where the exhaust gas is burned or in the previous chamber zones is lower, the degree of corrosion of the apparatus materials is significantly reduced. This allows the system to be maintained less frequently and provides an obvious cost advantage in terms of prolonging the life of the system.

The combustion treated exhaust gas is finally fed to wet abatement equipment such as an alkali scrubber connected to the exhaust duct of the combustion-type abatement tower for absorption treatment of hydrogen halides such as hydrogen fluoride, NO_x or other decomposed substances such as silicon tetrafluoride.

The exhaust gas treatment system of the invention is equipped with an exhaust gas introduction port, a fuel introduction port, a precombustion chamber, a combustion chamber, an air introduction port and an exhaust duct, and a fluoride passivation film is formed on at least the surface of the combustion chamber.

Fig. 1 shows an embodiment of a treatment system for carrying out the exhaust gas treatment process of the invention, which employs a combustion decomposition treatment system whereby a mixed exhaust gas containing fluorine gas or halogen fluoride gases is passed through a flame wall and introduced into a supporting gas vortex stream.

The material of the system shown in Fig. 1 must be a highly corrosion resistant material to withstand a flow of fluorine gas or halogen fluoride gases. As the combustion chamber 8 is at high temperature due to the heat of combustion, it is preferably formed of nickel or a nickel-rich alloy or Monel metal, and a fluoride passivation film is preferably formed on its surface. As another preferred mode, the combustion chamber 8 may be

formed of ordinary stainless steel or a steel material,
with the surface thereof having a thin-film composed of
nickel, nickel alloy electroplating, electrocast plating
or nickel alloy electroless plating or a ceramic thin-
5 film composed of alumina or aluminum nitride, which are
materials with excellent fluorine gas resistance and heat
resistance for spray coating or the like, and a fluoride
passivation film formed over the surface of the thin-
film. For nickel plating, a nickel-boron based
10 electroless plating treatment is preferred to achieve
excellent heat resistance. The precombustion chamber 7
also preferably has a fluoride passivation film formed on
its surface in the same manner.

The system parts are preferably subjected to
15 passivation treatment with fluorine gas beforehand. The
proximity of the zone in which the exhaust gas is burned
is exposed to particularly high temperatures by heat
radiation and heat transmission from the combustion zone.
These areas are therefore preferably constructed with
20 nickel or a nickel-rich alloy or Monel metal. An
ordinary stainless steel or steel material may be
subjected to anti-corrosion treatment such as nickel
electroplating, electrocast plating or nickel alloy
electroless plating. The system members are also
25 preferably subjected to passivation treatment with
fluorine gas, beforehand, in the same manner.

The passivation treatment with fluorine gas may be
according to a publicly known method, and for example,
the method described in Japanese Unexamined Patent
30 Publication No. 11-92912 may be used. Specifically, for
example, the surface of the nickel used for the system
parts may be first subjected to forced oxidation and the
oxidized film then reacted with fluorine gas to form a
fluoride passivation film. As another example where the
35 system part used is a stainless steel surface with a
nickel thin-film formed thereover, it may be subjected to
oxidation and fluorination treatment in the same manner

to form a fluoride passivation film on the surface.

According to the present invention as described above, exhaust gas containing fluorine gas or halogen fluoride gases which is emitted from etching or cleaning steps is introduced into a combustion apparatus equipped with a combustion chamber having a fluoride passivation film formed on its surface, and combustion of the exhaust gas therein allows efficient treatment of the exhaust gas.

The invention further provides a semiconductor device fabrication process comprising an etching or cleaning step employing fluorine gas or halogen fluoride gases as the etching gas or cleaning gas and an abatement step wherein the gas containing fluorine gas or halogen fluoride gases emitted from the previous step is burned, the abatement step being carried out in a combustion chamber having a fluoride passivation film formed on its surface.

The present invention will now be explained in greater detail through the following examples and comparative examples, with the understanding that these examples are in no way limitative on the invention.

Example 1

The stainless steel combustion chamber of a combustion-type abatement system and the parts surrounding it were subjected to nickel plating and fluoride passivation treatment, and a combustion-abatement experiment was conducted using fluorine gas. The combustion-type abatement system operating conditions and fluorine introduction conditions are shown in Table 1, and the results of compositional analysis of the exhaust gas emitted after combustion and abatement are shown in Table 2. The combustion chamber temperature was measured with a thermocouple attached to the combustion chamber outer wall. The nitrogen monoxide and nitrogen dioxide concentrations in the exhaust gas after combustion were measured with a gas detector tube, and

the hydrogen fluoride gas concentration was measured by infrared spectroscopy. The nitrogen trifluoride was measured using a detector. Sampling was performed with an aqueous potassium iodide solution, the fluorine gas concentration of the sample solution was measured by titration with aqueous sodium thiosulfate, and the metal concentration of the sample solution was measured by inductively coupled plasma-atomic emission spectroscopy.

Table 1

Fuel methane flow rate	Supporting air flow rate	Cooling air emission flow	Fluorine flow rate	Diluting nitrogen flow rate	Combustion chamber temperature
(L/min)	(L/min)	(m ³ /min)	(L/min)	(L/min)	(°C)
25	30	30	13.5	240	305-315

Table 2

Calculated hydrogen fluoride gas concentration	Measured hydrogen fluoride gas concentration	Measured fluorine concentration	Measured nitrogen monoxide concentration	Measured nitrogen dioxide concentration	Other combustion reaction products
(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	
900	900	<10	<0.1	<0.1	Not detected

As can be seen in Table 2, the exhaust gas after combustion contained absolutely no nitrogen monoxide or nitrogen dioxide, and the total amount of fluorine introduced into the combustion-type abatement system reacted and was converted to hydrogen fluoride gas. The absence of combustion reaction products other than hydrogen fluoride gas, water vapor and carbon dioxide in the combustion exhaust gas was confirmed by infrared spectroscopy and inductively coupled plasma-atomic emission spectroscopy of the sample solution.

Comparative Example 1

A combustion-abatement experiment was conducted using nitrogen trifluoride as the introduction gas instead of fluorine gas, with a nitrogen trifluoride flow

rate of 9.0 L/min. The combustion-type abatement system operating conditions and nitrogen trifluoride introduction conditions are shown in Table 3, and the results of compositional analysis of the combustion exhaust gas are shown in Table 4.

Table 3

Fuel methane flow rate	Supporting air flow rate	Cooling air emission flow	Nitrogen trifluoride flow rate	Diluting nitrogen flow rate	Combustion chamber temperature
(L/min)	(L/min)	(m ³ /min)	(L/min)	(L/min)	(°C)
30	311	30	9.0	240	350-360

Table 4

Calculated hydrogen fluoride gas concentration	Measured hydrogen fluoride gas concentration	Measured nitrogen trifluoride concentration	Measured nitrogen monoxide concentration	Measured nitrogen dioxide concentration	Other combustion reaction products
(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	
900	900	<1	72	12	not detected

The operating conditions shown in Table 3 are indicated as the combustion operating conditions under which no nitrogen trifluoride gas was detected in the exhaust gas. Thus, the total amount of the nitrogen trifluoride introduced into the combustion-type abatement system reacted and was converted to hydrogen fluoride gas, but nitrogen monoxide and nitrogen dioxide were both produced in the exhaust gas far in excess of permissible concentrations.

Comparative Example 2

A combustion-abatement experiment was conducted in the same manner as Example 1, except that the fuel methane flow rate was increased to 30 L/min and the combustion chamber temperature was increased to above 350°C. The combustion-type abatement system operating conditions and fluorine introduction conditions are shown in Table 5, and the results of compositional analysis of

the combustion exhaust gas are shown in Table 6.

Table 5

Fuel methane flow rate	Supporting air flow rate	Cooling air emission flow	Fluorine flow rate	Diluting nitrogen flow rate	Combustion chamber temperature
(L/min)	(L/min)	(m ³ /min)	(L/min)	(L/min)	(°C)
30	341	30	13.5	240	360-370

5

Table 6

Calculated hydrogen fluoride gas concentration	Measured hydrogen fluoride gas concentration	Measured fluorine concentration	Measured nitrogen monoxide concentration	Measured nitrogen dioxide concentration	Other combustion reaction products
(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	
900	850	<10	0.5	1.0	Not detected

As can be seen in Table 6, part of the fluorine introduced into the combustion-type abatement system was consumed by reaction with the surface of the members of combustion chamber and its surrounding area without being emitted as hydrogen fluoride. A portion thereof was confirmed to have formed metal fluorides as a fine powder. The results of analysis of the exhaust gas also confirmed production of nitrogen monoxide and nitrogen dioxide.

Comparative Example 3

A combustion-abatement experiment was conducted in the same manner as Example 1, except that stainless steel (SUS304 material) was used by itself for the combustion chamber without coating (fluoride passivation treatment). The combustion-type abatement system operating conditions and fluorine introduction conditions are shown in Table 7, and the results of compositional analysis of the combustion exhaust gas are shown in Table 8.

Table 7

Fuel methane flow rate	Supporting air flow rate	Cooling air emission flow	Fluorine flow rate	Diluting nitrogen flow rate	Combustion chamber temperature
(L/min)	(L/min)	(m ³ /min)	(L/min)	(L/min)	(°C)
25	308	30	13.5	240	310-320

Table 8

5

Calculated hydrogen fluoride gas concentration	Measured hydrogen fluoride gas concentration	Measured fluorine concentration	Measured nitrogen monoxide concentration	Measured nitrogen dioxide concentration	Other combustion reaction products
(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	
900	700	<10	<0.1	<0.1	chromium compounds

As can be seen in Table 8, a significant proportion of the fluorine introduced into the combustion-type abatement system was not confirmed as hydrogen fluoride, and there was no production of gas components such as chromium fluoride.

Comparative Example 4

A combustion-abatement experiment was conducted in the same manner as the example except that the combustion chamber coating was nickel plating alone and no fluorine treatment was carried out. The combustion-type abatement system operating conditions and fluorine introduction conditions are shown in Table 9, and the results of compositional analysis of the combustion exhaust gas are shown in Table 10.

Table 9

Fuel methane flow rate	Supporting air flow rate	Cooling air emission flow	Fluorine flow rate	Diluting nitrogen flow rate	Combustion chamber temperature
(L/min)	(L/min)	(m ³ /min)	(L/min)	(L/min)	(°C)
25	299	30	13.5	240	310-320

Table 10

Calculated hydrogen fluoride gas concentra- tion	Measured hydrogen fluoride gas concentra- tion	Measured fluorine concentra- tion	Measured nitrogen monoxide concentra- tion	Measured nitrogen dioxide concentra- tion	Other combustion reaction products
(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	
900	820	<10	<0.1	<0.1	Not detected

As can be seen in Table 10, the fluorine gas introduced into the combustion-type abatement system was slightly consumed by reaction with the combustion apparatus material surface.

Comparative Example 5

A combustion-abatement experiment was conducted in the same manner as Example 1 except that nitrogen trifluoride was used as the introduction gas and the nitrogen trifluoride flow rate was 9.0 L/min. Also, the surface treatment of the combustion chamber was stainless steel (SUS304) alone. The combustion-type abatement system operating conditions and nitrogen trifluoride introduction conditions are shown in Table 11, and the results of compositional analysis of the combustion exhaust gas are shown in Table 12.

Table 11

Fuel methane flow rate	Supporting air flow rate	Cooling air emission flow	Nitrogen trifluoride flow rate	Diluting nitrogen flow rate	Combustion chamber temperature
(L/min)	(L/min)	(m ³ /min)	(L/min)	(L/min)	(°C)
30	305	30	9.0	240	350-360

Table 12

Calculated hydrogen fluoride gas concentra- tion	Measured hydrogen fluoride gas concentra- tion	Measured nitrogen trifluoride concentra- tion	Measured nitrogen monoxide concentra- tion	Measured nitrogen dioxide concentra- tion	Other combustion reaction products
(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	(vol-ppm)	
900	860	<1	70	11	Not detected

As can be seen in Table 12, the nitrogen trifluoride introduced into the combustion-type abatement system reacted and was converted to hydrogen fluoride gas, but a portion thereof disappeared by reaction with the apparatus material while nitrogen monoxide and nitrogen dioxide were both produced far in excess of permissible concentrations.

After completing operation of the combustion and abatement, the metal surfaces inside the combustion chambers of Example 1 and Comparative Examples 1, 2, 3, 4 and 5 were analyzed. The measurement was conducted with an energy dispersive X-ray spectroscope.

Table 13 Detected metals (mass%)

	Ni	Fe	Cr	Other
Example 1	100	0	0	0
Comp. Ex. 1	100	0	0	0
Comp. Ex. 2	100	0	0	0
Comp. Ex. 3	7.7	75.8	16.5	0
Comp. Ex. 4	100	0	0	0
Comp. Ex. 5	7.5	73.5	19	0
Reference SUS316L	12	69.5	16	Mo 2.5
Reference SUS304	8	74	18	0

The combustion chambers which were surface treated with nickel had no significant damage and exhibited high corrosion resistance against fluorine gas and nitrogen trifluoride.

The inner surfaces of the precombustion chambers were also subjected to metal surface analysis after the combustion-abatement experiments of Example 1 and Comparative Examples 1, 2, 3, 4 and 5. The measurement

was conducted with an energy dispersive X-ray spectroscope.

Table 14 Detected metals (mass%)

	Ni	Fe	Cr	Other
Example 1	100	0	0	0
Comp. Ex. 1	100	0	0	0
Comp. Ex. 2	100	0	0	0
Comp. Ex. 3	7.9	88.1	7.9	0
Comp. Ex. 4	100	0	0	0
Comp. Ex. 5	9.6	75.8	14.7	0
Reference SUS316L	12	69.5	16	Mo 2.5
Reference SUS304	8	74	18	0

Comparative Example 3 was confirmed to have considerable loss of Cr from the material. The Cr concentration was slightly lower in Comparative Example 5 as well. Microscopic observation revealed cracks and peeling of the fluoride formed film, by formation and gasification of Cr fluorides as well as by secondary fluoride-forming reactions converting the stainless steel material Fe from the bivalent to trivalent form.

Upon examining the condition of damage of the stainless steel of the combustion chambers and precombustion chambers, in comparing fluorine gas and nitrogen trifluoride, the change in Cr concentration in Comparative Example 3 in which fluorine gas was burned was greater, and the appearance was also notably impaired.

When the stainless steel damage conditions of the combustion chambers and precombustion chambers were compared, the precombustion chambers all had greater changes in Cr concentration than the combustion chambers, whether with fluorine gas or nitrogen trifluoride, and the appearances were also notably impaired. This is attributed to predominance of oxidation reaction by oxidizing flame during combustion of the fuel gas in the combustion chamber, and particularly at the wall sections.

Industrial Applicability

As explained above, by using the treatment process of the invention, it is possible to accomplish treatment of fluorine gas or halogen fluoride gases when these are
5 emitted at high concentration or high volume, or when they are in combination with other gases having differing properties, to accomplish simultaneous treatment using the same abatement system. The process of the invention is preferably used in a semiconductor fabrication process
10 and, because, it allows efficient and economical abatement treatment with due consideration to safety and preservation of the environment, it has high potential value for industry.

CLAIMS

1. An exhaust gas treatment process which comprises burning exhaust gas containing fluorine gas or halogen fluoride gases emitted from etching or cleaning steps in a combustion chamber having a fluoride passivation film formed on its surface.

2. The process as claimed in claim 1, wherein the fluoride passivation film is composed of nickel fluoride.

3. The process as claimed in claim 1 or 2, wherein the concentration of fluorine gas or halogen fluoride gases is no greater than 5 vol%.

4. The process as claimed in any one of claims 1 to 3, wherein the content of nitrogen oxides in the exhaust gas after combustion is less than 5 volppm.

5. An exhaust gas treatment system equipped with an exhaust gas introduction port, a fuel introduction port, a precombustion chamber, a combustion chamber, an air introduction port and an exhaust duct, and having a fluoride passivation film formed on at least the surface of the combustion chamber.

6. The system as claimed in claim 5, wherein the combustion chamber is formed of at least one type of material selected from the group consisting of nickel, nickel-rich alloys and Monel metal, and a fluoride passivation film is formed on the surface of the material.

7. The system as claimed in claim 5, wherein the combustion chamber is formed of at least one type of material selected from the group consisting of stainless steel and steel materials, with the surface of the material having a thin-film composed of nickel, nickel alloy electroplating, electrocast plating or nickel alloy electroless plating or a ceramic thin-film composed of alumina or aluminum nitride, and a fluoride passivation film, formed over the surface of the thin-film.

8. A semiconductor device fabrication process comprising an etching or cleaning step employing fluorine

gas or halogen fluoride gas as the etching gas or
cleaning gas and an abatement step wherein the gas
containing fluorine gas or halogen fluoride gases emitted
from the previous step is burned, the abatement step
5 being carried out in a combustion chamber having a
fluoride passivation film formed on its surface.

9. The process as claimed in claim 8, wherein the
fluoride passivation film is composed of nickel fluoride.

10. The process of claim 8, wherein the combustion
chamber is formed of at least one type of material
selected from the group consisting of nickel, nickel-rich
alloys and Monel metal, and a fluoride passivation film
is formed on the surface of the material.

11. The process as claimed in claim 8, wherein the
15 combustion chamber is formed of at least one type of
material selected from the group consisting of stainless
steel and steel materials, with the surface of the
material having a thin-film composed of nickel, nickel
alloy electroplating, electrocast plating or nickel alloy
20 electroless plating or a ceramic thin-film composed of
alumina or aluminum nitride, and a fluoride passivation
film formed over the surface of the thin-film.