METHOD OF PROCESSING SUBSTRATE, METHOD OF MANUFACTURING SEMICONDUCTOR DEVICE, PROGRAM AND SUBSTRATE PROCESSING APPARATUS

TECHNICAL FIELD

[0001] The present disclosure relates to a method of processing a substrate, a method of manufacturing a semiconductor device, a program, and a substrate processing apparatus.

BACKGROUND

[0002] As a manufacturing process of a semiconductor device, a processing of supplying a predetermined gas to a substrate to form a film on the substrate may be performed (*see*, for example, Patent Document 1).

[Prior Art Documents]

[Patent Documents]

[0003] Patent Document 1: Japanese Laid-Open Patent Publication No. 2016-18907

SUMMARY

[0004] The present disclosure provides a technique capable of improving controllability of a composition ratio of a predetermined element added into a film.

[0005] According to some embodiments of the present disclosure, there is provided a technique that includes: forming a film containing a first element and a second element on a substrate by performing: a first process of forming a first layer containing the first element by performing a cycle a first number of times, the cycle for performing the first process including: (a-1) supplying a first precursor gas containing the first element to the substrate; and (a-2) supplying a first reaction gas to the substrate; and a second process of forming a second layer containing the first element and the second element by performing a cycle a second number of times, the cycle for performing the second process including: (b-1) supplying a second precursor gas containing

the first element and a first halogen element to the substrate; (b-2) supplying a third precursor gas, which contains the second element not contained in the first layer and a second halogen element, to the substrate, after the supply of the second precursor gas is performed for a first period in (b-1); and (b-3) supplying a second reaction gas to the substrate, after the supply of the third precursor gas is performed for a second period in (b-2).

[0006] According to the present disclosure, it is possible to improve controllability of a composition ratio of a predetermined element added into a film.

BRIEF DESCRIPTION OF DRAWINGS

[0007] FIG. 1 is a schematic configuration diagram of a vertical process furnace of a substrate processing apparatus suitably used in some embodiments of the present disclosure, illustrating a portion of the process furnace 202 in a vertical cross-sectional view.

FIG. 2 is a schematic configuration diagram of the vertical process furnace of the substrate processing apparatus suitably used in some embodiments of the present disclosure, illustrating a portion of the process furnace 202 in a cross-sectional view taken along line A-A of FIG. 1.

FIG. 3 is a schematic configuration diagram of a controller of the substrate processing apparatus suitably used in some embodiments of the present disclosure, illustrating a control system of the controller in a block diagram.

FIG. 4 is a diagram illustrating a processing sequence in some embodiments of the present disclosure.

FIG. 5 is a diagram illustrating an example of a cross-sectional structure of a NAND memory cell.

FIG. 6A is a diagram illustrating a processing sequence in Modification 1 of the present disclosure. FIG. 6B is a diagram illustrating a processing sequence in Modification 2 of the present disclosure.

FIG. 7A is a diagram illustrating one example of a processing sequence in Modification

3 of the present disclosure. FIG. 7B is a diagram illustrating another example of a processing sequence in Modification 3 of the present disclosure.

FIG. 8A is a diagram illustrating a processing sequence in Modification 4 of the present disclosure. FIG. 8B is a diagram illustrating a processing sequence in Modification 5 of the present disclosure. FIG. 8C is a diagram illustrating a processing sequence in Modification 6 of the present disclosure.

FIG. 9 is a diagram illustrating a charge trap film formed by the processing sequence in Modification 1 of the present disclosure.

DETAILED DESCRIPTION

[0008] <Embodiments of Present Disclosure>

Hereinafter, some embodiments of the present disclosure are described mainly with reference to FIGS. 1 to 5. The drawings used in the following description are schematic, and dimensional relationships, proportions, and the like of respective elements shown in the drawings may not coincide with those of actual ones. Further, dimensional relationships, proportions, and the like of respective elements may not be consistent among multiple drawings.

[0009] (1) Configuration of Substrate Processing Apparatus

As shown in FIG. 1, a process furnace 202 includes a heater 207 that serves as a temperature regulator (heating part). The heater 207 is formed in a cylindrical shape and is vertically installed by being supported by a holding plate. The heater 207 also functions as an activator (exciter) that activates (excites) a gas with heat.

[0010] Inside the heater 207, a reaction tube 203 is disposed concentrically with the heater 207. Below the reaction tube 203, a manifold 209 is disposed concentrically with the reaction tube 203. An upper end of the manifold 209 is engaged with a lower end of the reaction tube 203 and is configured to support the reaction tube 203. An O-ring 220a is installed as a seal between the manifold 209 and the reaction tube 203. A process container (reaction container) mainly includes the reaction tube 203 and the manifold 209. A process chamber 201 is formed

in a cylindrical hollow region of the process container. The process chamber 201 is configured to be capable of accommodating wafers 200 as substrates. The wafers 200 are processed inside the process chamber 201.

[0011] Nozzles 249a and 249b serving as a first supplier and a second supplier, respectively, are installed inside the process chamber 201 so as to penetrate a sidewall of the manifold 209. The nozzles 249a and 249b are also referred to as a first nozzle and a second nozzle, respectively. Gas supply pipes 232a and 232b are connected to the nozzles 249a and 249b, respectively. The nozzles 249a and 249b are different nozzles from each other, and the nozzles 249a and 249b are installed adjacent to each other.

[0012] The gas supply pipes 232a and 232b are installed, respectively, with mass flow controllers (MFCs) 241a and 241b, which are flow rate controllers (flow rate control parts), and valves 243a and 243b, which are opening/closing valves, in order from an upstream side of a gas flow. Gas supply pipes 232c to 232e and 232g are connected on a downstream side of the valve 243a of the gas supply pipe 232a, respectively. Gas supply pipes 232f and 232h are connected on a downstream side of the valve 243b of the gas supply pipe 232b, respectively. The gas supply pipes 232c to 232h are provided with MFCs 241c to 241h and valves 243c to 243h, respectively, in order from an upstream side of a gas flow.

[0013] As shown in FIG. 2, each of the nozzles 249a and 249b is installed in a space, formed in an annular shape in plane view, between an inner wall of the reaction tube 203 and the wafers 200 so as to extend upward in an arrangement direction of the wafers 200 from a lower portion to an upper portion of the inner wall of the reaction tube 203. That is, the nozzles 249a and 249b are respectively installed along the wafer arrangement region, in a region horizontally surrounding the wafer arrangement region, on a lateral side of the wafer arrangement region in which the wafers 200 are arranged. Gas supply holes 250a and 250b that supply gases are formed on side surfaces of the nozzles 249a and 249b, respectively. The gas supply holes 250a and 250b are opened toward centers of the wafers 200 in plane view, respectively, thereby being capable of supplying gases toward the wafers 200. A plurality of the gas supply holes 250a and

250b are formed from a lower portion to an upper portion of the reaction tube 203.

[0014] A first precursor gas containing a first element is supplied from the gas supply pipe 232a into the process chamber 201 via the MFC 241a, the valve 243a, and the nozzle 249a.

[0015] A first reaction gas is supplied from the gas supply pipe 232b into the process chamber 201 via the MFC 241b, the valve 243b, and the nozzle 249b.

[0016] A second precursor gas containing the first element and a first halogen element is supplied from the gas supply pipe 232c into the process chamber 201 via the MFC 241c, the valve 243c, the gas supply pipe 232a, and the nozzle 249a.

[0017] A third precursor gas containing a second halogen element and a predetermined second element is supplied from the gas supply pipe 232d into the process chamber 201 via the MFC 241d, the valve 243d, the gas supply pipe 232a, and the nozzle 249a.

[0018] A fourth precursor gas containing the first element, a third halogen element, and hydrogen (H) is supplied from the gas supply pipe 232e into the process chamber 201 via the MFC 241e, the valve 243e, the gas supply pipe 232a, and the nozzle 249a.

[0019] A second reaction gas is supplied from the gas supply pipe 232f into the process chamber 201 via the MFC 241f, the valve 243f, the gas supply pipe 232b, and the nozzle 249b.

[0020] An inert gas is supplied respectively from the gas supply pipes 232g and 232h into the process chamber 201 via the MFCs 241g and 241h, the valves 243g and 243h, the gas supply pipes 232a and 232b, and the nozzles 249a and 249b. The inert gas acts as a purge gas, a carrier gas, a dilution gas, or the like.

[0021] A first precursor gas supply system mainly includes the gas supply pipe 232a, the MFC 241a, and the valve 243a. A first reaction gas supply system mainly includes the gas supply pipe 232b, the MFC 241b, and the valve 243b. A second precursor gas supply system mainly includes the gas supply pipe 232c, the MFC 241c, and the valve 243c. A third precursor gas supply system mainly includes the gas supply pipe 232d, the MFC 241d, and the valve 243d. A fourth precursor gas supply system mainly includes the gas supply pipe 232e, the MFC 241e, and the valve 243e. A second reaction gas supply system mainly includes the gas supply pipe 232f,

the MFC 241f, and the valve 243f. An inert gas supply system mainly includes the gas supply pipes 232g and 232h, the MFCs 241g and 241h, and the valves 243g and 243h. A gas supply system includes the entirety or any one of the above-described various supply systems. A nozzle connected to the gas supply pipes constituting the above-described various supply systems may be included in each of the supply systems.

[0022] Any one or the entirety of the above-described various supply systems may be configured as an integrated supply system 248 in which the valves 243a to 243h, the MFCs 241a to 241h, and so on are integrated.

[0023] An exhaust port 231a that exhausts an internal atmosphere of the process chamber 201 is installed below a sidewall of the reaction tube 203. An exhaust pipe 231 is connected to the exhaust port 231a. A vacuum pump 246, which serves as a vacuum exhauster, is connected to the exhaust pipe 231 via a pressure sensor 245, which serves as a pressure detector (pressure detection part) that detects internal pressure of the process chamber 201, and an auto pressure controller (APC) valve 244, which serves as a pressure regulator (pressure regulation part). The APC valve 244 is configured to be capable of performing or stopping vacuum exhaust inside the process chamber 201 by opening or closing the valve while the vacuum pump 246 is in operation, and is further configured to be capable of regulating the internal pressure of the process chamber 201 by adjusting a degree of valve opening based on pressure information detected by the pressure sensor 245 while the vacuum pump 246 is in operation. An exhaust system mainly includes the exhaust pipe 231, the APC valve 244, and the pressure sensor 245. The vacuum pump 246 may also be considered as included in the exhaust system.

[0024] A seal cap 219 is installed below the manifold 209 as a furnace opening lid capable of airtightly closing an opening at a lower end of the manifold 209 via an O-ring 220b. A rotator 267 that rotates a boat 217 to be described later is installed below the seal cap 219. A rotation shaft 255 of the rotator 267 passes through the seal cap 219 and is connected to the boat 217. The rotator267 is configured to rotate the wafers 200 by rotating the boat 217. The seal cap 219 is configured to be vertically raised or lowered by a boat elevator 115 serving as a lift installed

outside the reaction tube 203. The boat elevator 115 is configured as a transferrer (transfer mechanism) that loads and unloads (transfers) the wafers 200 into and out of the process chamber 201 by raising and lowering the seal cap 219.

[0025] Below the manifold 209, a shutter 219s is installed as a furnace opening lid that is capable of airtightly closing the opening at the lower end of the manifold 209 via an O-ring 220c while the seal cap 219 is lowered and the boat 217 is unloaded from the process chamber 201. An opening/closing operation (raising/lowering operation, rotating operation, etc.) of the shutter 219s is controlled by a shutter opening/closing mechanism 115s.

[0026] A boat 217 as a substrate support is configured to support a plurality of wafers 200, for example, 25 to 200 wafers 200, in such a state that the wafers are arranged in a horizontal posture and in multiple stages along a vertical direction with the centers of the wafers 200 aligned with one another, i.e., so as to arrange the wafers 200 at intervals. Heat insulating plates 218 are supported in multiple stages at a lower portion of the boat 217.

[0027] A temperature sensor 263 serving as a temperature detector is provided inside the reaction tube 203. By regulating a state of supply of electric power to the heater 207 based on temperature information detected by the temperature sensor 263, an internal temperature of the process chamber 201 achieves a desired temperature distribution. The temperature sensor 263 is installed along the inner wall of the reaction tube 203.

[0028] As shown in FIG. 3, the controller 121, which is a control part (control means), is configured as a computer including a central processing unit (CPU) 121a, a random access memory (RAM) 121b, a memory 121c, and an I/O port 121d. The RAM 121b, the memory 121c, and the I/O port 121d are configured to be capable of exchanging data with the CPU 121a via an internal bus 121e. An input/output device 122, formed of, for example, a touch panel or the like, is connected to the controller 121. In addition, the controller 121 is configured to be capable of being connected to an external memory 123. The substrate processing apparatus may be configured to include one controller or a plurality of controllers. That is, a control to perform a processing sequence to be described later may be performed using one controller, or

may be performed using a plurality of controllers. In addition, the plurality of controllers may be configured as a control system in which the controllers are connected to one another via a wired or wireless communication network, and a control to perform the processing sequence to be described later may be performed by the control system as a whole. In the present disclosure, when the term "controller" is used, it may refer to a case of including one controller, a case of including a plurality of controllers, or a case of including a control system constituted by a plurality of controllers.

[0029] The memory 121c includes, for example, a flash memory, a hard disk drive (HDD), a solid state drive (SSD), or the like. In the memory 121c, a control program that controls an operation of a substrate processing apparatus, a process recipe describing procedures or conditions of substrate processing to be described later, and the like are readably recorded and stored. The process recipe is a combination that causes, by the controller 121, the substrate processing apparatus to execute respective substrate processing procedures, which are described later, so as to obtain predetermined results, and functions as a program. Hereinafter, the process recipe, the control program, or the like may be generally and simply referred to as a "program." In addition, the process recipe may also be simply referred to as a "recipe." When the term "program" is used herein, it may refer to a case of including the recipe alone, a case of including the control program alone, or a case of including both. The RAM 121b is configured as a memory area (work area) where programs, data, and others read by the CPU 121a are temporarily held.

[0030] The I/O port 121d is connected to the above-described MFCs 241a to 241h, the valves 243a to 243h, the pressure sensor 245, the APC valve 244, the vacuum pump 246, the temperature sensor 263, the heater 207, the rotator 267, the boat elevator 115, the shutter opening/closing mechanism 115s, and so on.

[0031] The CPU 121a is configured to be capable of reading and executing the control program from the memory 121c, as well as reading the recipe from the memory 121c in response to an input of an operation command from the input/output device 122 or the like. The CPU 121a is

configured to be capable of controlling, according to contents of the read recipe, flow rate regulating operations of various substances (various gases) by the MFCs 241a to 241h, opening/closing operations of the valves 243a to 243h, an opening/closing operation of the APC valve 244, a pressure regulating operation by the APC valve 244 based on the pressure sensor 245, starting and stopping of the vacuum pump 246, a temperature regulating operation of the heater 207 based on the temperature sensor 263, a rotation and rotation speed adjusting operation of the boat 217 by the rotator 267, a raising/lowering operation of the boat 217 by the boat elevator 115, an opening/closing operation of the shutter 219s by the shutter opening/closing mechanism 115s, and so on.

[0032] The controller 121 may be configured by installing on the computer the above-described program recorded and stored in the external memory 123. The external memory 123 includes, for example, a magnetic disk such as a HDD, an optical disk such as a CD, a magneto-optical disk such as a MO, a semiconductor memory such as a USB memory or a SSD, and the like. The memory 121c or the external memory 123 is configured as a computer-readable recording medium. Hereinafter, the memory 121c and the external memory 123 are collectively and simply referred to as a recording medium. As used herein, the term "recording medium" may refer to a case of including the memory 121c alone, a case of including the external memory 123 alone, or a case of including both. In addition, the program may be provided to the computer by using communication means such as the Internet or a dedicated line, without using the external memory 123.

[0033] (2) Substrate Processing Process

As a manufacturing process of a semiconductor device, an example of a processing sequence for forming a film on a surface of the wafer 200 as a substrate, using the above-described substrate processing apparatus, is described mainly with reference to FIG. 4. In the following description, operations of respective components constituting the substrate processing apparatus are controlled by the controller 121.

[0034] In the processing sequence of the present embodiments, a film containing a first element

and a second element is formed on the wafer 200 by performing:

a first process of forming a first layer containing the first element by performing a cycle a first number of times (m times, where m is an integer of 1 or 2 or more), the cycle including:

step A1 of supplying a first precursor gas containing the first element to the wafer 200; and

step A2 of supplying a first reaction gas to the wafer 200; and

a second process of forming a second layer containing the first element and the second element by performing a cycle a second number of times (n times, where n is an integer of 1 or 2 or more), the cycle including:

step B1 of supplying a second precursor gas containing the first element and a first halogen element to the wafer 200;

step B2 of supplying a third precursor gas, which contains the second element not contained in the first layer and a second halogen element, to the wafer 200, after the supply of the second precursor gas is performed for a first period in step B1; and

step B3 of supplying a second reaction gas to the wafer 200, after the supply of the third precursor gas is performed for a second period in step B2.

[0035] In the present embodiments, an example is described in which a charge trap film of a non-volatile memory cell is formed as a film containing the first element and the second element (hereinafter, also simply referred to as a "film"). The charge trap film is, for example, a SiN film in an ONO film, i.e., a three-layer insulating film of SiO film/SiN film/SiO film, constituting a NAND-type flash memory (*see* FIG. 5). In the present embodiments, as an example, a case is described in which a SiN film is formed as the film.

[0036] In FIG. 4, the first precursor gas, the second precursor gas, and the third precursor gas are denoted as 1, 2, and 3, respectively, and the first reaction gas and the second reaction gas are denoted as i and ii, respectively. In addition, P shown in FIG. 4 indicates that purging is performed inside the process chamber 201. The same applies to FIGS. 6A to 8C.

[0037] In the present disclosure, the term "wafer" may refer to a wafer itself, or may refer to a

stack including a wafer and a predetermined layer or film formed on a surface of the wafer. In the present disclosure, the term "surface of a wafer" may refer to a surface of a wafer itself, or may refer to a surface of a predetermined layer or the like formed on a wafer. When it is stated in the present disclosure that " a predetermined layer is formed on a wafer," it may refer to a case in which a predetermined layer is directly formed on a surface of a wafer itself, or a case in which a predetermined layer is formed on a layer or the like already formed on a wafer. In the present disclosure, the term "substrate" is used synonymously with the term "wafer."

[0038] In the present disclosure, the term "layer" includes at least one selected from the group of a continuous layer and a discontinuous layer. For example, the first layer and the second layer described later may include a continuous layer, a discontinuous layer, or both.

[0039] In the present disclosure, when describing adsorption or reaction of the first precursor gas, the second precursor gas, or the like to the surface of the wafer 200, this may include an embodiment in which the gases are adsorbed on or react with the surface of the wafer in an undecomposed state, as well as an embodiment in which intermediates, generated by decomposition of the gases or detachment of ligands of the gases, are adsorbed on or react with the surface of the wafer 200.

[0040] (Wafer Charge and Boat Loading)

When a plurality of wafers 200 are charged into the boat 217, the shutter 219s is moved, and the opening at the lower end of the manifold 209 is opened. Thereafter, the boat 217 supporting the plurality of wafers 200 is lifted by the boat elevator 115 and loaded into the process chamber 201.

[0041] (Pressure Regulation and Temperature Regulation)

After the boat loading is completed, an inside of the process chamber 201, that is, a process space in which the wafers 200 are present, is subjected to vacuum exhaust (decompression exhaust) by the vacuum pump 246 so as to reach a desired pressure (degree of vacuum). At this time, the internal 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 (pressure regulation). In addition, the wafers 200 in the process chamber 201 are heated by the heater 207 such that the wafers 200 reach a desired processing temperature. At this time, the state of supply of electric power to the heater 207 is feedback-controlled based on the temperature information detected by the temperature sensor 263 so that the inside of the process chamber 201 reaches a desired temperature distribution (temperature regulation). In addition, rotation of the wafers 200 by the rotator 267 is started. The exhaust of the inside of the process chamber 201, the heating of the wafers 200, and the rotation of the wafers 200 are continued at least until processing of the wafers 200 is completed.

[0042] (First Process (First Processing))

Thereafter, step A1 and step A2 are sequentially performed.

[0043] [Step A1]

In step A1, the first precursor gas is supplied to the wafer 200 in the process chamber 201.

[0044] Specifically, the valve 243a is opened to flow the first precursor gas into the gas supply pipe 232a. The precursor is regulated in flow rate by the MFC 241a, supplied into the process chamber 201 via the nozzle 249a, and exhausted through the exhaust port 231a. At this time, the first precursor gas is supplied to the wafer 200. At this time, the valves 243g and 243h may be opened to supply an inert gas into the process chamber 201 via the nozzle 249a and the nozzle 249b, respectively.

[0045] A processing condition in this step is exemplified as follows:

Processing temperature: 350 to 800 degrees C, specifically 500 to 700 degrees C;

Processing pressure: 10 to 1,333 Pa, specifically 10 to 133 Pa;

Supply flow rate of first precursor gas: 0.1 to 3 slm, specifically 0.1 to 0.5 slm;

Supply time of first precursor gas: 1 to 180 seconds, specifically 10 to 80 seconds; and

Supply flow rate of inert gas (for each gas supply pipe): 0 to 20 slm.

[0046] In addition, the notation of a numerical range such as "350 to 800 degrees C" as used in the present disclosure means that a lower limit value and an upper limit value are included in the

range. Thus, for example, "350 to 800 degrees C" means "350 degrees C or higher and 800 degrees C or lower." The same applies to other numerical ranges. Further, in the present disclosure, the processing temperature refers to a temperature of the wafer 200 or the internal temperature of the process chamber 201, and the processing pressure refers to the internal pressure of the process chamber 201, in other words, a pressure of a space in which the wafer 200 is present. Also, a processing time refers to a time during which that processing is continued. In addition, when a supply flow rate includes 0 slm, 0 slm refers to a case in which the substance (gas) is not supplied. The same applies to the following description.

[0047] By supplying, for example, a chlorosilane-based gas as the first precursor gas under the above-mentioned processing condition to the wafer 200, a silicon (Si)-containing layer containing chlorine (Cl) is formed on the surface of the wafer 200. The Si-containing layer containing Cl is formed by physical adsorption or chemical adsorption of molecules of the chlorosilane-based gas, physical adsorption or chemical adsorption of molecules of a substance obtained by partial decomposition of the chlorosilane-based gas, and the like, on an outermost surface of the wafer 200. The Si-containing layer containing Cl may be an adsorption layer (physical adsorption layer or chemical adsorption layer) of molecules of the chlorosilane-based gas or molecules of a substance obtained by partial decomposition of the chlorosilane-based gas. In the present disclosure, the Si-containing layer containing Cl is also simply referred to as a Si-containing layer. The Si-containing layer formed in this step is also referred to as a first Si-containing layer.

[0048] After the first Si-containing layer is formed, the valve 243a is closed to stop the supply of the first precursor gas into the process chamber 201. Then, the inside of the process chamber 201 is vacuum-exhausted, and gases and the like remaining in the process chamber 201 are removed from the process chamber 201 (purge). At this time, the valves 243g and 243h are opened to supply an inert gas into the process chamber 201 through the nozzles 249a and 249b. The inert gas acts as a purge gas.

[0049] As the first precursor gas, for example, a silane-based gas containing Si as the first

element, which is a main element constituting the film formed on the wafer 200, may be used. As the silane-based gas, for example, a gas containing Si and a halogen element, that is, a halosilane-based gas, may be used. The halogen element includes Cl, fluorine (F), bromine (Br), iodine (I), and the like. As the halosilane-based gas, for example, the above-described chlorosilane-based gas containing Si and Cl may be used.

[0050] As the first precursor gas, for example, H-free chlorosilane gases such as tetrachlorosilane ($SiCl_4$) gas, hexachlorodisilane (Si_2Cl_6) gas, octachlorotrisilane (Si_3Cl_8) gas, and the like may be used.

[0051] As the first precursor gas, for example, H-containing chlorosilane gases such as monochlorosilane (SiH_3Cl) gas, dichlorosilane (SiH_2Cl_2) gas, trichlorosilane ($SiHCl_3$) gas, and the like may be used.

[0052] As the first precursor gas, H-free fluorosilane-based gases such as tetrafluorosilane (SiF_4) gas, hexafluorodisilane (Si_2F_6) gas, and the like, H-free bromosilane-based gases such as tetrabromosilane ($SiBr_4$) gas, hexabromodisilane (Si_2Br_6) gas, and the like, or H-free iodosilane-based gases such as tetraiodosilane (SiI_4) gas, hexaiododisilane (Si_2I_6) gas, and the like may also be used.

[0053] As the first precursor gas, in addition to chlorosilane-based gases, H-containing fluorosilane-based gases such as difluorosilane (SiH_2F_2) gas, trifluorosilane ($SiHF_3$) gas, and the like, H-containing bromosilane-based gases such as dibromosilane (SiH_2Br_2) gas, tribromosilane ($SiHBr_3$) gas, and the like, or H-containing iodosilane-based gases such as diiodosilane (SiH_2I_2) gas, triiodosilane ($SiHI_3$) gas, and the like may also be used.

[0054] As the first precursor gas, aminosilane-based gases such as tetrakis(dimethylamino)silane ($Si[N(CH_3)_2]_4$) gas, tris(dimethylamino)silane ($Si[N(CH_3)_2]_3H$) gas, bis(diethylamino)silane ($Si[N(C_2H_5)_2]_2H_2$) gas, bis(tertiary-butylamino)silane ($SiH_2[NH(C_4H_9)]_2$) gas, (diisopropylamino)silane ($SiH_3[N(C_3H_7)_2]$) gas, and the like may also be used. As the first precursor gas, organic silane gases containing no amino group, such as tetraethoxysilane ($Si(OC_2H_5)_4$) gas, and the like may also be used.

[0055] As the first precursor gas, one or more of these gases may be used.

[0056] As the inert gas, nitrogen (N_2) gas or rare gases such as argon (Ar) gas, helium (He) gas, neon (Ne) gas, xenon (Xe) gas, and the like may be used. As the inert gas, one or more of these may be used. The same applies to respective steps to be described later.

[0057] [Step A2]

After step A1 is completed, the first reaction gas is supplied to the wafer 200 in the process chamber 201, that is, to the first Si-containing layer formed on the wafer 200.

[0058] Specifically, the valve 243b is opened to flow the first reaction gas into the gas supply pipe 232b. The first reaction gas is regulated in flow rate by the MFC 241b, supplied into the process chamber 201 via the nozzle 249b, and exhausted through the exhaust port 231a. At this time, the first reaction gas is supplied to the wafer 200. At this time, the valves 243g and 243h may be opened to supply an inert gas into the process chamber 201 via the nozzles 249a and 249b, respectively.

[0059] A processing condition in this step is exemplified as follows:

Processing pressure: 10 to 3,750 Pa, specifically 10 to 1,333 Pa;

Supply flow rate of first reaction gas: 1 to 10 slm, specifically 3 to 6 slm;

Supply time of first reaction gas: 1 to 180 seconds, specifically 10 to 60 seconds.

The other processing condition may be the same as the processing condition in step A1.

[0060] By supplying the first reaction gas to the wafer 200 under the above-described condition, at least a portion of the first Si-containing layer formed on the wafer 200 is modified. When, for example, a hydrogen nitride-based gas containing nitrogen (N) as a third element and H is used as the first reaction gas, at least a portion of the first Si-containing layer formed on the wafer 200 is nitrided, and a silicon nitride layer (SiN layer), which contains N as the third element and Si, is formed on the outermost surface of the wafer 200.

[0061] After the SiN layer is formed, the valve 243b is closed to stop the supply of the first reaction gas into the process chamber 201. Then, by a processing procedure similar to the purge in step A1, gases and the like remaining in the process chamber 201 are removed from the

process chamber 201.

[0062] As the first reaction gas, for example, a nitriding gas (nitriding agent) may be used. As the first reaction gas, for example, a hydrogen nitride-based gas such as ammonia (NH_3) gas, diazene (N_2H_2) gas, hydrazine (N_2H_4) gas, N_3H_8 gas, and the like may be used. As the first reaction gas, one or more of these gases may be used.

[0063] [Execution for Predetermined Number of Times]

By performing a cycle in which the above-described steps A1 and A2 are performed non-simultaneously, i.e., without synchronization, the first number of times (m times, where m is an integer of 1 or 2 or more, specifically an integer of 1 or more and 10 or less), a SiN layer as the first layer may be formed on the surface of the wafer 200. It is desirable to repeat the above-mentioned cycle multiple times. That is, it is desirable that a thickness of the SiN layer formed per cycle be thinner than a desired film thickness, and that the above-described cycle be performed multiple times until a film thickness of the first layer formed by stacking the SiN layers reaches the desired film thickness.

[0064] (Second Process (Second Processing))

Thereafter, steps B1 to B3 are sequentially performed.

[0065] [Step B1]

In step B1, the second precursor gas containing the first element and the first halogen element is supplied to the wafer 200 in the process chamber 201, i.e., to the first layer formed on the wafer 200.

[0066] Specifically, the valve 243c is opened to flow the second precursor gas into the gas supply pipe 232c. The second precursor gas is regulated in flow rate by the MFC 241c, supplied into the process chamber 201 via the nozzle 249a, and exhausted through the exhaust port 231a. At this time, the second precursor gas is supplied to the wafer 200. At this time, the valves 243g and 243h may be opened to supply an inert gas into the process chamber 201 via the nozzles 249a and 249b, respectively.

[0067] A processing condition in this step is exemplified as follows:

Gas supply flow rate of second precursor gas: 0.1 to 3 slm, specifically 0.1 to 0.5 slm;

Supply time (first period) of second precursor gas: 1 to 180 seconds, specifically 10 to 30 seconds.

The other processing condition may be the same as the processing condition in step A1. However, the processing condition in this step may differ from the processing condition in step A1 in order to regulate a composition ratio of the second element contained in (doped into) the second layer formed in this process. For example, the composition ratio of the second element may be regulated to be larger by making the supply flow rate of the second precursor gas smaller than the supply flow rate of the first precursor gas. Also, for example, the composition ratio of the second element may be regulated to be larger by making the supply time of the second precursor gas shorter than the supply time of the first precursor gas.

[0068] By supplying, under the above-mentioned processing condition to the wafer 200, for example, the second precursor gas containing Si as the first element and the first halogen element, a Si-containing layer that contains Si and includes a surface on which terminations of the first halogen element are formed may be formed on the SiN layer, which is formed on the wafer 200 as the first layer. In the present disclosure, the termination of the first halogen element is also referred to as a first halogen termination. In addition, the Si-containing layer formed in this step is also referred to as a second Si-containing layer.

[0069] After the second precursor gas is supplied for the first period to form the second Si-containing layer, the valve 243c is closed to stop the supply of the second precursor gas into the process chamber 201. Then, by a processing procedure similar to the purge in step A1, gases and the like remaining in the process chamber 201 are removed from the process chamber 201. However, the purge step of the process chamber 201 between step B1 and step B2 may be omitted. That is, step B1 and step B2 may also be performed consecutively.

[0070] As the second precursor gas, for example, a halosilane-based gas containing Si as the first element, which is a main element constituting the film formed on the wafer 200, and the first halogen element may be used. The first halogen element includes Cl, F, Br, I, and the like.

As the halosilane-based gas, for example, a chlorosilane-based gas containing Si and Cl may be used.

[0071] As the second precursor gas, for example, a gas containing one or more halosilane-based gases listed as examples of the first precursor gas may be used. The second precursor gas is desirably the same gas as the first precursor gas, but a gas different from the first precursor gas may also be used. However, the second precursor gas is desirably a H-free gas.

[0072] [Step B2]

In step B2, the third precursor gas, which contains the second element not included in the first layer and the second halogen element, is supplied to the wafer 200 in the process chamber 201, that is, to the second Si-containing layer on the wafer 200.

[0073] Specifically, valve 243d is opened to flow the third precursor gas into the gas supply pipe 232d. The third precursor gas is regulated in flow rate by the MFC 241d, supplied into the process chamber 201 via nozzle 249a, and exhausted through the exhaust port 231a. At this time, the third precursor gas is supplied to the wafer 200. At this time, the valves 243g and 243h may be opened to supply an inert gas into the process chamber 201 via the nozzles 249a and 249b, respectively.

[0074] A processing condition in this step is exemplified as follows:

Supply flow rate of third precursor gas: 0.05 to 6 slm, specifically 0.5 to 2 slm; and

Supply time (second period) of third precursor gas: 2 to 60 seconds, specifically 4 to 30 seconds.

The other processing condition may be the same as the processing condition in step A1.

[0075] By supplying the third precursor gas containing the second halogen element and a predetermined second element to the wafer 200 under the above-mentioned processing condition, for example, titanium (Ti) as the second element may be adsorbed onto regions (adsorption sites) on the second Si-containing layer where the first halogen terminations are not formed, thereby forming terminations of the second halogen element. In this manner, for example, it is possible to add (dope) Ti to the second Si-containing layer. This allows the

second Si-containing layer formed on the wafer 200 in step B1 to be changed into a second Si-containing layer doped with Ti. In the present specification, the termination of the second halogen element is also referred to as a second halogen termination.

[0076] After the third precursor gas is supplied for the second period and the second Si-containing layer doped with Ti is formed, the valve 243d is closed to stop the supply of the third precursor gas into the process chamber 201. Then, by a processing procedure similar to the purge in step A1, gases and the like remaining in the process chamber 201 are removed from the process chamber 201.

[0077] As the third precursor gas, for example, a halide (titanium halide) gas containing the second halogen element and Ti as the second element may be used. The second halogen element includes Cl, F, Br, I, and the like. The second halogen element may be the same element as the first halogen element or a different element. The second element is an element different from the first element. The third precursor gas is a gas different from the first precursor gas and the second precursor gas.

[0078] As the third precursor gas, for example, a H-free titanium halide gas such as tetrachlorotitanium ($TiCl_4$) gas, tetrafluorotitanium (TiF_4) gas, tetrabromotitanium ($TiBr_4$) gas, tetraiodotitanium (TiI_4) gas, and the like may be used.

[0079] As the third precursor gas, for example, a H-containing titanium halide gas such as monochlorotitanium (TiH_3Cl) gas, difluorotitanium (TiH_2F_2) gas, dibromotitanium (TiH_2Br_2) gas, diiodotitanium (TiH_2I_2) gas, and the like may be used.

[0080] As the third precursor gas, one or more of these substances may be used. It is desirable that the third precursor gas is a H-free gas.

[0081] [Step B3]

In step B3, the second reaction gas is supplied to the wafer 200 in the process chamber 201, that is, to the Ti-doped second Si-containing layer formed on the wafer 200.

[0082] Specifically, the valve 243f is opened to flow the second reaction gas into the gas supply pipe 232f. The second reaction gas is regulated in flow rate by an MFC 241f, supplied into the

process chamber 201 via the nozzle 249b, and exhausted through the exhaust port 231a. At this time, the second reaction gas is supplied to the wafer 200. At this time, the valves 243g and 243h may be opened to supply an inert gas into the process chamber 201 via the nozzles 249a and 249b, respectively.

[0083] A processing condition in this step is exemplified as follows:

Processing pressure: 10 to 3,750 Pa, specifically 10 to 1,333 Pa;

Supply flow rate of second reaction gas: 1 to 10 slm, specifically 3 to 6 slm;

Supply time of second reaction gas: 1 to 180 seconds, specifically 10 to 60 seconds.

The other processing condition may be the same as the processing condition in step A1.

[0084] By supplying the second reaction gas to the wafer 200 under the condition described above, at least a portion of the Ti-doped second Si-containing layer formed on the wafer 200 is modified. When, for example, a hydrogen nitride-based gas, which contains N as the third element and H, is used as the second reaction gas, similarly to the first reaction gas, at least a portion of the Ti-doped second Si-containing layer formed on the wafer 200 is nitrided, and a SiN layer containing Si and N as the third element and doped with Ti is formed.

[0085] After the Ti-doped SiN layer is formed, the valve 243f is closed to stop the supply of the second reaction gas into the process chamber 201. Then, by a processing procedure similar to the purge in step A1, gases and the like remaining in the process chamber 201 are removed from the process chamber 201.

[0086] As the second reaction gas, for example, a gas containing one or more of the gases among the gases listed as examples of the first reaction gas may be used. The second reaction gas is desirably the same gas as the first reaction gas, but a gas different from the first reaction gas may also be used. The second reaction gas is desirably a gas that reacts with the first halogen termination or the second halogen termination.

[0087] [Execution for Predetermined Number of Times]

By performing a cycle in which steps B1 to B3 described above are performed non-simultaneously, i.e., without synchronization, a second number of times (n times, where n is an

integer of 1 or 2 or more, specifically an integer of 1 or more and 10 or less), a Ti-doped SiN layer as the second layer may be formed, for example, on a SiN layer as the first layer. It is desirable to repeat the above-mentioned cycle multiple times. That is, it is desirable that a thickness of the Ti-doped SiN layer formed per cycle be thinner than a desired film thickness, and that the above-described cycle be performed multiple times until a film thickness of the second layer formed by stacking the Ti-doped SiN layers reaches the desired film thickness.

[0088] By performing a cycle including the first process and the second process described above a predetermined number of times (p times, where p is an integer of 1 or 2 or more, specifically a third number of times that is an integer of 2 or more), a Ti-doped SiN film (hereinafter also simply referred to as a "SiN film") including, for example, a SiN layer as the first layer (i.e., a SiN layer not doped with Ti) and a Ti-doped SiN layer as the second layer may be formed on the wafer 200. The Ti-doped SiN film may also be described as a film that contains the first element and the third element and doped with the second element. In the present embodiments, it is desirable that a thickness of the SiN film formed per cycle be thinner than a desired film thickness, and that the above-described cycle be performed multiple times until a thickness of the SiN film formed by stacking the SiN films reaches the desired thickness.

[0089] It is desirable to set (i.e., select) a ratio of the second number of times (n times) in the second process to the first number of times (m times) in the first process (i.e., n/m) such that a composition ratio of Ti in the SiN film reaches a predetermined ratio.

[0090] It is desirable to set a supply amount of the second precursor gas in step B1 such that a composition ratio of Ti in the Ti-doped SiN layer reaches a predetermined ratio. Specifically, at least one selected from the group of the supply flow rate of the second precursor gas and the supply time of the second precursor gas in step B1 is desirably set such that the composition ratio of Ti in the Ti-doped SiN layer reaches a predetermined ratio.

[0091] A thickness of the SiN layer serving as the first layer is desirably a thickness at which Ti, contained in the Ti-doped SiN layer serving as the second layer, is capable of diffusing throughout an entire thickness direction of the adjacent SiN layer (i.e., a thickness equal to or

less than such a thickness).

[0092] (After-Purge and Atmospheric Pressure Recovery)

After step B3 is completed, an inert gas as a purge gas is supplied into the process chamber 201 from each of the nozzles 249a and 249b, and is exhausted through the exhaust port 231a. As a result, the inside of the process chamber 201 is purged, and gases remaining in the process chamber 201, reaction by-products, and the like are removed from the process chamber 201. Thereafter, an internal atmosphere of the process chamber 201 is replaced with the inert gas, and the internal pressure of the process chamber 201 is returned to atmospheric pressure.

[0093] (Boat Unloading and Wafer Discharge)

Thereafter, the seal cap 219 is lowered by the boat elevator 115, and the lower end of the manifold 209 is opened. Then, the processed wafers 200 are unloaded from the lower end of the manifold 209 to an outside of the reaction tube 203 while being supported by the boat 217. After the boat unloading, the opening at the lower end of the manifold 209 is sealed by the shutter 219s. The processed wafers 200 are unloaded to the outside of the reaction tube 203 and then discharged from the boat 217.

[0094] (3) Effects of Present Embodiments

According to the present embodiments, one or more effects set forth below are obtained.

[0095] (a) By performing a cycle that includes the first process that does not include a step of supplying a gas containing the second element and the second process that includes a step of supplying a gas containing the second element, it is possible to improve controllability of a composition ratio of the second element doped into the film (i.e., a ratio of the second element to the entire elements constituting the film). In particular, in a region where the composition ratio of the doped second element is low (e.g., less than 5 atomic%, specifically less than 1 atomic%), fine regulation of the composition ratio of the second element may be performed easily. This makes it possible to easily obtain desired film characteristics, for example, desired charge trap characteristics.

[0096] (b) By performing a cycle, including the first process and the second process, two or

more times, the controllability of the composition ratio of the second element added into the film may be further improved.

[0097] (c) In step B1, by supplying the second precursor gas, which is a H-free gas, it is possible to reduce H-terminations (adsorption sites) present on a surface of the second Si-containing layer prior to the supply of the third precursor gas, to which the third precursor gas is capable of being adsorbed. This makes it possible to suppress adsorption of the second element, contained in the third precursor gas, on the second Si-containing layer. As a result, the composition ratio of the second element in the film may be controlled to be lower.

[0098] (d) In step B2, by supplying the third precursor gas, which is a H-free gas, i.e., a gas that does not react with halogen terminations, it is possible to suppress desorption of the first halogen element from the second Si-containing layer on which the first halogen terminations are formed after the supply of the second precursor gas. This makes it possible to suppress adsorption (doping) of the second element contained in the third precursor gas on the second Si-containing layer. As a result, the composition ratio of the second element in the film may be controlled to be lower.

[0099] (e) In step B3, by supplying the second reaction gas that reacts with both the first halogen terminations and the second halogen terminations, it is possible to desorb the first halogen element or the second halogen element bonded to the first element from the second Si-containing layer doped with the second element. As a result, impurities such as the first halogen element and the second halogen element in the film may be reduced. In addition, by desorbing the first halogen element or the second halogen element bonded to the first element from the second Si-containing layer doped with the second element, and forming dangling bonds of the first element, adsorption of the second precursor gas in step B1 of the subsequent cycle may be promoted. As a result, it is possible to promote film formation.

[0100] (f) By using the same gas for the first precursor gas and the second precursor gas, the composition of the first layer and the composition of the second layer may be brought closer to each other, except for the second element. That is, characteristics of the film in a thickness

direction may be brought closer to being uniform, except for the second element.

[0101] (g) By using the same gas for the first reaction gas and the second reaction gas, the composition of the first layer and the composition of the second layer may be brought closer to each other, except for the second element. That is, the characteristics of the film in the thickness direction may be brought closer to being uniform, except for the second element.

[0102] (h) The ratio of the second number of times in the second process to the first number of times in the first process is set such that the composition ratio of the second element in the film reaches a predetermined ratio. This allows the composition ratio of the second element in the film to be controlled to a desired value by regulating a ratio of the number of stacked layers of the first layer, which does not contain the second element, and the second layer, which contains the second element.

[0103] (i) The supply amount of the second precursor gas in step B1 is set such that the composition ratio of the second element in the second layer reaches a predetermined ratio. For example, by regulating the supply amount of the second precursor gas in step B1, it is possible to regulate a ratio of adsorption sites on the surface of the wafer 200 at which the third precursor gas (specifically, the second element) can be adsorbed (i.e., sites that are not terminated with the first halogen element). This allows the composition ratio of the second element in the second layer to be controlled. Specifically, for example, in step B1, by performing at least one selected from the group of reducing the supply flow rate of the second precursor gas and shortening the supply time of the second precursor gas, the ratio of adsorption sites on the surface of the wafer 200 for the second element is increased. This increases an amount of adsorption of the second element, thereby increasing the composition ratio of the second element in the film. Also, for example, in step B1, by performing at least one selected from the group of increasing the supply flow rate of the second precursor gas and lengthening the supply time of the second precursor gas, the ratio of adsorption sites on the surface of the wafer 200 for the second element is decreased. This decreases the amount of adsorption of the second element, thereby decreasing the composition ratio of the second element in the film.

[0104] (j) By setting the thickness of the first layer to a thickness at which the second element contained in the second layer is able to diffuse throughout the entire thickness direction of the adjacent first layer (a thickness equal to or less than such a thickness), it is possible for the second element to be diffused throughout the entire film (throughout the entire thickness direction of the film). A distribution of the composition ratio in the thickness direction of the film may be controlled.

[0105] (k) By setting the first number of times (m times) and the second number of times (n times) to 1 or more and 10 or less, it is possible for the second element to be diffused throughout the thickness direction of the film, making the composition ratio of the second element substantially uniform. When the first number of times and the second number of times exceed 10, the diffusion of the second element may not reach throughout the thickness direction of the film, and the composition ratio of the second element may become uneven.

[0106] (4) Modifications

The substrate processing sequence in the present embodiments may be modified as shown in the following modifications. These modifications may be combined arbitrarily. Unless otherwise specified, the processing procedure and processing condition in each step of each modification may be the same as the processing procedure and processing condition in each step of the substrate processing sequence described above.

[0107] (Modification 1)

As shown in FIG. 6A, in addition to performing a first cycle including the first process and the second process, a second cycle including the first process and the second process may be further performed. At this time, a ratio of the second number of times (n times) to the first number of times (m times) in the first cycle may be made different from a ratio of the second number of times (n' times) to the first number of times (m' times) in the second cycle. That is, the ratio of the second number of times to the first number of times may be varied depending on how many times the cycle including the first process and the second process is executed so far. Also, at this time, the number of times the first cycle is performed (p times) and the number of

times the second cycle is performed (p' times) may be the same or different. m, m', n, n', p, and p' are each an integer of 1 or 2 or more.

[0108] Specifically, for example, the process of performing the second cycle may be performed after the process of performing the first cycle, and the ratio of the second number of times to the first number of times in the first cycle (n/m) may be set greater than the ratio of the second number of times to the first number of times in the second cycle (n'/m'). That is, the composition ratio of the second element in the film formed in the preceding cycle (first cycle) may be set greater than the composition ratio of the second element in the film formed in the subsequent cycle (second cycle). Also, for example, the number of times the second cycle is performed (p' times) may be set greater than the number of times the first cycle is performed (p times).

[0109] In addition to the first cycle and the second cycle, a process of performing a third cycle including the first process sand the second process may be further performed. At this time, the ratios of the second number of times to the first number of times in the first cycle, the second cycle, and the third cycle may be different from one another.

[0110] According to this modification, effects similar to those obtained by the above-described embodiments may be obtained. In this modification, it is further possible to form a plurality of layers with mutually different composition ratios of the second element. This makes it possible to vary the composition ratio of the second element in the thickness direction of the film and to impart a gradient to the composition ratio.

[0111] In this modification, it is further possible, by setting the ratio of the second number of times to the first number of times in the first cycle (n/m) greater than the ratio of the second number of times to the first number of times in the second cycle (n/m'), to form, in a process of forming a charge trap film on a blocking film as one of manufacturing processes of a non-volatile memory cell such as a NAND-type flash memory, a layer with a larger composition ratio of the second element and a higher charge trap density on a side closer to the blocking film, and a layer with a smaller composition ratio of the second element and a lower charge trap density on

a side farther from the blocking film (*see* FIG. 9). This makes it possible to improve electrical characteristics of the charge trap film.

[0112] In this modification, it is further possible, by setting the number of times the second cycle is performed (p' times) greater than the number of times the first cycle is performed (p times), to make a thickness of the layer with a smaller composition ratio of the second element greater than a thickness of the layer with a larger composition ratio of the second element (*see* FIG. 9).

[0113] In this modification, it is further possible, by changing the ratio of the second number of times to the first number of times in the first cycle, the second cycle, and the third cycle, to change the composition ratio of the second element in a stepwise manner in the thickness direction of the film.

[0114] (Modification 2)

As shown in FIG. 6B, step B1 may further include, after the first period, a period during which the supply of the second precursor gas is continued while the third precursor gas is supplied. That is, step B1 and step B2 may include a period during which the second precursor gas and the third precursor gas are supplied simultaneously. The notation "2+3" shown in FIG. 6B indicates an overlapping period between a supply period of the second precursor gas (an execution period of step B1) and a supply period of the third precursor gas (an execution period of step B2). The same applies to the notation "2+4" shown in FIG. 7B.

[0115] In this modification, the supply flow rate of the second precursor gas during the first period (specifically, at least one selected from the group of a length of the first period in step B1 and the supply flow rate of the second precursor gas during the first period) may be set such that the composition ratio of the second element in the second layer reaches a predetermined ratio.

[0116] According to this modification, effects similar to those obtained by the above-described embodiments may be obtained.

[0117] (Modification 3)

A H-free gas may be used as the second precursor gas, and the cycle including steps B1, B2, and B3 described above may further include step B4 of supplying the fourth precursor gas

containing the first element, the third halogen element, and H, before supplying the third precursor gas (*see* FIG. 7A). In FIG. 7A, the fourth precursor gas is denoted as "4." The same applies to FIG. 7B and FIG. 8B described later.

[0118] As the second precursor gas in this modification, for example, one or more of the H-free halosilane-based gases listed in the above-described embodiments may be used.

[0119] As the fourth precursor gas, for example, a H-containing halosilane-based gas, which contains Si as the first element, the third halogen element, and H, may be used. The third halogen element includes Cl, F, Br, I, and the like. The third halogen element may be the same element as the first halogen element or the second halogen element, or may be a different element. As the fourth precursor gas, for example, one or more of the H-containing halosilane-based gases listed in the above-described embodiments may be used.

[0120] In this modification, the composition ratio of the second element contained in the second layer may be regulated by regulating a ratio of the supply amount of the second precursor gas to a supply amount of the fourth precursor gas. Specifically, the composition ratio of the second element contained in the second layer may be regulating by regulating at least one selected from the group of a supply flow rate and a supply time of either the second precursor gas or the fourth precursor gas.

[0121] In this modification, the ratio of the supply amount of the second precursor gas to the supply amount of the fourth precursor gas may be varied in accordance with the number of times the cycle including the first process and the second process is executed so far (i.e., in accordance with which execution number the cycle is at).

[0122] According to this modification, the same effects as those obtained by the above-described embodiments may be obtained. Further, in this modification, by supplying, prior to supplying the third precursor gas, the fourth precursor gas capable of forming H-terminations on the surface of the wafer 200 that serve as adsorption sites for the third precursor gas (specifically, the second element), it is possible to increase the composition ratio of the second element in the film.

[0123] Further, in this modification, it is also possible to regulate the composition ratio of the second element contained in the second layer may by regulating the ratio of the supply amount of the second precursor gas to the supply amount of the fourth precursor gas.

[0124] Further, in this modification, it is also possible to vary the composition ratio of the second element in the thickness direction of the film by varying the ratio of the supply amount of the second precursor gas to the supply amount of the fourth precursor gas in accordance with the number of times the cycle is executed so far.

[0125] Further, in this modification, an example in which a purge is performed between step B1 and step B4 is described; however, as shown in FIG. 7B, at least a portion of an execution period of step B1 and an execution period of step B4 may overlap. In this modification as well, the same effects as those of the above-described embodiments may be obtained.

[0126] (Modification 4)

As shown in FIG. 8A, a third process of forming a third layer containing the first element and the second element may be further included by performing a cycle a third number of times (r times), the cycle including: step C1 of supplying the second precursor gas to the wafer 200; step C2 of supplying the second reaction gas after supply of the second precursor gas is performed for a third period in step C1; and step C3 of supplying the third precursor gas after the supply of the second reaction gas is performed for a fourth period in step C2. A film that includes the first layer, the second layer, and the third layer and contains the first element and the second element may be formed on the wafer 200 by performing a cycle a predetermined number of times (p times), the cycle including the first process, the second process, and the third process. r and p are each an integer of 1 or 2 or more.

[0127] In this modification, a ratio of the first number of times (m times), the second number of times (n times), and the third number of times (r times) may be set such that the composition ratio of the second element in the film reaches a predetermined ratio. The first number of times (m times) may be set to zero in accordance with a desired composition ratio of the second element.

[0128] According to this modification, effects similar to those obtained by the above-described embodiments may be obtained. Further, in this modification, in the third process, halogen terminations formed on the outermost surface of the wafer 200 by the supply of the second precursor gas may be desorbed by the reaction gas, thereby increasing adsorption sites (e.g., N-H terminations) at which the third precursor gas can be adsorbed. For this reason, in the third process, it is possible to make adsorption probability of the third precursor gas greater compared to the second process, thus increasing a composition ratio of the second element contained in the third layer compared to the second layer.

[0129] Further, according to this modification, it is possible to control the composition ratio of the second element in the film to a desired value by regulating a ratio of the number of stacked layers of the first layer, which does not contain the second element, and the second layer and the third layer, which contain the second element at mutually different composition ratios.

[0130] (Modification 5)

As shown in FIG. 8B, a third process of forming a third layer containing the first element and the second element may be further included by performing a cycle a third number of times (r times, where r is an integer of 1 or 2 or more), the cycle including: step D1 of supplying the fourth precursor gas containing the first element, the third halogen element, and H; step D2 of supplying the third precursor gas after the supply of the fourth precursor gas is performed for a first period in step D1; and step D3 of supplying the second reaction gas after the supply of the third precursor gas is performed for a second period in step D2. A film that includes the first layer, the second layer, and the third layer and contains the first element and the second element may be formed on the wafer 200 by performing a cycle including the first process, the second process, and the third process. As the fourth precursor gas, for example, one or more of the H-containing halosilane-based gases listed in the above-described embodiments may be used.

[0131] In this modification, a ratio of the first number of times (m times), the second number of times (n times), and the third number of times (r times) may be set such that the composition ratio of the second element in the film reaches a predetermined ratio. The first number of times

(m times) may be set to zero in accordance with a desired composition ratio of the second element.

[0132] According to this modification, effects similar to those obtained by the above-described embodiments may be obtained. Further, in this modification, in the third process, since it is possible to form, on the surface of the wafer 200, a H-termination to which the third precursor gas can be adsorbed, before supplying the third precursor gas, an adsorption rate of the third precursor gas may be increased compared to the second process, and a composition ratio of the second element contained in the third layer may be increased compared to the second layer.

[0133] According to this modification, by regulating a ratio of the number of stacked layers of the first layer, which does not contain the second element, and the second layer and the third layer, which contain the second element at mutually different composition ratios, it is possible to control the composition ratio of the second element in the film to a desired value.

[0134] (Modification 6)

As shown in FIG. 8C, a third process of forming a third layer containing the first element may be further included by performing a cycle including step A1 and step A2 a third number of times (s times); and a fourth process of forming a fourth layer containing the first element and the second element may be further included by performing a cycle a fourth number of times (t times), the cycle including: step C1 of supplying the second precursor gas; step C2 of supplying the second reaction gas after the supply of the second precursor gas is performed for a third period in step C1; and step C3 of supplying the third precursor gas after the supply of the second reaction gas is performed for a fourth period in step C2. A film that includes the first layer, the second layer, the third layer, and the fourth layer and contains the first element and the second element may be formed on the wafer 200 by performing a process of performing a first cycle including the first process and the second process, and a process of performing a second cycle including the third process and the fourth process. s and t are an integer of 1 or 2 or more.

[0135] According to this modification, effects similar to those obtained by the above-described embodiments may be obtained. Further, in this modification, in the fourth process, similarly to

the third process in Modification 4 described above, the adsorption probability of the third precursor gas may be increased compared to the second process, and a composition ratio of the second element contained in the fourth layer may be increased compared to the second layer. Therefore, by further performing the second cycle in which the fourth process is performed, it is possible to vary the composition ratio of the second element in the thickness direction of the film.

[0136] <Other Embodiments of Present Disclosure>

The embodiments of the present disclosure are specifically described above. However, the present disclosure is not limited to the above-described embodiments, and various changes may be made without departing from the scope of the present disclosure.

[0137] In the present disclosure, for example, as the first reaction gas and the second reaction gas, oxidizing gases (i.e., gases containing oxygen (O) as the third element) such as oxygen (O_2) gas, ozone (O_3) gas, water vapor (H_2O gas), nitrogen monoxide (NO) gas, nitrous oxide (N_2O) gas, hydrogen peroxide (H_2O_2) gas, hydrogen (H_2) gas + oxygen (O_2) gas, H_2 gas + ozone (O_3) gas, and the like or H-containing gases such as NH_3 gas, hydrogen (H_2) gas, H_2 gas + O_2 gas, and the like may be used. The H-containing gas may partially overlap with oxidizing gases or hydrogen nitride-based gases. The notation of two gases written together, such as "H_2 gas + O_2 gas" in the present disclosure, means a mixed gas of H_2 gas and O_2 gas. In this embodiment as well, the same effects as those of the above-described embodiments may be obtained.

[0138] In the present disclosure, for example, it is desirable that at least one selected from the group of the first element and the second element is a metal element or a half metal element. The half metal element in the present disclosure refers to boron (B), germanium (Ge), arsenic (As), antimony (Sb), and tellurium (Te), in addition to Si. As the metal element, for example, zirconium (Zr), hafnium (Hf), tantalum (Ta), niobium (Nb), aluminum (Al), molybdenum (Mo), and tungsten (W), in addition to Ti, may be used. As the first precursor gas, the second precursor gas, and the third precursor gas, for example, gases containing halides of the above-described metal elements or half metal elements may be used. As the first precursor gas, the

second precursor gas, and the third precursor gas, one or more of these substances may be used. However, the first element and the second element are metal elements or half metal elements that are different from each other. In this embodiment as well, the same effects as those of the above-described embodiments may be obtained.

[0139] In the present disclosure, as the film formed, a half metal nitride film doped with the above-described metal element (for example, a SiN film doped with the above-described metal element) may be exemplified. The film formed may be a metal nitride film doped with a half metal element (for example, a titanium nitride film (TiN film) doped with the above-described half metal element). The film formed may be a metal nitride film doped with a metal element (for example, a TiN film doped with the above-described metal element). The film formed may be a half metal nitride film doped with a half metal element (for example, a SiN film doped with the above-described half metal element). Also, an oxide film may be formed instead of a nitride film. In this modification as well, the same effects as those of the above-described embodiments may be obtained.

[0140] In the present disclosure, for example, the first number of times (m times) and the second number of times (n times) may be 11 or more. By setting the first number of times and the second number of times to 11 or more, a bias may be introduced in the composition ratio of the second element in the thickness direction of the film, so as to form layers with different composition ratios of the second element.

[0141] The present disclosure may be suitably applied to, for example, a case where a film is formed using a single-substrate type substrate processing apparatus that processes one or several substrates at a time. The present disclosure may also be suitably applied to a case where a film is formed using a substrate processing apparatus with a cold-wall type process furnace. The present disclosure may also be suitably applied to, for example, a case where a gas is activated by plasma generated inside or outside the process chamber 201, or a case where a gas is activated by irradiating the gas with electromagnetic waves using a lamp or the like.

[0142] Even when these substrate processing apparatuses are used, each processing may be

performed under the same processing sequences and processing conditions as in the above-described embodiments and modifications. The same effects as in the above-described embodiments and modifications may be obtained.

[0143] The above-described embodiments and modifications may be used in combination as appropriate. The processing procedures and process conditions at this time may be the same as, for example, the processing procedures and process conditions in the above-described embodiments and modifications.

EXPLANATION OF REFERENCE NUMERALS

[0144] 200: wafer (substrate)

WHAT IS CLAIMED IS:

1. A method of processing a substrate, comprising:

forming a film containing a first element and a second element on the substrate by performing:

a first process of forming a first layer containing the first element by performing a cycle a first number of times, the cycle for performing the first process including:

(a-1) supplying a first precursor gas containing the first element to the substrate; and

(a-2) supplying a first reaction gas to the substrate; and

a second process of forming a second layer containing the first element and the second element by performing a cycle a second number of times, the cycle for performing the second process including:

(b-1) supplying a second precursor gas containing the first element and a first halogen element to the substrate;

(b-2) supplying a third precursor gas, which contains the second element not contained in the first layer and a second halogen element, to the substrate, after the supply of the second precursor gas is performed for a first period in (b-1); and

(b-3) supplying a second reaction gas to the substrate, after the supply of the third precursor gas is performed for a second period in (b-2).

2. The method of Claim 1, wherein the third precursor gas is a gas containing no hydrogen.

3. The method of Claim 1 or 2, wherein the second precursor gas is a gas containing no hydrogen.

4. The method of any one of Claims 1 to 3, wherein a ratio of the second number of times to the first number of times is set such that a composition ratio of the second element in the film becomes a predetermined ratio.

5. The method of any one of Claims 1 to 4, wherein at least one selected from the group of a supply flow rate of the second precursor gas and a supply time of the second precursor gas in (b-1) is set such that a composition ratio of the second element in the second layer becomes a predetermined ratio.

6. The method of any one of Claims 1 to 5, wherein the film is formed by performing a cycle including the first process and the second process a third number of times of two or more.

7. The method of any one of Claims 1 to 6, further comprising:

performing a first cycle including the first process and the second process; and

performing a second cycle including the first process and the second process,

wherein a ratio of the second number of times to the first number of times in the first cycle is different from a ratio of the second number of times to the first number of times in the second cycle.

8. The method of any one of Claims 1 to 7, wherein (b-1) further includes, after the first period, a period during which the supply of the second precursor gas is continued while the third precursor gas is being supplied.

9. The method of any one of Claims 1, 2, and 4 to 8, wherein the second precursor gas is a gas containing no hydrogen, and

wherein the cycle including (b-1), (b-2), and (b-3) further includes:

(b-4) supplying a fourth precursor gas, which contains the first element, a third

halogen element, and hydrogen, to the substrate, before supplying the third precursor gas to the substrate.

10. The method of any one of Claims 1 to 8, further comprising:

a third process of forming a third layer containing the first element and the second element by performing a cycle a third number of times, the cycle for performing the third process including:

(c-1) supplying the second precursor gas to the substrate;

(c-2) supplying the second reaction gas to the substrate, after the supply of the second precursor gas is performed for a third period in (c-1); and

(c-3) supplying the third precursor gas to the substrate, after the supply of the second reaction gas is performed for a fourth period in (c-2),

wherein the film containing the first element and the second element is formed on the substrate by performing a cycle including the first process, the second process, and the third process.

11. The method of any one of Claims 1 to 8, further comprising:

a third process of forming a third layer containing the first element and the second element by performing a cycle a third number of times, the cycle for performing the third process including:

(d-1) supplying a fourth precursor gas, which contains the first element, a third halogen element, and hydrogen, to the substrate;

(d-2) supplying the third precursor gas to the substrate, after the supply of the fourth precursor gas is performed for a first period in (d-1); and

(d-3) supplying the second reaction gas to the substrate, after the supply of the third precursor gas is performed for a second period in (d-2),

wherein the film containing the first element and the second element is formed on the

substrate by performing a cycle including the first process, the second process, and the third process.

12. The method of Claim 1, further comprising:

a third process of forming a third layer containing the first element by performing a cycle including (a-1) and (a-2) a third number of times; and

a fourth process of forming a fourth layer containing the first element and the second element by performing a cycle a fourth number of times, the cycle for performing the fourth process including:

(c-1) supplying the second precursor gas to the substrate;

(c-2) supplying the second reaction gas to the substrate, after the supply of the second precursor gas is performed for a third period in (c-1); and

(c-3) supplying the third precursor gas to the substrate, after the supply of the second reaction gas is performed for a fourth period in (c-2),

wherein the film containing the first element and the second element is formed on the substrate by performing a first cycle including the first process and the second process, and a second cycle including the third process and the fourth process.

13. A method of manufacturing a semiconductor device, comprising:

forming a film containing a first element and a second element on a substrate by performing:

a first process of forming a first layer containing the first element by performing a cycle a first number of times, the cycle for performing the first process including:

(a-1) supplying a first precursor gas containing the first element to the substrate; and

(a-2) supplying a first reaction gas to the substrate; and

a second process of forming a second layer containing the first element and the second element by performing a cycle a second number of times, the cycle for performing the second process including:

(b-1) supplying a second precursor gas containing the first element and a first halogen element to the substrate;

(b-2) supplying a third precursor gas, which contains the second element not contained in the first layer and a second halogen element, to the substrate, after the supply of the second precursor gas is performed for a first period in (b-1); and

(b-3) supplying a second reaction gas to the substrate, after the supply of the third precursor gas is performed for a second period in (b-2).

14. A program that causes, by a computer, a substrate processing apparatus to perform:

forming a film containing a first element and a second element on a substrate by performing:

a first process of forming a first layer containing the first element by performing a cycle a first number of times, the cycle for performing the first process including:

(a-1) supplying a first precursor gas containing the first element to the substrate; and

(a-2) supplying a first reaction gas to the substrate; and

a second process of forming a second layer containing the first element and the second element by performing a cycle a second number of times, the cycle for performing the second process including:

(b-1) supplying a second precursor gas containing the first element and a first halogen element to the substrate;

(b-2) supplying a third precursor gas, which contains the second element not contained in the first layer and a second halogen element, to the

substrate, after the supply of the second precursor gas is performed for a first period in (b-1); and

(b-3) supplying a second reaction gas to the substrate, after the supply of the third precursor gas is performed for a second period in (b-2).

15. A substrate processing apparatus comprising:

a gas supply system configured to supply, to a substrate, a first precursor gas containing a first element, a second precursor gas containing the first element and a first halogen element, a third precursor gas containing a second halogen element and a second element, a first reaction gas, and a second reaction gas; and

a controller configured to be capable of controlling the gas supply system so as to perform:

forming a film containing the first element and the second element on the substrate by performing:

a first process of forming a first layer containing the first element by performing a cycle a first number of times, the cycle for performing the first process including:

(a-1) supplying the first precursor gas to the substrate; and

(a-2) supplying the first reaction gas to the substrate; and

a second process of forming a second layer containing the first element and the second element by performing a cycle a second number of times, the cycle for performing the second process including:

(b-1) supplying the second precursor gas to the substrate;

(b-2) supplying the third precursor gas, which contains the second element not contained in the first layer, to the substrate, after the supply of the second precursor gas is performed for a first period in (b-1); and

(b-3) supplying the second reaction gas to the substrate, after the supply of the third precursor gas is performed for a second period in (b-2).