

[DESCRIPTION]

[Title]

VAPORIZER, SUBSTRATE PROCESSING APPARATUS AND METHOD
5 OF MANUFACTURING SEMICONDUCTOR DEVICE

[Technical Field]

[0001]

The present disclosure relates to a vaporizer, a substrate processing apparatus and a method of manufacturing a semiconductor device.

[Related Art]

[0002]

As a method of obtaining a denser film from a film formed by a process such as a SOD (spin on dielectric) method and a CVD (chemical vapor deposition) method, the film is modified into the denser film by supplying a modifying gas to the film. For
15 example, as in a technique disclosed in Patent Document 1, as a method of obtaining a denser oxide film such as a silicon oxide (SiO) film from an insulating material film, a gas containing hydrogen peroxide (H₂O₂) is supplied to the insulating material film to modify the insulating material film.

[Related Art Document]

[Patent Document]

[0003]

Patent Document 1: International Publication No. WO2013/077321

[Disclosure]

[Technical Problem]

25 [0004]

As one of the methods of generating a desired process gas such as the gas containing H_2O_2 , it is conceivable to vaporize a liquid source by a vaporizer to obtain the desired process gas. However, according to the conventional vaporizer, it is difficult to precisely control or to manage a temperature of the liquid source introduced into the vaporizer.

Described herein is a technique capable of precisely controlling or managing the temperature of the liquid source introduced into the vaporizer.

[Technical Solution]

[0005]

According to one aspect of the technique of the present disclosure, there is provided a vaporizer including: a liquid source supplier configured to supply a liquid source; a vaporization vessel constituting a vaporization chamber in which the liquid source supplied through the liquid source supplier is vaporized; a first heater configured to heat the vaporization vessel; and a heat insulating material provided to prevent heat emitted from the first heater from transferring to the liquid source supplier.

[Advantageous Effects]

[0006]

According to some embodiments in the present disclosure, it is possible to precisely control or to manage a temperature of a liquid source introduced into a vaporizer.

[Brief Description of Drawings]

[0007]

FIG. 1 schematically illustrates a configuration of a substrate processing apparatus according to an embodiment described herein.

FIG. 2 schematically illustrates a vertical cross-section of a process furnace of

the substrate processing apparatus according to the embodiment described herein.

FIG. 3 schematically illustrates a vertical cross-sectional structure of a vaporizer of the substrate processing apparatus according to the embodiment described herein.

5 FIG. 4(A) schematically illustrates the vertical cross-sectional structure of the vaporizer of the substrate processing apparatus according to the embodiment described herein, and FIG. 4(B) schematically illustrates a gap of the vaporizer shown in FIG. 4A.

FIG. 5(A) illustrates a calculation result of a temperature of a gas flowing between parallel flat plates of 1.0 mm, and FIG. 5(B) illustrates a calculation of the
10 temperature of the gas flowing between parallel flat plates of 0.8 mm.

FIG. 6 illustrates a calculation result of a pressure increase amount when water vapor flows through the gap at 25 slm.

FIG. 7 illustrates a schematic configuration of a controller of the substrate processing apparatus according to the embodiment described herein.

15 FIG. 8 is a flowchart schematically illustrating a pre-processing step of a substrate processing according to the embodiment described herein.

FIG. 9 is a flowchart schematically illustrating the substrate processing according to the embodiment described herein.

FIG. 10 schematically illustrates a vertical cross-sectional structure of a
20 vaporizer of the substrate processing apparatus according to a second embodiment described herein.

FIG. 11(A) schematically illustrates the vertical cross-sectional structure of the vaporizer of the substrate processing apparatus according to the second embodiment described herein, and FIG. 11(B) schematically illustrates a vertical cross-sectional
25 structure of a vaporizer of the substrate processing apparatus according to a comparative

example.

[Detailed Description]

[0008]

<Embodiment of Technique of Present Disclosure>

5 Hereinafter, a preferred embodiment of the technique of the present disclosure will be described with reference to the drawings.

[0009]

(1) Configuration of Substrate Processing Apparatus

First, an exemplary configuration of a substrate processing apparatus 10 in
10 which a method of manufacturing a semiconductor device according to the present embodiment is performed will be described with reference to FIGS. 1 and 2. The substrate processing apparatus 10 is an apparatus of processing a substrate using a process gas generated by vaporizing a liquid source containing hydrogen peroxide (H_2O_2), that is, a hydrogen peroxide solution. For example, the substrate processing
15 apparatus 10 is an apparatus of processing a wafer 200 serving as the substrate made of a material such as silicon. Preferably, the substrate processing apparatus 10 is used when processing the wafer 200 of a concave-convex structure (grooves) which is a microstructure. According to the present embodiment, an oxide film is formed by filling the grooves with a polysilazane film, which is a silicon-containing film, and processing
20 the polysilazane film with the process gas.

[0010]

According to the present embodiment, the H_2O_2 vaporized or converted to be in a mist state (that is, the H_2O_2 in a gaseous phase) is referred to as a “ H_2O_2 gas”, a gas containing at least the H_2O_2 gas is referred to as “process gas”, and an aqueous solution
25 of the H_2O_2 is referred to as

to suppress the heat from a first heating apparatus 207 from being transferred to the seal cap 219.

[0015]

<Elevator>

5 A boat elevator serving as an elevator configured to elevate and lower the boat 217 is provided under the process vessel 203. When the boat 217 is elevated by the boat elevator, the seal cap 219 then airtightly closes the furnace opening. A boat rotator 267 configured to rotate the boat 217 is provided at the seal cap 219 opposite to the process chamber 201.

10 [0016]

<First Heating Apparatus>

 The first heater 207 is provided outside the process vessel 203. The first heater 207 is of a concentric ring shape surrounding a side wall surface of the process vessel 203. The first heater 207 is configured to heat the plurality of the wafers including the wafer 200 accommodated in the process vessel 203. The first heater 207 is supported by
15 a heater base 206. As shown in FIG. 2, the first heater 207 includes a first sub-heater 207a, a second sub-heater 207b, a third sub-heater 207c and a fourth sub-heater 207d. A first temperature sensor 263a, a second temperature sensor 263b, a third temperature sensor 263c and a fourth temperature sensor 263d are provided in the process vessel 203.
20 The first temperature sensor 263a through the fourth temperature sensor 263d serve as temperature detectors configured to detect temperatures of the plurality of the wafers including the wafer 200, respectively, or to detect an ambient temperature, and are provided for the first sub-heater 207a through the fourth sub-heater 207d serving as sub-heaters, respectively. For example, the first temperature sensor 263a through the fourth
25 temperature sensor 263d such as thermocouples may be provided between the process vessel 203 and the boat 217, respectively.

[0017]

The first heating apparatus 207 and the first temperature sensor 263a through the fourth temperature sensor 263d are electrically connected to a controller 121 which will be described later. A first external temperature sensor 264a, a second external temperature sensor 264b, a third external temperature sensor 264c and a fourth external temperature sensor 264d may be further provided at the first sub-heater 207a through the fourth sub-heater 207d, respectively. The first external temperature sensor 264a through the fourth external temperature sensor 264d constituted by thermocouples and serving as temperature detectors are configured to detect temperatures of the first sub-heater 207a through the fourth sub-heater 207d, respectively. The first external temperature sensor 264a through the fourth external temperature sensor 264d are electrically connected to the controller 121.

[0018]

<Gas Supplier (Gas Supply System)>

As shown in FIGS. 1 and 2, a process gas supply nozzle 501a and an oxygen-containing gas supply nozzle 502a are provided between the process vessel 203 and the first heating apparatus 207 along an outer sidewall of the process vessel 203. Tips (downstream ends) of the process gas supply nozzle 501a and the oxygen-containing gas supply nozzle 502a are inserted into the process vessel 203 through a ceiling of the process vessel 203 in an airtight manner. A supply hole 501b and a supply hole 502b are provided at the tips of the process gas supply nozzle 501a and the oxygen-containing gas supply nozzle 502a located in the process vessel 203, respectively.

[0019]

A gas supply pipe 602c is connected to an upstream end of the oxygen-containing gas

supply pipe 289a as the process gas together with the carrier gas.

[0022]

The liquid source supply system 300 includes a liquid source supply 301, a valve 302 and a liquid mass flow controller (LMFC) 303 configured to control a flow rate of the liquid source supplied to the vaporizer 100, which are sequentially provided in order on the upstream side to a downstream side of the liquid source supply system 300. The carrier gas supply supplier is constituted at least by a carrier gas supply pipe 601c, a carrier gas valve 601a, an MFC 601b serving as a carrier gas flow rate controller and a carrier gas valve 601d. According to the present embodiment, the oxygen-containing gas such as the O₂ gas may be used as the carrier gas. However, a gas including at least one of oxygen-containing gases (for example, the O₃ gas and the NO gas as well as the O₂ gas) may be used as the carrier gas. In addition, a gas whose reactivity with the wafer 200 or films formed on the wafer 200 is low may be used as the carrier gas. For example, N₂ gas or a rare gas may be used as the carrier gas.

15 [0023]

According to the present embodiment, a process gas supplier (process gas supply system) is constituted at least by the process gas supply nozzle 501a and the supply hole 501b. The process gas supplier may further include the process gas supply pipe 289a, the valve 289b and the vaporizer 100. An oxygen-containing gas supplier (oxygen-containing gas supply system) is constituted at least by the oxygen-containing gas supply nozzle 502a and the supply hole 502b. The oxygen-containing gas supplier may further include the gas supply pipe 602c, the oxygen-containing gas heater 602e, the valve 602d, the MFC 602b and the valve 602a. A gas supply supplier (gas supply system) is constituted by the process gas supplier and the oxygen-containing gas supplier.

25

[0024]

<Vaporizer>

concentration of the compound in the liquid source before vaporized in the vaporization chamber 112 may fluctuate without being controlled or managed, and as a result, the concentration of the compound in the vaporized gas generated in the vaporization chamber 112 may vary unintentionally.

5 [0041]

Therefore, according to the present embodiment, by providing the heat insulating material 160, it is possible to suppress the interference of the heat from the vaporizer heater 113 to the liquid source supplier 150, and as a result, it is possible to easily control or manage the temperature of the liquid source in the liquid source
10 supplier 150. According to the present embodiment, the vaporizer heater 113 is controlled so that the vaporization vessel 111 is heated to a temperature ranging from 180 °C to 210 °C. On the other hand, by providing the heat insulating material 160, it is possible to suppress the interference of the heat from the vaporizer heater 113, and as a result, it is possible to manage the temperature of the liquid source in the liquid source
15 supplier 150 to 100 °C or lower. In addition, according to the present embodiment, it is possible to suppress the temperature of the liquid source in the liquid source supplier 150 to a predetermined temperature (for example, 100 °C) or less without providing a cooler. According to the verification by the disclosers, when the temperature of the liquid source containing the H₂O₂ is 100 °C or lower, the concentration of the H₂O₂ in
20 the liquid source is stable, and the concentration of the obtained vaporized gas is also stable. In the present specification, a notation of a numerical range such as “from 180 °C to 210 °C” means that a lower limit and an upper limit are included in the numerical range. Therefore, for example, a numerical range “from 180 °C to 210 °C” means a range equal to or higher than 180 °C and equal to or lower than

In addition, when the temperature measured by the temperature sensor 119 exceeds a desired temperature due to the interference of the heat emitted from the vaporizer heater 113, the temperature of the vaporizer heater 113 may be controlled based on the temperature data measured by the temperature sensor 115 and the temperature sensor 119. In such a case, the temperature data measured by the temperature sensor 115 and the temperature sensor 119 are output to a temperature controller 106, and the temperature controller 106 is configured to control the temperature of the vaporizer heater 113 based on the temperature data. However, when the heat insulating material 160 sufficiently suppresses the interference of the heat supplied from the vaporizer heater 113 to the liquid source supplier 150 (that is, when the liquid source supplier 150 is thermally substantially isolated from the vaporizer heater 113), the control of the vaporizer heater 113 based on the temperature data measured by the temperature sensor 119 may not be performed.

[0047]

In addition, as in a second embodiment of the technique of the present disclosure described later, by providing a heater configured to heat the liquid source supplier 150 separately from the vaporizer heater 113, it is also possible to control the temperature of the liquid source to maintain the desired temperature of 100 °C or lower.

[0048]

<Double Tube Structure of Vaporization Vessel>

In addition, according to the present embodiment, as described above, the vaporization vessel 111 is configured as the double tube structure in order to more efficiently transfer the heat from the heater to the liquid source. The droplets of the liquid source supplied from the liquid source supplier 150 are heated and vaporized by passing through the upper space 112a and the gap 112b of a cylindrical shape constituting a gas flow path of a cylindrical shape. In addition, according to the present embodiment, the vaporization vessel 111 is configured as the double tube structure as

described above in order to more efficiently transfer the heat from the heater such as the vaporizer heater 113 to the liquid source.

[0049]

5 In order to prevent the vaporization vessel 111 from being damaged by directly contacting with the metal block 116, an O-ring 118 made of a heat resistant material is provided between the metal block 116 of the outer block 110a and the vaporization vessel 111.

[0050]

10 Similar to the vaporization vessel 111, the exhaust port 114 is made of the quartz material. A connection interface of the exhaust port 114 whereat the process gas supply pipe 289a is connected thereto is configured as a flange structure. The exhaust port 114 seals the connection interface to the process gas supply pipe 289a by an O-ring interposed therebetween.

[0051]

15 According to the present embodiment, a width of the gap 112b (that is, a width of the gas flow path of a cylindrical shape) is set to 0.6 mm or more and 0.8 mm or less. Hereinafter, the basis of setting the width of the gap 112b will be described with reference to FIGS. 4 through 6.

[0052]

20 In order to analyze a temperature of the gas flowing through the gap 112b shown in FIG. 4(A), let us assume that it is the convection heat transfer problem of the gas flowing between heated parallel flat plates as shown in FIG 4(B). Then, the temperature of the gas flowing between the parallel flat plates is calculated by the following difference equation.

25 [Equation 1]

inner pressure of the process vessel 203 is returned to the atmospheric pressure and a predetermined time has elapsed, the temperature of wafer 200 is lowered until a predetermined temperature (for example, a temperature at which the wafer 200 can be unloaded) is reached.

5 [0077]

<Substrate Unloading Step S60>

Thereafter, the boat 217 charged with the processed wafers including the wafer 200 is unloaded out of the process vessel 203 through the lower end of the process vessel 203. The processed wafers including the wafer 200 are then discharged from the
10 boat 217. Thereby, the substrate processing according to the present embodiment is completed.

[0078]

<Second Embodiment of Technique of Present Disclosure>

Subsequently, a second embodiment of the technique of the present disclosure
15 will be described with reference to FIG. 10. In the second embodiment, the detailed description of the same configurations and steps as those of the embodiment described above will be omitted.

[0079]

In a substrate processing apparatus according to the present embodiment, a
20 vaporizer 400 is used instead of the vaporizer 100. The vaporizer 400 according to the present embodiment is provided with an atomizing heater 162 serving as a second heater configured to heat the liquid source supplier 150 around the liquid source supplier 150.

[0080]

25 According to the vaporizer 400, a metal block 163 serving as a second metal block is inserted between the atomizing heater 162 and the liquid source supplier 150 in order to conduct the heat emitted from the atomizing heater 162 to the quartz material of the liquid source

The vaporizer 400 is covered with the heat insulating material 160 formed as a single body therewith, and the heat insulating material 165 is provided between the metal block 116 and the metal block 163 in addition to the heat insulating material 160. That is, the heat insulating material 165 is provided between the outer heater 113a serving as the first heater and the atomizing heater 162 serving as the second heater. In addition, the heat insulating material 165 is provided between the ceiling wall 161 of the vaporization vessel 111 connected to the liquid source supplier 150 and the upper surface of the metal block 116.

[0087]

As described above, the heat insulating material 165 is provided below the liquid source supplier 150, and is configured to prevent the heat emitted from the vaporizer heater 113 from transferring to the metal block 163 and the liquid source supplier 150 via the metal block 116. In other words, by configuring the liquid source supplier 150 and the vaporization chamber 112 as separated and independent structures, it is possible to reduce the temperature interference between the liquid source supplier 150 and the vaporization chamber 112.

[0088]

<Other Embodiments of Technique of Present Disclosure>

While the technique of the present disclosure is described in detail by way of the embodiments, the technique of the present disclosure is not limited thereto. The technique of the present disclosure may be modified in various ways without departing from the gist thereof.

[0089]

While the embodiments are described by way of an example in which the wafer 200 with the polysilazane film formed thereon is processed, the technique of the present disclosure is not limited thereto. The technique of the present disclosure may also be

applied when the wafer 200 with a film containing a silazane bond (-Si-N-) formed thereon is processed. The vaporizer described above may also be used when a coating film containing materials such as hexamethyldisilazane (HMDS), hexamethylcyclotrisilazane (HMCTS), polycarbosilazane and polyorganosilazane is
5 processed.

[0090]

In addition, the vaporizer described above may also be used when a film such as a plasma polymerized film of tetrasilylamine and ammonia is processed. In addition, the vaporizer described above may also be used when a silicon-containing film formed by a
10 CVD method, for example, a silicon-containing film formed by the CVD method using a silicon source such as monosilane (SiH_4) gas and trisilylamine (TSA) gas is processed. In particular, the silicon-containing film may be formed by a flowable CVD method.

[0091]

In addition, the embodiments are described by way of an example in which a
15 substrate processing apparatus including a vertical type process furnace is used. However, for example, the vaporizer described above may also be applied when a single type substrate processing apparatus, a substrate processing apparatus including a hot wall type process furnace, a substrate processing apparatus including a cold wall type process furnace or a substrate processing apparatus capable of processing the wafer 200
20 by activating the process gas is used.

[0092]

<Example>

Hereinafter, examples of the technique of the present disclosure will be described.

25 [0093]

As the example of the technique of the present disclosure, the vaporizer 400

shown in FIGS. 10 and 11(A) is used, and as a comparative example, a vaporizer 500 shown in FIG. 11(B) is used to supply water H₂O) serving as the liquid source. Experiments in which the liquid source is supplied to the liquid source supplier 150 and vaporized are performed. The vaporizer 500 is configured without the heat insulating material 165 of the vaporizer 400, and the liquid source supplier 150 and the vaporization vessel 111 of the vaporizer 500 are not thermally separated and independent. The processing conditions of the example and the comparative example are the same.

[0094]

According to the vaporizer 500 shown in FIG. 11(B), it is confirmed that it is possible to vaporize a maximum of 20 g/min of the liquid source when a liquid supplier temperature (the temperature of the liquid source supplier 150) is 143 °C. On the other hand, according to the vaporizer 400 shown in FIG. 11(A), it is confirmed that it is possible to vaporize a maximum of 20 g/min of the liquid source when the liquid supplier temperature is 89 °C.

[0095]

That is, according to the present embodiments, it was confirmed that, by providing the heat insulating material 165 between the atomizing heater 162 configured to heat the liquid source supplier and the vaporizer heater 113 configured to heat the vaporization chamber 112, it is possible to maintain the liquid supplier temperature to 100 °C or lower, and even when the liquid supplier temperature is 100 °C or lower, it is possible to vaporize the same amount of the liquid source as when the liquid supplier temperature is higher than 100 °C.

[Description of Reference Numerals]

[0096]

substrate processing apparatus

[CLAIMS]

[Claim 1]

A vaporizer comprising:

- 5 a liquid source supplier configured to supply a liquid source;
- a vaporization vessel constituting a vaporization chamber in which the liquid source supplied through the liquid source supplier is vaporized;
- a first heater configured to heat the vaporization vessel; and
- a heat insulating material provided to prevent heat emitted from the first heater
- 10 from transferring to the liquid source supplier.

[Claim 2]

The vaporizer of claim 1, further comprising:

- a second heater configured to heat the liquid source supplier; and
- 15 a controller configured to individually control a temperature of the first heater and a temperature of the second heater.

[Claim 3]

The vaporizer of claim 2, wherein the heat insulating material is provided

- 20 between the first heater and the second heater.

[Claim 4]

The vaporizer of any one of claims 1 through 3, wherein the vaporization vessel

comprises:

an outer vessel of a cylindrical shape; and

an inner vessel provided at an inner side of the outer vessel and being of a column shape,

5 wherein a gap is provided between an outer wall of the inner vessel and an inner wall of the outer vessel to define a flow path of a cylindrical shape in which the liquid source is vaporized, and a width of the flow path is 0.6 mm or more and 0.8 mm or less.

10 [Claim 5]

The vaporizer of any one of claims 1 through 4, wherein the heat insulating material is configured such that a temperature of the liquid source supplier is 100 °C or lower.

15 [Claim 6]

The vaporizer of claim 2 or 3, wherein the controller is further configured to control the temperature of the second heater such that the temperature of the liquid source supplier is 80 °C or higher and 100 °C or lower.

20 [Claim 7]

The vaporizer of any one of claims 1 through 6, wherein the liquid source supplier comprises:

an outlet port configured to eject the liquid source into the vaporization

chamber; and

a liquid source introducing pipe configured to introduce the liquid source to the outlet port.

5 [Claim 8]

The vaporizer of claim 7, wherein the liquid source supplier further comprises:

a carrier gas outlet port provided adjacent to the outlet port and configured to eject a carrier gas into the vaporization vessel; and

a carrier gas introducing pipe configured to introduce the carrier gas to the
10 carrier gas outlet port.

[Claim 9]

The vaporizer of any one of claims 1 through 8, wherein the vaporization vessel and the liquid source supplier are formed as a single body made of quartz.

15

[Claim 10]

The vaporizer of any one of claims 1 through 9, further comprising:

a first metal block inserted between the first heater and the vaporization vessel,
and configured to be heated by the first heater and transfer the heat to the vaporization
20 vessel,

wherein the heat insulating material is configured to cover at least a part of a surface of the first metal block so as to prevent the heat emitted from the first metal block from transferring to the liquid source supplier.

[Claim 11]

The vaporizer of claim 10, wherein the vaporization vessel comprises an outer vessel of a cylindrical shape, and

5 the first metal block is provided so as to cover an outer surface of the outer vessel from below the outer vessel to a height position same as a ceiling wall of the vaporization vessel connected to the liquid source supplier, or from below the outer vessel to a height position lower than the ceiling wall.

10 [Claim 12]

The vaporizer of claim 10 or 11, further comprising:

a second metal block inserted between the second heater and the liquid source supplier, and configured to be heated by the second heater and transfer the heat to the liquid source supplier,

15 wherein the heat insulating material is provided between the first metal block and the second metal block.

[Claim 13]

20 The vaporizer of any one of claims 1 through 12, wherein the liquid source contains hydrogen peroxide.

[Claim 14]

A substrate processing apparatus comprising:

a process chamber in which a substrate is processed;

a vaporizer comprising:

- a liquid source supplier configured to supply a liquid source;
- a vaporization vessel constituting a vaporization chamber in which the
- 5 liquid source supplied through the liquid source supplier is vaporized;
- a first heater configured to heat the vaporization vessel; and
- a heat insulating material provided to prevent heat emitted from the
- first heater from transferring to the liquid source supplier; and
- a vaporized gas pipe configured to supply a vaporized gas generated by the
- 10 vaporizer into the process chamber.

[Claim 15]

A method of manufacturing a semiconductor device comprising:

- (a) loading a substrate into a process chamber;
- 15 (b) supplying a liquid source into a vaporization vessel constituting a vaporization chamber in which the liquid source supplied by a liquid source supplier configured to supply the liquid source is vaporized;
- (c) heating the vaporization vessel by a first heater configured to heat the vaporization vessel while preventing heat emitted from the first heater from transferring
- 20 to the liquid source supplier by a heat insulating material; and
- (d) generating a vaporized gas by vaporizing the liquid source supplied into the heated vaporization vessel and supplying the vaporized gas into the process chamber.