

[DESCRIPTION]

[Title]

METHOD OF MANUFACTURING SEMICONDUCTOR DEVICE, SUBSTRATE
PROCESSING APPARATUS AND NON-TRANSITORY COMPUTER-READABLE
5 RECORDING MEDIUM

[Technical Field]

[0001]

The present invention relates to a method of manufacturing a semiconductor
device, a substrate processing apparatus and a non-transitory computer-readable
10 recording medium.

[Related Art]

[0002]

As one of manufacturing processes of a semiconductor device, a substrate
processing of processing a film formed on a surface of a substrate by supplying a
15 process gas containing hydrogen peroxide to the substrate may be performed (refer to,
for example, patent documents 1 and 2).

[Related Art Document]

[Patent Document]

[0003]

20 Patent Document 1: International Publication No. 2014/069826
Patent Document 2: International Publication No. 2013/070343

[Disclosure]

[Technical Problem]

[0004]

25 It is an object of the present invention to provide a technique capable of
improving the quality of an oxide film processed using hydrogen peroxide.

[Technical Solution]

[0005]

According to one aspect of the present invention, there is provided a technique including:

a first step of modifying a silicon-containing film into a silicon oxide film by supplying a first process gas containing hydrogen peroxide to a substrate with the silicon-containing film formed on a surface thereof; and

a second step of modifying the silicon oxide film by supplying a second process gas containing a compound containing an NH group to the substrate after the first step.

[Advantageous Effects]

[0006]

According to the present invention, it is possible to improve the quality of a substrate processing using hydrogen peroxide.

[Brief Description of Drawings]

[0007]

FIG. 1 is a diagram schematically illustrating a vertical cross-section of a vertical type process furnace of a substrate processing apparatus preferably used in an embodiment of the present invention.

FIG. 2 is a block diagram schematically illustrating a configuration of a controller and related components of the substrate processing apparatus preferably used in the embodiment of the present invention.

FIGS. 3(a) and 3(b) are flow charts schematically illustrating an example of a pre-processing step.

FIG. 4 is a flow chart schematically illustrating a substrate processing performed after the pre-processing step.

FIG. 5 is one of diagrams schematically illustrating results of analyzing compositions of films formed according to a first comparative example, a second comparative example and an

example of the embodiment by Fourier-transform infrared spectroscopy (FTIR).

FIG. 6 is one of the diagrams schematically illustrating the results of analyzing the compositions of the films formed according to the first comparative example, the second comparative example and the example of the embodiment by the FTIR.

FIG. 7 is one of diagrams schematically illustrating results of analyzing compositions of the films formed according to the first comparative example, a third comparative example and the example of the embodiment by the FTIR.

FIG. 8 is one of the diagrams schematically illustrating the results of analyzing the compositions of the films formed according to the first comparative example, the third comparative example and the example of the embodiment by the FTIR.

FIG. 9 is a diagram schematically illustrating a molecular structure of a polysilazane film formed by the pre-processing step.

FIG. 10 is a diagram schematically illustrating a molecular structure of an ideal film obtained by modifying (oxidizing) the polysilazane film.

FIG. 11 is a diagram schematically illustrating a molecular structure of an actual film obtained by modifying (oxidizing) the polysilazane film.

[Detailed Description]

[0008]

<First Embodiment of Present Invention>

Hereinafter, a first embodiment of the present invention will be described with reference to FIGS. 1, 2, 3(a) and 4.

[0009]

(1) Configuration of Substrate Processing Apparatus

As shown in FIG. 1, a process furnace 202 of a substrate processing apparatus includes a

reaction tube 203. For example, the reaction tube 203 is made of a heat resistant material such as quartz (SiO_2) and silicon carbide (SiC), and is configured as a cylindrical member provided with a first gas supply port 242a and a second gas supply port 242c at an upper end thereof and a furnace opening (hole) at a lower end thereof. A process chamber 201 is provided in a hollow cylindrical portion of the reaction tube 203. The process chamber 201 is configured to accommodate a plurality of wafers including a wafer 200 serving as a substrate.

[0010]

A seal cap 219 serving as a lid part capable of airtightly closing the lower end opening of the reaction tube 203 is provided under the reaction tube 203. For example, the seal cap 219 is made of a non-metallic material such as quartz, and of a disk shape. A rotating mechanism 267 is installed below the seal cap 219. A rotating shaft 255 of the rotating mechanism 267 is connected to a boat 217 through the seal cap 219. The rotating mechanism 267 is configured to rotate the wafer 200 accommodated in the boat 217 by rotating the boat 217. The seal cap 219 is configured to be elevated or lowered in the vertical direction by a boat elevator 115 installed outside the reaction tube 203. The boat elevator 115 is configured as a transfer mechanism that loads (transfers) the wafer 200 into the process chamber 201 or unloads (transfers) the wafer 200 out of the process chamber 201 by elevating or lowering the seal cap 219.

[0011]

The boat 217 serving as a substrate retainer aligns the plurality of the wafers including the wafer 200, for example, from 25 to 200 wafers in the vertical direction and supports the plurality of the wafers in a multi-stage manner, while the plurality of the wafers is horizontally oriented with their centers aligned with each other. That is, the boat 217 supports the plurality of the wafers with predetermined intervals therebetween. For example, the boat 217 is made of a heat resistant material

such as quartz and SiC. The boat 217 includes a top plate 217a and a bottom plate 217b at a top and a bottom thereof. A plurality of heat insulators including a heat insulator 218 is supported in a multi-stage manner under the boat 217. For example, the heat insulator 218 is made of a heat resistant material such as quartz and SiC.

[0012]

A heater 207 serving as a heating apparatus is provided outside the reaction tube 203. The heater 207 is vertically installed so as to surround a wafer accommodation region in the process chamber 201. The heater 207 heats the wafer 200 accommodated in the wafer accommodation region to a predetermined temperature. In addition, the heater 207 may function as a liquefaction suppressing mechanism that applies thermal energy to a gas supplied into the process chamber 201 to suppress its liquefaction, or may function as an excitation mechanism that activates the gas by heat. A temperature sensor 263 serving as a temperature detector is provided in the process chamber 201 along an inner wall of the reaction tube 203. Based on temperature information detected by the temperature sensor 263, an output of the heater 207 is adjusted.

[0013]

A first gas supply pipe 232a and a third gas supply pipe 232c are connected to the first gas supply port 242a and the second gas supply port 242c provided at the upper end of the reaction tube 203, respectively.

[0014]

A gas generator 250a, a mass flow controller (MFC) 241a serving as a flow rate controller (flow rate control mechanism) and a valve 243a serving as an opening/closing valve are installed in order at the first gas supply pipe 232a. A first gas supply system of supplying a first process gas such as a H₂O₂-containing gas described later is constituted mainly by the gas supply pipe 232a, the MFC

241a and the valve 243a. The first gas supply system may further include the gas generator 250a.

[0015]

The gas generator 250a is configured to generate a process gas by heating hydrogen peroxide solution serving as a liquid source to a predetermined temperature (vaporization temperature), for example, within a range from 120 °C to 200 °C under approximately atmospheric pressure to vaporize the hydrogen peroxide solution or to convert the hydrogen peroxide solution into a mist state. In the present specification, the hydrogen peroxide solution refers to an aqueous solution obtained by dissolving hydrogen peroxide (H_2O_2) which is a liquid at normal temperature in water (H_2O) serving as a solvent. The gas obtained by vaporizing the hydrogen peroxide solution contains each of the H_2O_2 and the H_2O at predetermined concentrations. Hereinafter, the gas is also referred to as the H_2O_2 -containing gas. In addition, the process gas used in a first modification step described later is also referred to as the “first process gas”, and the process gas used in a second modification step described later is also referred to as a “second process gas”. The H_2O_2 contained in the process gas is a kind of active oxygen, is unstable and easily releases oxygen (O), and generates hydroxyl radical (OH radical) having a very strong oxidizing power. Therefore, the H_2O_2 -containing gas serves as a strong oxidizing agent in a substrate processing described later.

[0016]

According to the present embodiment, when the hydrogen peroxide solution is vaporized or converted into the mist state, the hydrogen peroxide solution is atomized by supplying oxygen (O_2) gas serving as a vaporization carrier gas together with the hydrogen peroxide solution to the gas generator 250a. A flow rate of the vaporization carrier gas is, for example, about 100 times to 500 times of a flow rate of the hydrogen peroxide solution. A gas similar to an oxygen (O)-containing gas described later may be used as the vaporization carrier gas, or a rare gas such as argon (Ar) gas,

helium (He) gas and neon (Ne) gas may be used as the vaporization carrier gas.

[0017]

An oxygen-containing gas supply source 251c, an MFC 241c and a valve 243c are installed in order at the third gas supply pipe 232c. An oxygen-containing gas supply system of supplying the oxygen-containing gas such as O₂ gas, ozone (O₃) gas and nitrous oxide (NO) gas is constituted mainly by the third gas supply pipe 232c, the MFC 241c and the valve 243c. The oxygen-containing gas supply system may further include the oxygen-containing gas supply source 251c.

[0018]

An inert gas supply pipe 232d is connected to the third gas supply pipe 232c between a downstream side of the valve 243c and an upstream side of the second gas supply port 242c. An inert gas supply source 251d, an MFC 241d and a valve 243d are installed in order at the inert gas supply pipe 232d. An inert gas supply system of supplying an inert gas such as N₂ gas is constituted mainly by the inert gas supply pipe 232d, the MFC 241d and the valve 243d. The inert gas supply system may further include the inert gas supply source 251d.

[0019]

A gas nozzle 242b is provided inside the reaction tube 203 so as to extend from a lower portion of a side wall of the reaction tube 203 to the vicinity of an upper end of the boat 217 in the vertical direction in the reaction tube 203. The gas nozzle 242b is made of a material such as quartz. A gas supply hole or a plurality of gas supply holes is opened in the gas nozzle 242b.

[0020]

A second gas supply pipe 232b is connected to an upstream end of the gas nozzle 242b. A second process gas supply source 251b, an MFC 241b and a valve 243b are installed in order at the second gas supply pipe 232b. A second process gas supply system of supplying the second process

gas such as ammonia (NH₃) gas described later is constituted mainly by the second gas supply pipe 232b, the MFC 241b and the valve 243b. The second process gas supply system may further include the second process gas supply source 251b.

[0021]

5 An exhaust pipe 231 configured to exhaust an inner atmosphere of the process chamber 201 is connected to a lower portion of the side wall of the reaction tube 203. A vacuum pump 246 serving as a vacuum exhausting apparatus is connected to the exhaust pipe 231 through a pressure sensor 245 and an APC (Automatic Pressure Controller) valve 244. The pressure sensor 245 serves as a pressure detector configured
10 to detect an inner pressure of the process chamber 201, and the APC valve 244 serves as a pressure adjustment device. With the vacuum pump 246 in operation, the APC valve 244 may be opened or closed to vacuum-exhaust the process chamber 201 or stop the vacuum exhaust. With the vacuum pump 246 in operation, an opening degree of the APC valve 244 may be adjusted based on pressure information detected by the pressure
15 sensor 245, in order to adjust the inner pressure of the process chamber 201. An exhaust system is constituted mainly by the exhaust pipe 231, the APC valve 244 and the pressure sensor 245. The exhaust system may further include the vacuum pump 246.

[0022]

 As shown in FIG. 2, a controller 121 serving as a control device is constituted by
20 a computer including a CPU (Central Processing Unit) 121a, a RAM (Random Access Memory) 121b, a memory device 121c and an I/O port 121d. The RAM 121b, the memory device 121c and the I/O port 121d may exchange data with the CPU 121a through an internal bus 121e. For example, an input/output device 122 such as a touch panel is connected to the controller 121.

25 [0023]

 The memory device 121c is configured by components such as a flash memory and a hard

disk drive (HDD). For example, a control program for controlling the operation of the substrate processing apparatus and a process recipe containing information on the sequences and the conditions of the substrate processing described later are readably stored in the memory device 121c. The process recipe is obtained by combining steps of the substrate processing described later such that the controller 121 can execute the steps to acquire a predetermine result, and functions as a program. Hereafter, the process recipe and the control program may be collectively or individually referred to as a “program”. The process recipe may also be simply referred to as a “recipe”. In the present specification, the term “program” may indicate only the recipe, may indicate only the control program, or may indicate both of the recipe and the control program. The RAM 121b functions as a memory area (work area) where a program or data read by the CPU 121a is temporarily stored.

[0024]

The I/O port 121d is connected to the above-described components such as the MFCs 241a through 241d, the valves 243a through 243d, the gas generator 250a, the pressure sensor 245, the APC valve 244, the vacuum pump 246, the heater 207, the temperature sensor 263, the rotating mechanism 267 and the boat elevator 115.

[0025]

The CPU 121a is configured to read the control program from the memory device 121c and execute the read control program. Furthermore, the CPU 121a is configured to read the recipe from the memory device 121c according to an operation command inputted from the input/output device 122. According to the contents of the read recipe, the CPU 121a may be configured to control various operations such as a gas generating operation by the gas generator 250a, gas flow rate adjusting operations by the MFCs 241a through 241d, opening/closing operations of the valves 243a through 243d, an opening/closing operation of the APC valve 244, a pressure adjusting operation by the APC valve 244 based on the pressure sensor 245, a start and stop of the vacuum pump 246, a

temperature adjusting operation by the heater 207 based on the temperature sensor 263, a rotation operation and a rotation speed adjusting operation of the boat 217 by the rotating mechanism 267 and an elevating and lowering operation of the boat 217 by the boat elevator 115.

[0026]

The controller 121 may be embodied by installing the above-described program stored in an external memory device 123 into a computer. For example, the external memory device 123 may include a magnetic disk such as a hard disk drive (HDD), an optical disk such as a CD, a magneto-optical disk such as MO and a semiconductor memory such as a USB memory. The memory device 121c or the external memory device 123 may be embodied by a non-transitory computer readable recording medium. Hereafter, the memory device 121c and the external memory device 123 may be collectively or individually referred to as the recording medium. In the present specification, the term “recording medium” may indicate only the memory device 121c, may indicate only the external memory device 123, and may indicate both of the memory device 121c and the external memory device 123. Instead of the external memory device 123, a communication means such as the Internet and a dedicated line may be used for providing the program to the computer.

[0027]

(2) Pre-processing Step and Substrate Processing

Subsequently, the pre-processing step and the substrate processing performed to the wafer 200 which is part of manufacturing processes of a semiconductor device will be described.

[0028]

(2-1) Pre-processing Step

The pre-processing step performed before performing the substrate processing to the wafer 200 will be described with reference to FIG. 3(a).

[0029]

As shown in FIG. 3(a), according to the pre-processing step, a polysilazane (PHPS) coating step and a prebaking step are sequentially performed to the wafer 200. In the PHPS coating step, a coating liquid (polysilazane solution) containing polysilazane is coated onto a surface of the wafer 200 by a method such as a spin coating method. In the prebaking step, the solvent is removed from the coated film by heating the wafer 200 with the coated film formed thereon. By heating the wafer 200 with the coated film formed thereon at a processing temperature (prebaking temperature) within a range from 70 °C to 250 °C, it is possible to volatilize the solvent from the coated film. For example, the prebaking temperature may be within a range from 70 °C to 250 °C. It is preferable that the wafer 200 is heated to about 150 °C.

[0030]

The coated film formed on the surface of the wafer 200 becomes a film with a silazane bond (-Si-N-), that is, a polysilazane film by performing the prebaking step. The polysilazane film contains nitrogen (N) and hydrogen (H) in addition to silicon (Si). The polysilazane film may further contain carbon (C) and other impurities in some cases. The polysilazane film has a molecular structure with irregular bonds between atoms and a relatively low film density. According to the substrate processing described later, by supplying the H₂O₂-containing gas to the polysilazane film formed on the wafer 200 under a predetermined temperature condition, the polysilazane film is modified (oxidized) into a silicon oxide film (SiO₂ film).

[0031]

According to the present embodiment, a concave-convex structure serving as a microstructure is formed on the surface of the wafer 200. After supplying the coating liquid to the wafer 200 so as to fill at least a groove (that is, a concave portion of the concave-convex structure), the polysilazane film serving as a silicon-containing film is formed in the groove by heating the

coated film filled in at least the groove according to the prebaking step. Therefore, in particular, a thickness of the polysilazane film formed in the groove is equal to or greater than a depth of the groove. For example, the thickness of the polysilazane film is 4 μm or more.

5 [0032]

(2-2) Substrate Processing

Subsequently, an example of the substrate processing performed using the substrate processing apparatus described above will be described with reference to FIG. 4. Hereinafter, the operations of the components constituting the substrate processing
10 apparatus are controlled by the controller 121.

[0033]

<Substrate Loading Step>

The plurality of the wafers including the wafer 200 with the polysilazane film formed on the surface thereof by the pre-processing step is loaded (charged) into the
15 boat 217. After the boat 217 is charged with the plurality of the wafers, the boat 217 accommodating the plurality of the wafers is elevated by the boat elevator 115 and loaded into the process chamber 201 as shown in FIG. 1. With the boat 217 loaded, the seal cap 219 seals the lower end opening of the reaction tube 203.

[0034]

20 <Pressure and Temperature Adjusting Step>

First, the process chamber 201 in which the plurality of the wafers including the wafer 200 is accommodated is vacuum-exhausted to, for example, about 1 Pa by the vacuum pump 246. Thereafter, the valve 243c is opened to supply the O_2 gas serving as the oxygen-containing gas into the process chamber 201 through the second gas supply
25 port 242c while a flow rate of the O_2 gas is adjusted by the MFC 241c. While supplying the O_2 gas, the inner pressure of the process chamber 201 is measured by the pressure sensor 245, and the APC valve 244 is feedback-controlled based on the measured pressure information such that the inner pressure of the process chamber reaches a

predetermined pressure (modification pressure). The heater 207 heats the process chamber 201 such that the temperature of the wafer 200 in the process chamber 201 reaches a predetermined temperature (first temperature). The state of electrical conduction to the heater 207 is feedback-controlled based on the temperature information detected by the temperature sensor 263 such that the temperature of the wafer 200 reaches the first temperature. The feedback control for the heater 207 is continuously performed according to target temperatures set in each step at least until the processing on the wafer 200 is completed. The rotating mechanism 267 starts to rotate the wafer 200. Until at least the processing of the wafer 200 is completed, the vacuum pump 246 continuously vacuum-exhausts the process chamber 201, the rotating mechanism 267 continuously rotates the wafer 200, and the heater 207 continuously heats the process chamber 201. In addition, according to the present embodiment, the inner pressure of the process chamber 201 is maintained at the same as the modification pressure, or maintained at one of the atmospheric pressure, a slightly depressurized pressure and a slightly pressurized pressure.

[0035]

<First Modification Step>

When the temperature of the wafer 200 reaches the first temperature and the boat 217 is rotated at a desired rotation speed, the valve 243a is opened to supply the H₂O₂-containing gas (first process gas) into the process chamber through the MFC 241a and the first gas supply pipe 232a. The first process gas supplied into the process chamber 201 flows downward in the process chamber 201, and is discharged out of the process chamber 201 through the exhaust pipe 231. Thereby, the first process gas is supplied onto the wafer 200. While supplying the first process gas, the valve 243c may be opened to supply the O₂ gas into the process chamber 201 through the third gas supply pipe 232c. The flow rate of the O₂ gas is adjusted by the MFC 241c. A concentration of the H₂O₂ in the first process gas supplied into the process chamber 201 may be adjusted by changing the flow rate of the vaporization carrier gas or the flow rate of the liquid source, which are supplied to the gas generator

250a.

[0036]

For example, the processing conditions of the first modification step are as follows:

The concentration of the H_2O_2 of the liquid source: from 20 % to 40 %, preferably from 25 % to 35 %;

The flow rate of the liquid source: from 1.0 sccm to 10 sccm, preferably from 1.6 sccm to 8 sccm;

The flow rate of the O_2 gas: from 0 SLM to 20 SLM, preferably from 5 SLM to 10 SLM;

The modification pressure: 700 hPa to 1,000 hPa (one of the atmospheric pressure, a slightly depressurized pressure and a slightly pressurized pressure.); and

The temperature of the wafer 200 (first temperature): from 40 °C to 120 °C, preferably from 40 °C to 80 °C.

In addition, the flow rate of the O_2 gas described above refers to a total flow rate of the O_2 gas serving as the vaporization carrier gas supplied to the gas generator 250a and the O_2 gas serving as the oxygen-containing gas supplied into the process chamber 201 through the third gas supply pipe 232c of the oxygen-containing gas supply system.

[0037]

By supplying the first process gas to the wafer 200 according to the above-described processing conditions and maintaining the supply of the first process gas for a predetermined first time duration (for example, a time duration within a range from 20 minutes to 720 minutes), it is possible to modify (oxidize) the polysilazane film, which serves as the silicon-containing film formed on the wafer 200, into the SiO_2 film. That is, it is possible to add oxygen (O) component contained in the first process gas into the silicon-containing film, and the impurities such as nitrogen (N) component, carbon (C) component and hydrogen (H) component contained in the polysilazane

film can be removed (desorbed) from the polysilazane film.

[0038]

The H_2O_2 contained in the first process gas has a very strong oxidizing power as described above. Therefore, even when the first temperature is set to the low temperature condition described above, it is possible to oxidize the polysilazane film at a practical rate.

[0039]

In addition, by performing the first modification step with the first temperature set to the low temperature condition described above, it is possible to suppress the hardening (condensation) of the surface of the polysilazane film. Therefore, according to the first modification step, it is possible to allow the H_2O_2 component or the H_2O component contained in the first process gas to efficiently permeate into not only the surface of the polysilazane film but also an inside of the polysilazane film (along a thickness direction of the polysilazane film). As a result, it is possible to obtain the effect of the modification described above not only on the surface of the polysilazane film but also in the deepest portion of the polysilazane film.

[0040]

In particular, when the temperature of the wafer 200 is 200 °C or higher, the hardening of the surface of the polysilazane film becomes remarkably, and it is difficult to permeate the H_2O_2 component or the H_2O component into the polysilazane film to obtain the effect of the modification. Therefore, it is preferable that the temperature of the wafer 200 is set to be lower than 200 °C, especially when the thickness of the polysilazane film is large.

[0041]

<Drying Step>

After the first time duration has elapsed and a modification process of modifying the

polysilazane film by the first process gas is completed, the valve 243a is closed to stop the supply of the first process gas to the wafer 200. When the O₂ gas is supplied through the third gas supply pipe 232c in the first modification step, with the valve 243c kept open, the O₂ gas is continuously supplied until the next temperature elevating step is started. When the first modification step is performed without supplying the O₂ gas through the third gas supply pipe 232c, the valve 243c is opened to supply the O₂ gas until the next temperature elevating step is started. Then, the wafer 200 is dried by supplying the O₂ gas to the wafer 200. It is preferable that the drying step is performed while the temperature of the wafer 200 is maintained at a predetermined second temperature higher than the first temperature described above. Therefore, it is possible to promote the drying of the wafer 200.

[0042]

By drying the wafer 200 as described above, it is possible to remove by-products such as ammonium chloride (NH₄Cl) desorbed from the polysilazane film, impurities such as carbon (C) and hydrogen (H) of the gas from the solvent and impurities from the H₂O₂, which are desorbed from a surface or an inside of the film modified by performing the first modification step, while suppressing reattaching to the wafer 200.

[0043]

According to the present embodiment, by performing the first modification step and the drying step, ideally, a film having a structure containing only silicon (Si) and oxygen (O) such as a molecular structure shown in FIG. 10 may be formed. However, when a modification process is performed under the low temperature condition of the wafer 200 as in the first modification step of the present embodiment, actually, as shown in a molecular structure of FIG 11, a film is formed with a structure where a ring structure of O-Si-O contains an OH bond, the H₂O is adsorbed to an OH

group, or the H₂O is adsorbed onto a surface of the film. The tendency described above is particularly remarkable when the modification process is performed under the low temperature condition of the wafer 200 of 120 °C or less as in the present embodiment. Therefore, according to the present embodiment, the temperature elevating step and a second modification step are performed to improve the characteristics of the film.

[0044]

The phenomenon that the OH group or the moisture remaining in the inside of the SiO₂ film or on the surface of the SiO₂ film is generally observed in the SiO₂ film formed or modified under the low temperature condition. The same effect of the modification of the next temperature elevating step and the second modification step may be obtained for these films.

[0045]

<Temperature Elevating Step>

After a predetermined time has elapsed and the drying step is completed, the supply of the O₂ gas to the wafer 200 is stopped and the temperature of the wafer 200 is elevated to a predetermined third temperature higher than the second temperature. When the second temperature is equal to the third temperature, the temperature of the wafer 200 is maintained. In addition, the valve 243d is opened to supply the N₂ gas serving as the inert gas into the process chamber 201 through the gas supply pipes 232d and 232c. Thereby, the inner atmosphere of the process chamber 201 is replaced (purged) with the N₂ gas.

[0046]

<Second Modification Step>

When the temperature of the wafer 200 reaches the third temperature and stabilized, the valve 243b is opened to supply the NH₃ gas (second process gas) into the process chamber 201 through the MFC 241b, the second gas supply pipe 232b and the gas nozzle 242b. The second

process gas supplied into the process chamber 201 is discharged out of the process chamber 201 through the exhaust pipe 231. Thereby, the second process gas is supplied onto the wafer 200. The supply of the second process gas is maintained for a predetermined second time duration, for example, within a range from 5 minutes to 480 minutes, preferably 10 minutes to 60 minutes. In the second modification step, it is preferable that the valve 243d is kept open and the N₂ gas is continuously supplied into the process chamber 201.

[0047]

By supplying the gas containing a compound containing an NH group, which serves as the second process gas (the NH₃ gas in the present embodiment), to the wafer 200 as described above, the NH group of the compound in the gas react with the OH group or the moisture remaining on the surface of the film or the inside of the film. Therefore, it is possible to effectively remove the OH group of the film or the moisture. As a result, it is possible to modify the film into the SiO₂ film having a low hydrogen (H) content and a good film quality. According to the present embodiment, by supplying the NH₃ gas serving as the gas containing the compound containing the NH group which includes a molecular structure smaller than a diameter of the ring structure of O-Si-O of the SiO₂ film to be processed to the wafer 200, the OH group bonded or coordinated to Si-O chain is removed.

[0048]

In the present specification, the NH group refers to at least one among an imino group (an imide group) and an amino group. Instead of the NH₃, for example, a compound such as the methylamine (CH₃NH₂), dimethylamine ((CH₃)₂NH) and trimethylamine ((CH₃)₃N) may be used as the compound containing the NH group.

[0049]

A flow rate of the NH_3 gas serving as the second process gas in the second modification step is, for example, from 5 SLM to 10 SLM, and a flow rate ratio with the N_2 gas supplied simultaneously is, for example, about 1: 1. The third temperature, which is a processing temperature of the second modification step, is, for example, a predetermined temperature within a range from 150 °C to 400 °C. It is preferable that the third temperature is set to 400 °C or less in consideration of conditions such as the influence of the thermal history on the semiconductor device formed on the wafer 200. Although it is preferable that the third temperature is set to a temperature equal to or lower than 400 °C depending on the semiconductor device, according to the present embodiment, it is possible to obtain the effect described above even under the low temperature condition of the wafer 200 of 300 °C or less by performing the second modification step using the gas containing the compound containing the NH group. However, when the third temperature is lower than 150 °C, it is difficult to sufficiently obtain the effect of removing the OH group in the film. Therefore, it is particularly preferable that the third temperature is set to a predetermined temperature within a range from 150 °C to 300 °C.

[0050]

It is preferable that the NH_3 gas actually used in the present embodiment has a moisture concentration of less than 0.1% (for example, 0.0001%) serving as impurities. When the moisture concentration is 0.1% or more, the effect of removing the OH groups by the second modification step is saturated in a short time, and it is difficult to sufficiently obtain the effect.

[0051]

<Temperature Lowering and Returning to Atmospheric Pressure Step>

After the second time duration has elapsed and the second modification step is completed, the valve 243b is closed to stop the supply of the second process gas to the wafer 200 (when the N_2 gas is supplied into the process chamber 201 in the second modification step, the supply of the N_2

gas is also stopped), the process chamber 201 is vacuum-exhausted to, for example, about 1 Pa. Thereafter, the valve 243d is opened to supply the N₂ gas into the process chamber 201, and the inner pressure of the process chamber 201 is returned to the atmospheric pressure. Thereby, even when the process chamber 201 is vacuum-exhausted to about 1 Pa, it is possible to reduce the concentration of the second process gas remaining in the process chamber 201 to 1 ppm or less. After the inner pressure of the process chamber 201 is returned to the atmospheric pressure and a predetermined time has elapsed, the inner temperature of the process chamber 201 is lowered to a predetermined temperature at which the wafer 200 can be unloaded

[0052]

<Substrate Unloading Step>

The seal cap 219 is lowered by the boat elevator 115 and the lower end opening of the reaction tube 203 is opened. Then, the boat 217 accommodating a plurality of processed wafers including the wafer 200 is unloaded out of the reaction tube 203 through the lower end opening of the reaction tube 203.

[0053]

(3) Effect According to Present Embodiment

Hereinafter, with reference to FIGS. 5 through 8, evaluation results of an example of the present embodiment and comparative examples thereof will be compared, and the effects of the present embodiment will be described.

[0054]

In each of the example of the embodiment and the comparative examples described below, the SiO₂ film is formed by performing the modification process using the first process gas containing the H₂O₂ to the polysilazane film formed on the surface of the wafer 200 by the pre-processing step described above. The main differences of the substrate processing and the processing conditions

between the comparative examples and the example of the embodiment are as follows: (a) the temperature of the wafer in the first modification step; and (b) whether the temperature elevating step and the second modification step are performed, and the processing conditions of the temperature elevating step and the second modification step when the temperature elevating step and the second modification step are performed. The other processing conditions and the steps of the substrate processing of the example of the embodiment and the comparative example are the same as the processing conditions and the steps of the substrate processing of the first embodiment described above.

[0055]

The differences between the comparative examples and the example of the embodiment are as follows:

<First Comparative Example>

(a) The temperature of the wafer (first temperature) and the processing time (first time duration) in the first modification step: 80 ° C and 60 minutes; and

(b) The temperature elevating step and the second modification step: not performed.

<Second Comparative Example>

(a) The temperature of the wafer (first temperature) and the processing time (first time duration) in the first modification step: 80 ° C and 60 minutes; and

(b) The temperature elevating step and the second modification step: the temperature of the wafer is 200 °C, and only the N₂ gas (in place of the NH₃ gas) is supplied as the second process gas for 60 minutes.

<Third Comparative Example>

(a) The temperature of the wafer (first temperature) and the processing time (first time

duration) in the first modification step: 200 ° C and 60 minutes; and

(b) The temperature elevating step and the second modification step: not performed.

<Example of Embodiment>

(a) The temperature of the wafer (first temperature) and the processing time (first time duration) in the first modification step: 80 ° C and 60 minutes; and

(b) The temperature elevating step and the second modification step: the temperature of the wafer is 200 °C, and the NH₃ gas serving as the second process gas is supplied for 60 minutes.

[0056]

First, the evaluation results of the first comparative example, the second comparative example and the example of the present embodiment will be described with reference to FIGS. 5 and 6.

[0057]

FIGS. 5 and 6 schematically illustrate the evaluation results of analyzing the compositions of each of the SiO₂ films formed according to the first comparative example, the second comparative example and the example of the embodiment by Fourier-transform infrared spectroscopy (FTIR). The vertical axes shown in FIGS. 5 and 6 represent the absorbance of the infrared, and the horizontal axes shown in FIGS. 5 and 6 represent the wave number. In FIGS. 5 and 6, components contained in the film and the amounts thereof are indicated by the position and height of the peak of the waveform in the horizontal axis. In particular, the heights of the peaks around 900 cm⁻¹ and around 3,000 cm⁻¹ to 3,500 cm⁻¹ indicate the amounts of the OH group contained in the film. FIG. 5 schematically illustrates the waveforms around 2700 cm⁻¹ to 3,900 cm⁻¹ at which the peaks indicating the OH group appear, and FIG. 6 schematically illustrates the waveforms around 600 cm⁻¹ to 1100 cm⁻¹ at which the peaks indicating the OH group appear.

[0058]

Referring to the waveform of the first comparative example indicated by solid lines, the peaks are observed at around 900 cm^{-1} and around $3,000^{-1}$ to $3,500\text{ cm}^{-1}$, respectively. That is, it is confirmed that a large amount of the OH group are contained in the SiO_2 film formed according to the first comparative example in which the temperature elevating step and the second modification step are not performed.

[0059]

Referring to the waveform of the second comparative example indicated by broken lines, the peaks are observed at around 900 cm^{-1} and around $3,000^{-1}$ to $3,500\text{ cm}^{-1}$, respectively, similar to the waveforms of the first comparative example, and almost no decrease in the peaks is observed. In other words, it is confirmed that the modification process using only the N_2 gas in second comparative example hardly contributes to the removal of the OH group in the film.

[0060]

On the other hand, referring to the waveform of the example of the embodiment indicated by dotted lines, it is confirmed that the height of each of the peaks at around 900 cm^{-1} and around $3,000^{-1}$ to $3,500\text{ cm}^{-1}$ is reduced by half with respect to the waveforms of the first comparative example and the second comparative example. That is, it is confirmed that it is possible to obtain the effect of removing the OH group in the SiO_2 film by performing the modification process using the NH_3 gas containing the compound containing the NH group as the second modification step as in the present embodiment.

[0061]

Subsequently, the evaluation results of the first comparative example, the third comparative example and the example of the present embodiment will be described with reference to FIGS. 7 and

8. FIGS. 7 and 8 schematically illustrate the evaluation results of analyzing the compositions of the SiO₂ films formed according to the first comparative example, the third comparative example and the example of the embodiment by the FTIR.

[0062]

In FIGS. 7 and 8, the waveform of the third comparative example is indicated by broken lines, and the waveform of the example of the embodiment is indicated by dotted lines. Comparing the waveform of the third comparative example with the waveform of the example of the embodiment, it is observed that the heights of the peaks at around 900 cm⁻¹ and around 3,000⁻¹ to 3,500 cm⁻¹ indicating the content of the OH group are almost the same. That is, by performing the modification process using the NH₃ gas as the second modification step as in the present embodiment, even when the first modification step is performed under the condition that the temperature of the wafer is as low as 80 °C, it is confirmed that it is possible to reduce the content of the OH group in the film as low as that of the OH group in the film when the first modification step is performed by heating the wafer to 200 °C according to the third comparative example.

[0063]

<Another Effect According to Present Embodiment>

In addition, in comparison between the third comparative example and the example of the embodiment, it is possible to obtain the following effects (advantage) according to the example of the embodiment.

[0064]

When the first modification step (that is, the modification process using the H₂O₂-containing gas) is performed under the condition of heating the wafer to 200 °C according to the third comparative example to the polysilazane film formed on the surface of the wafer by the

pre-processing step described above, there is a problem that a surface layer of the polysilazane film is solidified first, and as a result, it is difficult to sufficiently obtain the effect of the modification on a portion equal to or deeper than 4 μm from the surface of the polysilazane film.

[0065]

On the other hand, when the temperature of the wafer in the first modification step is set to 80 °C as in the example of the embodiment, according to the analysis of the composition of the film formed in the first modification step in the depth direction by secondary ion mass spectrometry (SIMS), it is confirmed that it is possible to sufficiently obtain the effect of the modification of the polysilazane film on the portion in the depth direction of 4 μm or more from the surface of the polysilazane film. Therefore, when the temperature of the wafer in the first modification step is set to 120 °C or lower as in the embodiment, it is thought to be possible to sufficiently obtain the effect of the modification on the portion of 4 μm or more from the surface of the polysilazane film. That is, the present embodiment has a clear advantage over the third comparative example in that it is possible to sufficiently perform the modification process even on the deeper portion (at least 4 μm) of the film to be processed. In other words, when the thickness of the polysilazane film is 4 μm or more, the temperature of the wafer in the first modification step of the present embodiment is preferably at most less than 200 °C, and more preferably 120 °C or less, still more preferably 80 °C or less.

[0066]

In addition, as can be seen from the comparison of the waveforms of the first comparative example and the third comparative example shown in FIGS. 7 and 8, when the first modification step for the polysilazane film is performed under the low temperature condition of 120 °C or less as in the embodiment (80 °C according to the first comparative example), there is a problem that the amount

of the OH group contained in the film is increased compared with that of the OH group contained in the film where the temperature is set to 200 °C as in the third comparative example. However, according to the example of the embodiment, it is possible to sufficiently modify the polysilazane film up to a depth of 4 μm or more from the surface thereof, and it is also possible to obtain the SiO₂ film equivalent to that of third comparative example in terms of the concentration of the OH group in the film by performing the second modification step of the present embodiment.

[0067]

That is, when the polysilazane film having a thickness of 4 μm or more (or a silazane bond-containing film that undergoes similar hardening under the high temperature condition) is modified into the SiO₂ film, it is particularly preferable to modify the polysilazane film (or the silazane bond-containing film) by combining the first modification step and the second modification step of the present embodiment.

[0068]

<Still Another Effect According to Present Embodiment>

In addition, as can be seen from the molecular structure shown in FIG. 9, the polysilazane film formed in the pre-processing step described above has a relatively small film density as compared with a silicon-containing film formed under other high temperature conditions. Therefore, the NH group component of the gas containing the compound containing the NH group used in the second modification step of the present embodiment is particularly likely to permeate into the polysilazane film. Therefore, even when the thickness of the film is large (for example, the thickness of the film is at least greater than 400 nm), it is preferable to apply the present embodiment to the polysilazane film since it is possible to obtain the effect of the modification by the second modification step to a deeper portion of the polysilazane film.

[0069]

<Other Embodiments of Present Invention>

While the embodiment of the present invention is described in detail by way of the embodiment and examples, the present invention is not limited thereto. For example, the embodiment described above and modified examples thereof may be used in appropriate combinations without departing from the gist thereof. The processing sequences and the processing conditions of the combinations may be substantially the same as those of the embodiment described above.

[0070]

While the embodiment described above is described by way of an example in which the polysilazane film formed by performing the PHPS coating step and the prebaking step is processed, the present invention is not limited thereto. For example, even when a silicon-containing film formed by a flowable CVD method as shown in FIG. 3(b) and not prebaked is processed, the substrate processing including the first modification step and the second modification step may be applied.

[0071]

While the embodiment described above is described by way of an example in which the modification process is performed to the polysilazane film, the present invention is not limited thereto. For example, the substrate processing including the first modification step and the second modification step may be applied to perform the modification process of a film such as another film containing silicon (Si), nitrogen (N) and hydrogen (H) (particularly, another film with a silazane bond) and another silicon-containing film formed by a CVD method. In particular, the substrate processing may be preferably applied to a film having a structure where a ring structure of O-Si-O contains -OH bond, the H₂O is adsorbed to an OH group, or the H₂O is adsorbed onto a surface of the film. For example, the silicon-containing film formed by the CVD method may include a plasma

polymerized film formed by using trisilylamine (TSA) gas and the NH_3 gas and an SiO_2 film formed by using an organic silane (particularly, tetraethoxysilane (TEOS)) gas and the O_3 gas.

[0072]

While the embodiment described above is described by way of an example in which the first modification step and the second modification step are performed in the same process chamber, the present invention is not limited thereto. For example, the present invention may include another example in which the substrate to be processed is processed in a process chamber according to the first modification step and then the substrate to be processed is processed in another process chamber (process space) according to the second modification step.

[0073]

While the embodiment described above is described by way of an example in which a batch type substrate processing apparatus configured to simultaneously process a plurality of substrates is used to form the film, the present invention is not limited thereto. For example, the present invention may be applied to form the film using a single type substrate processing apparatus configured to simultaneously process a single substrate or a small number of substrates. In addition, while a substrate processing apparatus having a hot wall type process furnace is exemplified in the embodiment described above, the present invention is not limited thereto. For example, the present invention may also be applied to form the film using a substrate processing apparatus having a cold wall type process furnace.

[Description of Reference Numerals]

[0074]

200: wafer (substrate)

201: process chamber

[CLAIMS]**[Claim 1]**

A method of manufacturing a semiconductor device comprising:

5 a first step of modifying a silazane-bond containing film, whose thickness is greater than 400 nm, into a silicon oxide film by supplying a first process gas containing hydrogen peroxide to a substrate with the silazane-bond containing film formed on a surface thereof; and

 a second step of removing an OH group bonded or coordinated to Si-O chain
10 from the silicon oxide film by supplying a second process gas containing a compound containing an NH group to the substrate after the first step.

[Claim 2]

 The method of claim 1, wherein a temperature of the substrate is equal to or less
15 than 120 °C in the first step.

[Claim 3]

 The method of claim 1, wherein the silazane-bond containing film comprises a polysilazane film.
20

[Claim 4]

 The method of claim 1, wherein the thickness of the silazane-bond containing film is greater than 4 μm.

[Claim 5]

The method of claim 4, wherein a temperature of the substrate is less than 200 °C in the first step.

5

[Claim 6]

The method of claim 1, wherein the compound containing the NH group is at least one compound selected from the group consisting of ammonia, methylamine, dimethylamine and trimethylamine.

10

[Claim 7]

The method of claim 1, wherein a temperature of the substrate is equal to or less than 400 °C in the second step.

15 [Claim 8]

The method of claim 7, wherein the temperature of the substrate is equal to or greater than 150 °C and equal to or less than 300 °C in the second step.

[Claim 9]

20

A substrate processing apparatus comprising:
a process chamber configured to accommodate a substrate;
a first process gas supply system configured to supply a first process gas containing hydrogen peroxide into the process chamber;

a second process gas supply system configured to supply a second process gas containing a compound containing an NH group into the process chamber; and

a controller configured to control the first process gas supply system and the second process gas supply system to perform:

5 a first process of modifying a silazane-bond containing film, whose thickness is greater than 400 nm, into a silicon oxide film by supplying the first process gas containing the hydrogen peroxide to the substrate with the silazane-bond containing film formed on a surface thereof; and

 a second process of removing an OH group bonded or coordinated to
10 Si-O chain from the silicon oxide film by supplying the second process gas containing the compound containing the NH group to the substrate after the first process.

[Claim 10]

A non-transitory computer-readable recording medium storing a program that
15 causes, by a computer, a substrate processing apparatus to perform:

a first sequence of modifying a silazane-bond containing film, whose thickness is greater than 400 nm, into a silicon oxide film by supplying a first process gas containing hydrogen peroxide to a substrate with the silazane-bond containing film formed on a surface thereof; and

20 a second sequence of removing an OH group bonded or coordinated to Si-O chain from the silicon oxide film by supplying a second process gas containing a compound containing an NH group to the substrate after the first sequence.

[Claim 11]

The method of claim 1, wherein the second process gas is supplied to the substrate at equal to or greater than 700 hPa and equal to or less than 1,000 hPa in the second step.