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 substrate processing process may be performed in which a precursor gas and a reaction gas are supplied to a substrate to form a film on the substrate (*see,* for example, Patent Document 1).

[Prior Art Document]

Patent Document

[0003] Patent Document 1: Japanese Laid-open Patent Publication 2014-135475

SUMMARY

[0004] The present disclosure provides a technique capable of improving characteristics of a film formed on a substrate.

[0005] According to one embodiment of the present disclosure, there is provided a technique that includes: (a) supplying a first material containing a first element constituting the film to the substrate; (b) supplying a second material containing a second element constituting the film to the

substrate; (c) supplying a third material containing a third element to be added to the film to the substrate; and (d) performing (a), (b), and (c) a predetermined number of times to form the film containing the first element, the second element, and the third element. A difference between an electronegativity of the third element and an electronegativity of the second element is greater than a difference between an electronegativity of the first element and the electronegativity of the second element.

[0006] According to the present disclosure, it is possible to provide the technique capable of improving characteristics of the film formed on the substrate.

BRIEF DESCRIPTION OF DRAWINGS

[0007] FIG. 1 is a vertical cross-sectional view schematically showing a vertical process furnace of a substrate processing apparatus according to one embodiment.

FIG. 2 is a schematic cross-sectional view taken along line A-A in FIG. 1.

FIG. 3 is a diagram showing a schematic configuration of a controller of a substrate processing apparatus according to one embodiment, and is a block diagram of a control system of the controller.

FIG. 4 is a diagram showing an example of a substrate processing process according to one embodiment.

DETAILED DESCRIPTION

[0008] Hereinafter, one embodiment of the present disclosure will be described mainly with reference to FIGS. 1 to 4. Drawings used in the following description are schematic. Dimensional relationships, ratios, and the like of various elements shown in the drawings may not match actual ones. Further, the dimensional relationships, ratios, and the like of various elements may not match one another among multiple drawings.

[0009] (1) Configuration of Substrate Processing Apparatus

The substrate processing apparatus 10 includes a process furnace 202 in which a heater 207 serving as a heating means (heating mechanism, heating system) is installed. The heater 207 is formed in a cylindrical shape and is vertically installed by being supported by a heater base (not shown) serving as a support plate.

[0010] Inside the heater 207, an outer tube 203 constituting a reaction tube (that is, reaction container and process container) is disposed concentrically with the heater 207. The outer tube 203 is made of a heat-resistant material such as quartz or silicon carbide (SiC.) The outer tube 203 is formed in a cylindrical shape with a closed upper end and an open lower end. Below the outer tube 203, a manifold 209 (hereinafter, MF 209) is disposed concentrically with the outer tube 203. The MF 209 is made of a metal such as stainless steel. The MF 209 is formed in a cylindrical shape with open upper and lower ends. An O-ring 220a is installed as a seal between the upper end of the MF 209 and the outer tube 203. With the MF 209 supported by the heater base, the outer tube 203 is in a vertically installed state.

[0011] Inside the outer tube 203, an inner tube 204 constituting a reaction container is disposed. The inner tube 204 is made of a heat-resistant material such as quartz or SiC. The inner tube 204 is formed in a cylindrical shape with a closed upper end and an open lower end. A process container (that is, reaction container) is mainly constituted by the outer tube 203, the inner tube 204, and the MF 209. A process chamber 201 is formed in a hollow cylindrical region of the process container (that is, inside the inner tube 204.)

[0012] The process chamber 201 is configured to be capable of accommodating wafers 200 serving as substrates. The wafers 200 are arranged in a horizontal posture and in multiple stages along a vertical direction by a boat 217 as a support.

[0013] Nozzles 410, 420, and 430 are installed inside the process chamber 201 so as to penetrate through a sidewall of the MF 209 and the inner tube 204. Gas supply pipes 310, 320, and 330 are connected to the nozzles 410, 420, and 430, respectively. However, the process furnace 202 of the present embodiment is not limited to the above-described configuration.

[0014] At the gas supply pipes 310, 320, and 330, mass flow controllers (MFCs) 312, 322, and 332, which are flow rate controllers (flow rate control parts), are respectively installed in order from an upstream side. At the gas supply pipes 310, 320, and 330, valves 314, 324, and 334, which are as opening/closing valves, are respectively installed. Gas supply pipes 510, 520, and 530 for supplying an inert gas are respectively connected to downstream sides of the valves 314, 324, and 334 of the gas supply pipes 310, 320, and 330. At the gas supply pipes 510, 520, and 530, MFCs 512, 522, and 532, which are flow rate controllers (flow rate control parts), and valves 514, 524, and 534, which are opening/closing valves, are respectively installed in order from an upstream side.

[0015] Nozzles 410, 420, and 430 are connected to tip end portions of the gas supply pipes 310, 320, and 330, respectively. The nozzles 410, 420, and 430 are configured as L-shaped nozzles. Horizontal portions of the nozzles 410, 420, and 430 are installed so as to penetrate through the sidewall of the MF 209 and the inner tube 204. Vertical portions of the nozzles 410, 420, and 430 are installed inside a preliminary chamber 201a. The preliminary chamber 201a is formed in a channel shape (groove shape), so as to protrude outward in a radial direction of the inner tube 204 and to extend in the vertical direction. The vertical portions of the nozzles 410, 420, and 430 are installed along an inner wall of the inner tube 204 in an upward direction of the preliminary chamber 201a (upward in the stacking direction of the wafers 200.)

[0016] The nozzles 410, 420, and 430 are installed so as to extend from a lower region of the process chamber 201 to an upper region of the process chamber 201. A plurality of gas supply holes 410a, 420a, and 430a are respectively installed at the nozzles 410, 420, and 430, at positions facing the wafers 200. Thus, a process gas is supplied from the gas supply holes 410a, 420a, and 430a of the respective nozzles 410, 420, and 430 to the wafers 200. The plurality of the gas supply holes 410a, 420a, and 430a are installed at height positions from a lower portion to an upper portion of the inner tube 204. Each of the gas supply holes 410a, 420a, and 430a is of the same aperture area. Further, the gas supply holes 410a, 420a, and 430a are arranged at the same pitch. However, the gas supply holes 410a, 420a, and 430a are not limited to the above-

described configuration. For example, the aperture area of the gas supply holes 410a, 420a, and 430a may be gradually increased from the lower portion toward the upper portion of the inner tube 204. Consequently, flow rates of the gas supplied from the gas supply holes 410a, 420a, and 430a to the wafers 200 can be made more uniform.

[0017] The plurality of the gas supply holes 410a, 420a, and 430a of the nozzles 410, 420, and 430 are installed at height positions from a lower portion to an upper portion of the boat 217. Therefore, the process gas supplied into the process chamber 201 from the gas supply holes 410a, 420a, and 430a of the nozzles 410, 420, and 430 is supplied to an entire region of the wafers 200 accommodated from the lower portion to the upper portion of the boat 217. The nozzles 410, 420, and 430 may be installed so as to extend from the lower region to the upper region of the process chamber 201, but may be installed so as to extend to a vicinity of a ceiling of the boat 217.

[0018] A first material is supplied from the gas supply pipe 310 into the process chamber 201 via the MFC 312, the valve 314, and the nozzle 410. In the present disclosure, the first material is also referred to as a precursor, a precursor agent, or a source. When the first material is in a gas state, the first material in the gas state is also referred to as a first gas, a precursor gas, a source gas, or the like.

[0019] A second material is supplied from the gas supply pipe 320 into the process chamber 201 via the MFC 322, the valve 324, and the nozzle 420. In the present disclosure, the second material is also referred to as a reacting agent, a reagent, or a reactant. When the second material is in a gas state, the second material in the gas state is also referred to as a second gas, a reaction gas, a reactant gas, or the like.

[0020] A third material is supplied from the gas supply pipe 330 into the process chamber 201 via the MFC 332, the valve 334, and the nozzle 430. In the present disclosure, the third material is also referred to as a dopant, a doping agent, an additive, or the like. When the third material is in a gas state, the third material in the gas state is also referred to as a third gas, a doping gas, an additive gas, or the like.

[0021] The term "agent" used in the present disclosure includes at least one selected from the group of a gaseous substance and a liquid substance. The liquid substance includes a mist-like substance. That is, a conditioning agent may include a gaseous substance, may include a liquid substance such as a mist-like substance, or may include both.

[0022] From the gas supply pipes 510, 520, and 530, an inert gas such as nitrogen (N_2) gas, is supplied into the process chamber 201 via the MFCs 512, 522, and 532, the valves 514, 524, and 534, and the nozzles 410, 420, and 430, respectively. Hereinafter, an example in which N_2 gas is used as the inert gas will be described. In the present disclosure, in addition to N_2 gas, a rare gas such as Ar gas, He gas, Ne gas, or Xe gas may be used as the inert gas.

[0023] When the first material flows from the gas supply pipe 310, a first material supply system (first gas supply system) mainly includes the gas supply pipe 310, the MFC 312, and the valve 314. The nozzle 410 may also be included in the first material supply system. When the second material flows from the gas supply pipe 320, a second material supply system (second gas supply system) mainly includes the gas supply pipe 320, the MFC 322, and the valve 324. The nozzle 420 may also be included in the second material supply system. When the third material flows from the gas supply pipe 330, a third material supply system (third gas supply system) mainly includes the gas supply pipe 330, the MFC 332, and the valve 334. The nozzle 430 may also be included in the conditioning agent supply system. A process gas supply system includes the first material supply system, the second material supply system, and the third material supply system. The nozzles 410, 420, and 430 may also be included in the process gas supply system. An inert gas supply system mainly includes the gas supply pipes 510, 520, and 530, the MFCs 512, 522, and 532, and the valves 514, 524, and 534.

[0024] A reservoir 701 configured to store the first material may be installed at the gas supply pipe 310, and a valve 702 may be installed at a downstream side of the reservoir 701 (that is, on a process chamber 201 side.)

[0025] In the present embodiment, the inner wall of the inner tube 204 and end portions of a plurality of wafers 200 define an annular, vertically elongated space. A gas is conveyed into the

inner tube 204 via the nozzles 410, 420, and 430 disposed in the preliminary chamber 201a within the annular, vertically elongated space. The gas is then ejected into the inner tube 204 from the plurality of gas supply holes 410a, 420a, and 430a installed at positions on the nozzles 410, 420, and 430 that face the wafers 200. More specifically, the gas and the like are ejected in a direction parallel to surfaces of the wafers 200 from the gas supply holes 410a of the nozzle 410, the gas supply holes 420a of the nozzle 420, and the gas supply holes 430a of the nozzle 430.

[0026] An exhaust hole (exhaust port) 204a is a through-hole formed in a sidewall of the inner tube 204 at a position facing the nozzles 410, 420, and 430. The exhaust hole 204a is, for example, a slit-shaped through-hole that is elongated in the vertical direction. The gas supplied into the process chamber 201 from the gas supply holes 410a, 420a, and 430a of the nozzles 410, 420, and 430 and flowing over the surfaces of the wafers 200 passes through the exhaust hole 204a and flows into a gap formed between the inner tube 204 and the outer tube 203 (that is, into an exhaust path 206.) The gas that flows into the exhaust path 206 then flows into an exhaust pipe 231 and is discharged to an outside of the process furnace 202.

[0027] The exhaust hole 204a is installed at a position facing the plurality of wafers 200. The gas supplied from the gas supply holes 410a, 420a, and 430a into the vicinity of the wafers 200 in the process chamber 201 flows in a horizontal direction and then passes through the exhaust hole 204a and flows into the exhaust path 206. The exhaust hole 204a is not limited to being configured as the slit-shaped through-hole, and may be configured as a plurality of holes.

[0028] The exhaust pipe 231 configured to exhaust an atmosphere inside the process chamber 201 is connected to the exhaust port 231a installed in the MF 209. A pressure sensor 245, which is a pressure detector (pressure detecting part) configured to detect a pressure inside the process chamber 201, an auto pressure controller (APC) valve 243, and a vacuum pump 246 serving as a vacuum-exhauster, are connected to the exhaust pipe 231 sequentially from an upstream side. The APC valve 243 can vacuum-exhaust or stop vacuum-exhausting the process chamber 201 by opening and closing the valve while the vacuum pump 246 is in operation. Further, the APC

valve 243 can regulate the pressure in the process chamber 201 by adjusting an opening degree of the valve while the vacuum pump 246 is in operation. An exhaust system mainly includes the exhaust hole 204a, the exhaust path 206, the exhaust pipe 231, the APC valve 243, and the pressure sensor 245. The vacuum pump 246 may also be included in the exhaust system.

[0029] A seal cap 219 (hereinafter also referred to as SC 219) serving as a furnace opening lid that is capable of hermetically sealing a lower end opening of the MF 209 is installed under the MF 209. The SC 219 is configured to come into contact with the lower end of the MF 209 from a lower side in the vertical direction. The SC 219 is made of, for example, a metal such as SUS, and is formed in a disc shape. An O-ring 220b serving as a seal making contact with the lower end of the MF 209 is installed at an upper surface of the SC 219. A rotator 267 configured to rotate the boat 217 in which the wafers 200 are accommodated is installed at an opposite side of the process chamber 201 with respect to the SC 219. A rotary shaft 255 of the rotator 267 passes through the SC 219 and is connected to the boat 217. The rotator 267 is configured to rotate the wafers 200 by rotating the boat 217. The SC 219, which serves as an elevation mechanism vertically installed outside the outer tube 203, is configured to be raised or lowered in the vertical direction by a boat elevator 115 (hereinafter also referred to as BE 115.). The BE 115 is configured to be capable of loading or unloading the boat 217 into or out of the process chamber 201 by raising or lowering the SC 219. The BE 115 is configured as a transfer apparatus (that is, a transfer mechanism and a transfer system) that transfers the boat 217 and the wafers 200 accommodated in the boat 217 into or out of the process chamber 201.

[0030] The boat 217 is configured such that the plurality of wafers 200, for example, 25 to 200 wafers, are arranged at intervals in the vertical direction in a horizontal posture with centers of the wafers 200 aligned with one another. The boat 217 is made of a heat-resistant material such as quartz or SiC. At the lower portion of the boat 217, dummy substrates 218 are supported in multiple stages in a horizontal posture. The dummy substrates 218 are made of a heat-resistant material such as quartz or SiC. This configuration makes it difficult for heat from the heater 207 to be transferred to the SC 219 side. However, the present embodiment is not limited to the

above-described configuration. For example, instead of the dummy substrates 218, a heat insulating cylinder may be installed at the lower portion of the boat 217. The heat insulating cylinder is a cylinder made of a heat-resistant material such as quartz or SiC.

[0031] As shown in FIG. 2, a temperature sensor 263 serving as a temperature detector is installed in the inner tube 204. The substrate processing apparatus 10 is configured to regulate an amount of electric power supplied to the heater 207 based on temperature information detected by the temperature sensor 263 such that a temperature inside the process chamber 201 falls within a desired temperature distribution. The temperature sensor 263 is configured in an L-shape, similarly to the nozzles 410, 420, and 430, and is installed along the inner wall of the inner tube 204.

[0032] As shown in FIG. 3, the controller 121 serving as a controller (control means or unit) is constituted by a computer including a central processing unit (CPU) 121a, a random access memory (RAM) 121b, a memory 121c, and an input/output (I/O) port 121d. The RAM 121b, the memory 121c, and the I/O port 121d are connected to the CPU 121a via an internal bus so as to be capable of exchanging data with the CPU 121a. An input/output device 122 such as a touch panel or the like is connected to the controller 121. The substrate processing apparatus may be configured to include a single controller or a plurality of controllers. That is, a control for executing a processing sequence to be described later may be performed by using a single controller, or may be performed by using a plurality of controllers. The plurality of controllers may be configured as a control system connected to one another via a wired or wireless communication network, and the control for executing the processing sequence to be described later may be performed by the control system as a whole. The term "controller" used in the present disclosure may include a case of including a single controller, a case of including a plurality of controllers, or a case including a control system constituted by a plurality of controllers.

[0033] The memory 121c is configured with, for example, a flash memory, a hard disk drive (HDD), or the like. A control program that controls an operation of a substrate processing

apparatus, and a process recipe describing procedures and conditions of a method of manufacturing a semiconductor device (method of processing a substrate) to be described later, and the like are readably stored in the memory 121c. The process recipe functions as a program that is combined to cause the controller 121 to execute each process (each step) in the method of manufacturing a semiconductor device (method of processing a substrate) to be described later. Hereinafter, the process recipe, the control program, and the like may be generally and simply referred to as a program. The term "program" used in the present disclosure may include the process recipe alone, the control program alone, or a combination of the process recipe and the control program. The RAM 121b is configured as a memory area in which programs, data, and the like read by the CPU 121a are temporarily held.

[0034] The I/O port 121d is connected to the MFCs 312, 322, 332, 512, 522, 532, valves 314, 324, 334, 514, 524, 534, 702, the pressure sensor 245, the APC valve 243, the vacuum pump 246, the heater 207, the temperature sensor 263, the rotator 267, and the BE 115 described above, and the like.

[0035] The CPU 121a is configured to read and execute the control program from the memory 121c, and to read the process recipe or the like 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 specific operations according to contents of the read process recipe. The specific operations include flow rate regulating operations for various gases by the MFCs 312, 322, 332, 512, 522, and 532; opening and closing operations of the valves 314, 324, 334, 514, 524, 534, and 702; a gas storing operation to the reservoir 701 by the valve 702; opening and closing operations of the APC valve 243; a pressure regulating operation based on the pressure sensor 245 by the APC valve 243; a temperature regulating operation of the heater 207 based on the temperature sensor 263; actuating and stopping of the vacuum pump 246; a rotation operation of the boat 217 and a rotational speed adjusting operation of the boat 217 by the rotator 267; raising and lowering operations of the boat 217 by the BE 115; and a loading operation of the wafers 200 into the boat 217.

[0036] The controller 121 may be configured by installing, on the computer, the above-described program stored in an external memory 123 (e.g., a magnetic disk such as a hard disk, an optical disk such as a CD or a DVD, or a semiconductor memory such as a flash memory or a memory card.) The memory 121c and the external memory 123 are each constituted as a computer-readable recording medium. Hereinafter, these are generally and simply referred to as a "recording medium." The term "recording medium" used in the present disclosure may include the memory 121c alone, the external memory 123 alone, or both the memory 121c and the external memory 123. The program (program product) may be provided to the computer using communication means such as the Internet or a dedicated line, instead of using the external memory 123.

[0037] (2) Substrate Processing Process

An example of a process of forming a silicon nitride (SiN) film used as, for example, a charge trap film of a 3D NAND, on a wafer 200, will be described with reference to FIG. 4 as one process of a manufacturing process of a semiconductor device (device). The process of forming the SiN film is performed using the process furnace 202 of the substrate processing apparatus 10 described above. In the present embodiment, an example in which a substrate (wafer) with recesses such as trenches or holes formed in a surface of the substrate is used as the wafer 200 will be described. In the following description, operations of each component constituting the substrate processing apparatus 10 are configured to be controllable by the controller 121.

[0038] The substrate processing process (manufacturing process of a semiconductor device) according to the present embodiment includes:

(a) supplying a first material containing a first element constituting a film to the wafer 200;

(b) supplying a second material containing a second element constituting the film to the wafer 200;

(c) supplying a third material containing a third element to be added to the film to the wafer 200; and

(d) performing (a), (b), and (c) a predetermined number of times to form, on the wafer 200, the film containing the first element, the second element, and the third element. A difference between an electronegativity of the third element and an electronegativity of the second element is greater than a difference between an electronegativity of the first element and the electronegativity of the second element.

[0039] In the present disclosure, the processing sequence described above includes sequences shown in (A) through (G) below. The same notation as described below is also used in the description of other embodiments.

[0040] (A) (first material → second material → third material) × X_a

(B) (first material → third material → second material) × X_b

(C) (second material → third material → first material) × X_c

(D) (third material → second material → first material) × X_d

(E) (first material + second material + third material) × X_e

(F) (first material + second material → third material) × X_f

(G) (second material + third material → first material) × X_g

Here, X_a through X_g are natural numbers (an integer of 1 or 2 or more.) "→" means supplying different types of materials sequentially, and "+" means supplying different types of materials simultaneously. Supplying different types of materials simultaneously means that there exists a period during which the supplies of different types of materials overlap. Note that between "→", a process of removing materials present on the wafers 200 (also simply referred to as a purge process) may be performed.

[0041] The term "wafer" used in the present disclosure may refer to "a wafer itself" or may refer to "a stack including a wafer and a predetermined layer, film, or the like formed on a surface of the wafer." The term "surface of a wafer" used in the present disclosure may refer to "a surface of a wafer itself" or may refer to "a surface of a predetermined layer, film, or the like formed on a wafer." The expression "forming a predetermined layer on a wafer" used in the present disclosure may mean forming a predetermined layer directly on a surface of the wafer itself, or

may mean forming a predetermined layer on a layer or the like already formed on the wafer. The term "substrate" used in the present disclosure is used synonymously with the term "wafer."

[0042] (Selection of Third Element)

A third element is selected. The element to be doped (that is, the third element) can be selected based on, for example, the following criteria A) through D).

A) Electronegativity

B) Atomic size

C) Coordination number

D) Type of element

[0043] (A: Selection Based on Electronegativity)

Here, a selection of the third element based on electronegativity in a case in which the film formed on the wafer 200 is the following film will be described. A case in which the first element contained in the film is a Group 14 element (e.g., silicon (Si)) and the second element contained in the film is a Group 15 element (e.g., nitrogen (N)) will be described.

[0044] The third element to be added to the film can be selected based on a relationship between the electronegativity of the third element and the electronegativity of the second element, and a relationship between the electronegativity of the first element and the electronegativity of the second element. For example, the third element is selected such that the difference between the electronegativity of the third element and the electronegativity of the second element is greater than the difference between the electronegativity of the first element and the electronegativity of the second element. By selecting the third element based on such a relationship, electrons of the third element in the film are attracted to the second element, so that the third element can easily become positively charged. When the film is composed of SiN and the third element is positively charged, electrons of the first element in the film are attracted to the third element, causing the first element to be slightly positively charged. As a result, an energy level at which electrons can be trapped is formed around the first element. By utilizing this effect to form a

charge trap layer of a semiconductor device, charge trap capability of the semiconductor device can be improved.

[0045] The third element may be an element with an electronegativity lower than the electronegativity of the second element. Specifically, the third element may be an element with an electronegativity lower than the electronegativity of the first element. By selecting the third element based on relative levels of electronegativities of respective elements, the above-described effects can be further enhanced.

[0046] (B: Selection Based on Atomic Size)

In selecting the third element based on atomic size, an atomic size of the third element may be substantially the same as an atomic size of the first element. In other words, it can be said that the atomic size of the third element is closer to the atomic size of the first element than to an atomic size of the second element. As the atomic size of the third element becomes closer to the atomic size of the first element, an atomic packing factor in the film can be made lower. By lowering the atomic packing factor in the film, spaces for trapping (capturing) electrons can be increased.

[0047] The third element may be an element with an atomic size that is larger than the atomic size of the first element and close to the atomic size of the first element. Specifically, the third element may be an element with an atomic size larger than the atomic size of the second element and smaller than the atomic size of another element that belongs to the same group as the first element but is different from the first element. For example, when the first element is Si, the second element is N, and the third element is an element with an atomic size larger than an atomic size of N and smaller than an atomic size of tin (Sn), which is a Group 14 element in the same group as Si, the third element can form the same four covalent bonds as Si, and Si can be substituted with the third element. Accordingly, spaces for trapping electrons can be increased. In other words, an amount of electron trapping can be increased.

[0048] (C: Selection Based on Coordination Number)

A case in which the film is composed of SiN will be described. The third element may be an

element capable of adopting a tricoordinate configuration or a tetracoordinate configuration. A tricoordinate configuration means that the third element is coordinated with three ligands. A tetracoordinate configuration means that the third element is coordinated with four ligands. The third element being capable of adopting a tricoordinate configuration means that the third element is capable of forming three ligands. The third element being capable of adopting a tetracoordinate configuration means that the third element is capable of forming four ligands. These ligands are bonded by at least one selected from the group of a covalent bond, a coordinate bond, and an ionic bond. By using an element capable of adopting a tricoordinate configuration or a tetracoordinate configuration as the third element, the spaces for trapping electrons can be increased. In other words, the amount of electron trapping can be increased. Specifically, the third element may be an element capable of adopting a tricoordinate configuration. When comparing a tetracoordinate element and a tricoordinate element, the tricoordinate element may be able to increase spaces for trapping electrons to a greater extent than the tetracoordinate element.

[0049] (D: Selection by Type of Element)

A case in which the film is composed of SiN will be described. The third element may be a metal element. By using a metal element as the third element, the same effects as described above can be obtained. Specifically, the third element may be at least one selected from the group of elements in Period 3, Period 4, and Period 5 of a periodic table. More specifically, the third element may be at least one selected from the group of elements in Period 3 and Period 4 of the periodic table. The third element may be a transition metal element. The third element may be a non-transition metal element. The non-transition metal element also satisfies selection conditions A), B), and C) described above as selection criteria, and can increase the amount of electron trapping. Examples of such non-transition metal elements include zinc (Zn), gallium (Ga), aluminum (Al), and indium (In.) The third element may be at least one selected from the group of Al, Zn, Ga, and In. Specifically, the third element may be at least one selected from the

group of Zn, Ga, and In. By using these elements as the third element, a greater number of electrons can be trapped. That is, the amount of electron trapping can be increased.

[0050] A process of preparing to supply the third material containing the third element selected based on the selection criteria described above to the wafers 200 is performed.

[0051] (Wafer Loading)

When the plurality of wafers 200 are loaded into the boat 217, as shown in FIG. 1, the boat 217 supporting the plurality of wafers 200 is raised by BE 115 and loaded into a process chamber 201. The boat 217 supporting the plurality of wafers 200 is then accommodated in the process container. In this state, SC 219 closes a lower end opening of the outer tube 203 via an O-ring 220b.

[0052] (Pressure Regulation and Temperature Regulation)

An interior of the process chamber 201 (that is, a space in which the wafers 200 exist) is exhausted by a vacuum pump 246 so as to reach a desired pressure. At this time, the pressure inside the process chamber 201 is measured by the pressure sensor 245. Then, the APC valve 243 is feedback-controlled based on the pressure information measured by the pressure sensor 245 (pressure regulation.) The vacuum pump 246 remains in operation until processing of the wafers 200 is completed. The process chamber 201 is heated by a heater 207 such that the interior of the process chamber 201 reaches a desired temperature. At this time, the amount of electric power supplied to the heater 207 is feedback-controlled based on the temperature information detected by a temperature sensor 263 such that the interior of the process chamber 201 reaches a desired temperature distribution (temperature regulation.) Heating the interior of the process chamber 201 by the heater 207 is continuously performed until the processing of the wafers 200 is completed.

[0053] (Film Formation Process)

Subsequently, a film formation process is performed. The film formation process includes supplying the first material, purging, supplying the second material, purging, supplying the third

material, purging, and determining whether these steps are performed a predetermined number of times (n times, where n is an integer of 1 or 2 or more.) Each of the steps is described below.

[0054] (Supplying First Material: First Step)

The controller 121 opens the valve 314 to allow the first material to flow into the gas supply pipe 310. After a flow rate of the first material is regulated by the MFC 312, the first material is supplied into the process chamber 201 from the gas supply hole 410a of the nozzle 410. The first material supplied into the process chamber 201 is exhausted from the exhaust pipe 231. This supplies the first material to the wafers 200. At this time, the controller 121 may open the valve 514 to allow an inert gas such as N_2 gas to flow into the gas supply pipe 510. After a flow rate of the N_2 gas flowing through the gas supply pipe 510 is regulated by the MFC 512, the N_2 gas is supplied into the process chamber 201 together with the first material. The N_2 gas supplied into the process chamber 201 is exhausted from the exhaust pipe 231. At this time, in order to prevent the first material from entering the nozzles 420 and 430, the controller 121 may open valves 524 and 534 and allow N_2 gas to flow into gas supply pipes 520 and 530. The N_2 gas is supplied into the process chamber 201 via gas supply pipes 320 and 330 and nozzles 420 and 430, and is then exhausted from the exhaust pipe 231.

[0055] At this time, the controller 121 regulates the APC valve 243 to set the pressure inside the process chamber 201 to a pressure within a range of, for example, 1 to 3,990 Pa. A supply flow rate of the precursor controlled by the MFC 312 is, for example, 1 to 2,000 sccm, specifically 10 to 1,000 sccm. Here, supply conditions for the first material are set such that an exposure amount of the first material to the wafers 200 is greater than an exposure amount of the third material to the wafers 200. The exposure amount of the first material in the present disclosure refers to, for example, a product of a partial pressure of the precursor in the process chamber 201 and a supply time of the precursor into the process chamber 201 (partial pressure × time.) Respective supply flow rates of N_2 gas controlled by MFCs 512, 522, and 532 are set to fall within a range of, for example, 0.1 to 5.0 slm. At this time, a temperature of the heater 207 is set such that a temperature of the wafers 200 falls within a range of, for example, 250 to 800 degrees

C, specifically 600 to 700 degrees C. The exposure amount of the first material in the present disclosure may also be a product of the supply flow rate of the first material into the process chamber 201 and the supply time (supply flow rate × supply time), a product of a total pressure in the process chamber 201 and the supply time of the first material into the process chamber 201 (total pressure × supply time), or a product of the partial pressure (total pressure) in the process chamber 201 and the supply flow rate and supply time of the first material into the process chamber 201 (partial pressure (total pressure) × supply flow rate × supply time.) The supply flow rate of the first material into the process chamber 201 is affected by factors such as a volume of the process container and a pattern of recesses formed in the wafers 200. For this reason, the exposure amount of the first material may be the product of the partial pressure in the process chamber 201 and the supply time of the precursor into the process chamber 201. An expression of a numerical range such as "1 to 3,990 Pa" in the present disclosure means that a lower limit value and an upper limit value are included in the range. Thus, for example, "1 to 3,990 Pa" means "1 Pa or more and 3,990 Pa or less." The same applies to other numerical ranges.

[0056] The exposure amount of the first material to the wafers 200 in the present disclosure can also be rephrased as an amount of adsorption of gas molecules adsorbed to the surfaces of the wafers 200. This amount of adsorption can be regulated by, for example, the product of the partial pressure of the first material in the process chamber 201 and the supply time of the first material into the process chamber 201 (partial pressure × time), as described above.

[0057] In order to make the exposure amount (amount of adsorption) of the first material in the present disclosure greater than the exposure amount (amount of adsorption) of the third material, at least one selected from the group of the partial pressure, total pressure, supply flow rate, and supply time with respect to the exposure amount of the first material can be set to be greater than at least one selected from the group of the partial pressure, total pressure, supply flow rate, and time with respect to the exposure amount of the third material.

[0058] Further, the first material may be stored in a reservoir 701 so that the first material is supplied from the reservoir 701 into the process chamber 201. When the first material stored in the reservoir 701 is supplied into the process chamber 201, the supply time of the first material into the process chamber 201 may be shorter than either a supply time of the second material or a supply time of the third material into the process chamber 201. In this case, exposure amounts of the first material, the second material, and the third material are each regulated such that, for example, the product of the partial pressure (total pressure) of the first material in the process chamber 201 and the supply time of the first material into the process chamber 201 is greater than the product of the partial pressure (total pressure) of the second material (third material) in the process chamber 201 and the supply time of the second material (third material) into the process chamber 201. Further, in the supplying of the first material, the supply of the first material into the process chamber 201 may be performed a plurality of times instead of once. When the supply of the first material into the process chamber 201 is performed a plurality of times, the supply of the first material into the process chamber 201 is stopped between a predetermined supply and the next supply. When the supply of the first material into the process chamber 201 is performed a plurality of times, the first material stored in the reservoir 701 may be supplied into the process chamber 201 at least once. For example, when the supply of the first material into the process chamber 201 is performed two or more times, the first material stored in the reservoir 701 is supplied into the process chamber 201 in the first supply, and the first material is supplied into the process chamber 201 without the precursor being stored in the reservoir 701 in the second supply. Further, the supply of the first material into the process chamber 201 is stopped between the first supply and the second supply. Simultaneously with the stopping of the supply of the first material into the process chamber 201, the interior of the process chamber 201 may be exhausted (depressurized), and simultaneously with the exhausting, an inert gas may be supplied into the process chamber 201. The supplying and stopping of the first material into the process chamber 201 are controlled by, for example, opening and closing of the valve 702.

[0059] The first material (precursor) supplied to the wafer 200 contains, for example, a main element constituting the film formed on the wafer 200. The first material contains a first element. The first element may be a Group 14 element. The main element of the first material may be, for example, Si. As the first material, for example, a silane-based gas containing Si may be used. As the silane-based gas, for example, a gas containing Si and a halogen (i.e., a halosilane gas) may be used. Halogens include chlorine (Cl), fluorine (F), bromine (Br), iodine (I), and the like. As the halosilane gas, for example, a chlorosilane gas containing Si and Cl may be used.

[0060] Examples of the precursor may include chlorosilane gases such as monochlorosilane (SiH_3Cl) gas, dichlorosilane (SiH_2Cl_2) gas, trichlorosilane ($SiHCl_3$) gas, tetrachlorosilane ($SiCl_4$) gas, hexachlorodisilane (Si_2Cl_6, abbreviated as HCDS) gas, and octachlorotrisilane (Si_3Cl_8) gas. One or more of these may be used as the first material.

[0061] As the first material, in addition to chlorosilane gases, fluorosilane gases such as tetrafluorosilane (SiF_4) gas and difluorosilane (SiH_2F_2) gas, bromosilane gases such as tetrabromosilane ($SiBr_4$) gas and dibromosilane (SiH_2Br_2) gas, and iodosilane gases such as tetraiodosilane (SiI_4) gas and diiodosilane (SiH_2I_2) gas may also be used. One or more of these may be used as the first material.

[0062] As the first material, in addition to those described above, a gas containing Si and an amino group (i.e., an aminosilane gas) may also be used. An amino group is a monovalent functional group in which hydrogen (H) is removed from ammonia, a primary amine, or a secondary amine, and can be represented as $-NH_2$, -NHR, and $-NR_2$. R represents an alkyl group, and the two R groups in $-NR_2$ may be the same or different.

[0063] As the first material, aminosilane 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, and (diisopropylamino)silane ($SiH_3[N(C_3H_7)_2]$) gas may also be used. One or more of these may be used as the first material.

[0064] In the present disclosure, an example in which HCDS gas is used as the first material will be described. When HCDS gas is used as the first material, a Si-containing layer containing Cl with a predetermined thickness may be formed as a first layer on an outermost surface of the wafer 200. The Si-containing layer containing Cl may be formed by physical adsorption or chemical adsorption of molecules of the first material to the outermost surface of the wafer 200, physical adsorption or chemical adsorption of molecules of a substance obtained by at least a portion of the molecules of the first material undergoing decomposition (also referred to as a decomposition product), deposition of Si by thermal decomposition of the first material, or the like. The decomposition product in the case where HCDS is used as the first material is, for example, $SiCl_x$. Here, x is 2, 3, or 4. The Si-containing layer containing Cl may be an adsorption layer (physical adsorption layer or chemical adsorption layer) of molecules of a chlorosilane gas or molecules of a substance obtained by the chlorosilane gas partially undergoing decomposition, or may be a deposition layer of Si containing Cl. When the above-described chemical adsorption layer or the above-described deposition layer is formed on the outermost surface of the wafer 200, Si contained in the chlorosilane gas is adsorbed to the outermost surface of the wafer 200. In the present disclosure, the Si-containing layer containing Cl is also simply referred to as a Si-containing layer.

[0065] (Purging (Residual Gas Removal))

After a predetermined time (e.g., 1 to 60 seconds) elapses from a start of the supply of the first material, the controller 121 closes the valve 314 (or valve 702) of the gas supply pipe 310 to stop the supply of the first material. That is, the supply time of the first material to the wafers 200 is, for example, within a range of 1 to 60 seconds. At this time, the controller 121 keeps the APC valve 243 of the exhaust pipe 231 open, causes the vacuum pump 246 to vacuum-exhaust the interior of the process chamber 201, and removes unreacted first material remaining in the process chamber 201 and first material that contributed to layer formation from the interior of the process chamber 201. That is, the controller 121 exhausts the atmosphere inside the process chamber 201. At this time, the controller 121 may keep the valves 514, 524, and 534 open to

continue supplying N_2 gas into the process chamber 201. The N_2 gas acts as a gas for suppressing entry of gas into each of the nozzles 410, 420, and 430, and also acts as a purge gas. When N_2 gas is supplied as a purge gas, the effect of removing the unreacted first material remaining in the process chamber 201 and the first material that contributed to layer formation from the interior of the process chamber 201 can be enhanced.

[0066] (Supplying Second Material: Second Step)

After removing the residual gas in the process chamber 201, the controller 121 opens the valve 324 and allows the second material to flow into the gas supply pipe 320. After a flow rate of the second material is regulated by the MFC 322, the second material is supplied into the process chamber 201 from the gas supply holes 420a of the nozzle 420. The second material supplied into the process chamber 201 is exhausted from the exhaust pipe 231. At this time, the second material is supplied to the wafers 200. At this time, the controller 121 keeps the valves 514, 524, and 534 open to continue supplying N_2 gas through the gas supply pipes 510, 520, and 530. Respective flow rates of the N_2 gas flowing through the gas supply pipes 510, 520, and 530 are regulated by the MFCs 512, 522, and 532. The N_2 gas flowing through the gas supply pipe 520 is supplied together with the second material into the process chamber 201 via the gas supply pipe 320 and the nozzle 420, and is then exhausted from the exhaust pipe 231. The N_2 gas flowing through the gas supply pipe 530 is supplied into the process chamber 201 via the gas supply pipe 330 and the nozzle 430, and is then exhausted from the exhaust pipe 231. The N_2 gas flowing through the gas supply pipe 510 is supplied into the process chamber 201 via the gas supply pipe 310 and the nozzle 410, and is then exhausted from the exhaust pipe 231. This suppresses entry of the second material into the nozzles 410 and 430.

[0067] At this time, the controller 121 regulates the APC valve 243 so that the pressure inside the process chamber 201 is set to fall within a range of, for example, 1 to 13,300 Pa (e.g., 5,000 Pa.) A supply flow rate of the second material controlled by the MFC 322 is set to fall within a range of, for example, 1 to 50 slm, specifically 15 to 40 slm. Respective supply flow rates of the

N_2 gas controlled by the MFCs 512, 522, and 532 are set to fall within the range of, for example, 0.1 to 5.0 slm.

[0068] The exposure amount (amount of adsorption) of the second material to the wafers 200 may be set to an amount at which adsorption of molecules of the second material to the wafers 200 reaches saturation. In other words, the exposure amount (amount of adsorption) of the second material to the wafer 200 may be set to an amount at which molecules of the second material are saturated and adsorbed to the wafers 200.

[0069] The second material contains a second element. The second element may be a Group 15 element. As the second material supplied to the wafers 200, for example, a N and H-containing gas that is a nitriding gas (nitriding agent) may be used. The N and H-containing gas is both a N-containing gas and a H-containing gas. The N and H-containing gas may include a N-H bond.

[0070] As the second material, for example, hydrogen nitride-based gases such as ammonia (NH_3) gas, diazene (N_2H_2) gas, hydrazine (N_2H_4) gas, and N_3H_8 gas may be used. One or more of these may be used as the second material.

[0071] As the second material, in addition to these, for example, a N, carbon (C), and H-containing gas may also be used. As the N, C, and H-containing gas, for example, an amine-based gas or an organic hydrazine-based gas may be used. The N, C, and H-containing gas is a N-containing gas, a C-containing gas, a H-containing gas, and also a N and C-containing gas.

[0072] As the second material, for example, ethylamine-based gases such as monoethylamine ($C_2H_5NH_2$) gas, diethylamine ($(C_2H_5)_2NH$) gas, and triethylamine ($(C_2H_5)_3N$) gas, methylamine-based gases such as monomethylamine (CH_3NH_2) gas, dimethylamine ($(CH_3)_2NH$) gas, and trimethylamine ($(CH_3)_3N$) gas, and organic hydrazine-based gases such as monomethylhydrazine ($(CH_3)HN_2H_2$) gas, dimethylhydrazine ($(CH_3)_2N_2H_2$) gas, and trimethylhydrazine ($(CH_3)_2N_2(CH_3)H$) gas may be used. One or more of these may be used as the second material. These gases are also referred to as amine-based gases.

[0073] (Purging: Residual Gas Removal)

After a predetermined time (e.g., 1 to 1,200 seconds) elapses since a start of the supply of the

second material, the controller 121 closes the valve 324 of the gas supply pipe 320 to stop the supply of the second material. Then, by the same processing procedure as the purging described above, unreacted second material or second material that contributed to layer formation, as well as reaction by-products remaining in the process chamber 201, are removed from the process chamber 201. That is, the controller 121 exhausts the atmosphere inside the process chamber 201.

[0074] (Supplying Third Material: Third Step)

The controller 121 opens the valve 334 and allows the third material to flow into the gas supply pipe 330. After a flow rate of the third material is regulated by the MFC 332, the third material is supplied into the process chamber 201 from the gas supply holes 430a of the nozzle 430. The third material supplied into the process chamber 201 is exhausted from the exhaust pipe 231. At this time, the third material is supplied to the wafers 200. At this time, the controller 121 may open the valve 534 and allow an inert gas such as N_2 gas to flow through the gas supply pipe 530. The N_2 gas flowing through the gas supply pipe 530 is supplied into the process chamber 201 together with the third material after the flow rate is regulated by the MFC 532. The N_2 gas supplied into the process chamber 201 is exhausted from the exhaust pipe 231. At this time, in order to prevent the third material from entering the nozzles 410 and 420, the controller 121 may open the valves 514 and 524 and allow N_2 gas to flow through the gas supply pipes 510 and 520. The N_2 gas is supplied into the process chamber 201 via the gas supply pipes 310 and 320 and the nozzles 410 and 420, and is exhausted from the exhaust pipe 231.

[0075] At this time, the controller 121 regulates the APC valve 243 to set the pressure inside the process chamber 201 to, for example, within the range of 1 to 3,990 Pa (e.g., 1,000 Pa). A supply flow rate of the third material controlled by the MFC 332 is, for example, within a range of 0.005 to 3.0 slm. Here, the controller 121 regulates the pressure inside the process chamber 201, as well as the supply flow rate and supply time of the third material into the process chamber 201, such that the exposure amount of the third material to the wafers 200 reaches a predetermined exposure amount. Note that the exposure amount of the third material in the

present disclosure is determined, for example, by a product of a partial pressure of the third material in the process chamber 201 and the supply time of the third material into the process chamber 201 (partial pressure × time.) The exposure amount of the third material is less than the exposure amount of the first material and the exposure amount of the second material. In order to suppress the third material from entering the nozzles 410 and 420, respective supply flow rates of N_2 gas controlled by the MFCs 512 and 522 is, for example, within the range of 0.1 to 5.0 slm. At this time, the temperature of the heater 207 is set such that the temperature of the wafers 200 falls within the range of, for example, 250 to 800 degrees C, specifically 600 to 700 degrees C.

[0076] As the third material, for example, gases of chlorides (i.e., gases of inorganic materials) such as aluminum chloride ($AlCl_3$), gallium chloride ($GaCl_3$), indium chloride ($InCl_3$), zinc chloride ($ZnCl_2$), titanium chloride ($TiCl_4$), zirconium chloride ($ZrCl_4$), and hafnium chloride ($HfCl_4$) may be used. A gas obtained by mixing such a chloride with another solvent and vaporizing the mixture may also be used. Organic gases containing an alkyl group, such as trimethylaluminum ($Al(CH_3)_3$), triethylaluminum ($Al(C_2H_5)_3$), trimethylgallium ($Ga(CH_3)_3$), triethylgallium ($Ga(C_2H_5)_3$), trimethylindium ($In(CH_3)_3$), triethylindium ($In(C_2H_5)_3$), dimethylzinc ($Zn(CH_3)_2$), diethylzinc ($Zn(C_2H_5)_2$), trisdimethylamidocyclopentadienylhafnium ($Hf(C_5H_5)(N(CH_3)_2)_3$), trisdimethylamidocyclopentadienylzirconium ($Zr(C_5H_5)(N(CH_3)_2)_3$), and tetrakisdimethylamidotitanium ($Ti((CH_3)_2N)_4$), may be used.

[0077] (Purging: Residual Gas Removal)

After a predetermined time (e.g., 1 to 1,200 seconds) elapses from a start of the supply of the third material, the controller 121 closes the valve 334 of the gas supply pipe 330 to stop the supply of the third material. Then, by the same processing procedure as the purging described above, unreacted third material or third material that contributed to layer formation, as well as reaction by-products remaining in the process chamber 201, are removed from the process chamber 201. That is, the controller 121 exhausts the atmosphere inside the process chamber 201.

[0078] (Performing a Predetermined Number of Times)

By performing a cycle in which the first step, the second step, and the third step described above are executed in sequence for a predetermined number of times (n times, where n is an integer of 1 or 2 or more), a film containing elements included in the first material is formed on the wafer 200 with a predetermined thickness. For example, a SiN film can be formed on the wafer 200. The above-described cycle may be repeated multiple times.

[0079] (Purging and Restoring to Atmospheric Pressure)

The controller 121 supplies N_2 gas from each of the gas supply pipes 510, 520, and 530 into the process chamber 201. The N_2 gas supplied into the process chamber 201 is exhausted through the exhaust pipe 231. The N_2 gas acts as a purge gas. As a result, the interior of the process chamber 201 is purged with an inert gas, and materials (gases) and reaction by-products remaining in the process chamber 201 are removed from the process chamber 201. Thereafter, the atmosphere inside the process chamber 201 is replaced with an inert gas, and the pressure inside the process chamber 201 is restored to normal pressure (atmospheric pressure.)

[0080] (Wafer Unloading)

Thereafter, the SC 219 is lowered by the BE 115, and the lower end of the outer tube 203 is opened. Then, the processed wafers 200 are unloaded from the lower end of the outer tube 203 to an outside of the outer tube 203 while being supported by the boat 217. Thereafter, the processed wafers 200 are discharged from the boat 217.

[0081] (3) Effects of the Present Embodiment

According to the present embodiment, one or more of the following effects can be obtained.

[0082] (a) The charge trap capability of a film formed on the wafer 200 can be improved.

(b) The difference between the electronegativity of the third element and the electronegativity of the second element is greater than the difference between the electronegativity of the first element and the electronegativity of the second element. By using a third material containing a third element that satisfies this condition, electrons of the third element in the film are attracted to the second element, so that the third element can easily become positively charged. When the

film is composed of SiN and the third element is positively charged, electrons of the first element in the film are attracted to the third element, causing the first element to be slightly positively charged. As a result, the energy level at which electrons can be trapped is formed around the first element. By utilizing this effect to form a charge trap layer of a semiconductor device, the charge trap capability of the semiconductor device can be improved.

(c) When the third element is an element with an electronegativity lower than the electronegativity of the second element, the effect of (b) can be further enhanced.

(d) When the atomic size of the third element is closer to the atomic size of the first element than to the atomic size of the second element, the atomic packing factor in the film can be lowered. By lowering the atomic packing factor in the film, spaces for trapping (capturing) electrons can be increased.

(e) The third element may be an element with an atomic size that is larger than the atomic size of the first element and close to the atomic size of the first element. Specifically, the third element may be an element with an atomic size that is larger than the atomic size of the second element and smaller than the atomic size of another element that belongs to the same group as the first element but is different from the first element, and therefore, the spaces for trapping electrons can be increased. In other words, the amount of electron trapping can be increased.

(f) When the film is composed of SiN, and the third element is an element capable of adopting a tricoordinate configuration or a tetracoordinate configuration, the spaces for trapping electrons in SiN can be increased. In other words, the amount of electron trapping can be increased.

(g) When the film is composed of SiN, the third element may be a metal element. By the third element being a metal element, the same effects as described above can be obtained. The metal element may be at least one selected from the group of zinc (Zn), gallium (Ga), aluminum (Al), and indium (In.) Specifically, the third element may be at least one selected from the group of Zn, Ga, and In. More specifically, the third element may be In. In the case of In, the number of electrons that can be trapped can be increased by a mechanism in which tricoordinate bonds are formed and electrons enter remaining unoccupied orbitals. When comparing trap depths of Zn,

Ga, Al, and In, a relationship of Zn < Ga < Al < In is established, with the trap depth of In being deepest. By increasing the trap depth, the electron retention capability can be improved. In addition, compared to other metal elements (e.g., Hf and Ti), these elements can make it difficult for shallow trap levels to be formed among energy levels at which electrons are retained. Here, a shallow trap level is an energy level close to a conduction band, and even when electrons are retained in the shallow trap level, the retained electrons may be released due to some influence, which can lead to a degradation in device performance. Elements such as Zn, Ga, Al, and In make it difficult for shallow trap levels to be formed. Further, for Al and In, levels capable of trapping electrons in a vicinity of these elements are formed at deeper levels than a trap level of the SiN material itself. Therefore, by forming a film using these elements, the electron retention capability of the device can be improved. A deep level refers to an energy level that is relatively closer to a valence band than the trap level of the SiN material itself.

[0083] <Other Embodiments of the Present Disclosure>

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

[0084] For example, in the above-described embodiment, the case where a gas containing Si element is used as the first material is described as an example, but the present disclosure is not limited thereto. For example, the present disclosure may also be applicable to a processing using, as the first material, a gas containing at least one element selected from Group 13 elements, Group 14 elements, Group 4 elements, Group 6 elements, and Group 8 elements.

[0085] In the above-described embodiment, the case where a gas containing nitrogen element is used as the second material is described as an example, but the present disclosure is not limited thereto. For example, a gas containing oxygen element may be used as the second material to form an oxide film on the wafer 200. Examples of the gas containing oxygen include oxygen (O_2) gas, water (H_2O), hydrogen peroxide (H_2O_2) gas, nitrous oxide (dinitrogen monoxide)

(N_2O) gas, nitric oxide (NO) gas, and ozone (O_3) gas. A gas obtained by activating or exciting one or more of these gases may also be used as the second material.

[0086] A gas containing hydrogen element may be used as the second material to form a film containing the above-described element as a main component on the wafer 200. Examples of the gas containing hydrogen element include gases composed of hydrogen elements such as hydrogen (H_2) gas and deuterium gas, and mononuclear parent hydride gases such as silane-based gases, borane-based gases, phosphane-based gases, and germane-based gases. A gas obtained by activating or exciting at least one of these gases may also be used as the reactant. Examples of silane-based gases include monosilane (SiH_4) gas, disilane (Si_2H_6) gas, and trisilane (Si_3H_8) gas. Examples of borane-based gases include monoborane (BH_3) gas and diborane (B_2H_6) gas. Examples of phosphane-based gases include phosphine (PH_3) gas and diphosphine (P_2H_6) gas. Examples of germane-based gases include monogermane (GeH_4) gas, digermane (Ge_2H_6) gas, and trigermane (Ge_3H_8) gas.

[0087] In the above-described embodiment, an example in which film formation is performed using a substrate processing apparatus that is a batch-type vertical apparatus configured to process a plurality of substrates at once is described. However, the present disclosure is not limited thereto, and may also be suitably applied to a case in which film formation is performed using a single-wafer-type substrate processing apparatus that processes at least one substrate at once. In the above-described embodiment, an example in which a film is formed using a substrate processing apparatus that includes a hot-wall-type process furnace is described. The present disclosure is not limited to the above-described embodiments, and may be suitably applied to a case in which a film is formed using a substrate processing apparatus that includes a cold-wall type process furnace. Even when these substrate processing apparatuses are used, film formation can be performed under the same processing sequence and processing conditions as those in the above-described embodiment.

[0088] Note that in the above-described embodiment, an example in which the above-described processing sequence is performed in the same process chamber of the same processing apparatus

(in-situ) is described. The present disclosure is not limited to the above-described embodiment. For example, any step and any other step of the above-described processing sequence may be performed in different process chambers of different processing apparatuses (ex-situ), or may be performed in different process chambers of the same processing apparatus.

[0089] Process recipes used for forming these various thin films (that is, programs describing processing procedures, processing conditions, and the like) may be prepared individually (that is, a plurality of process recipes be prepared) according to details of the substrate processing (e.g., the film type, composition ratio, film quality, film thickness, processing procedure, or processing conditions of the thin film to be formed.) When starting substrate processing, a suitable process recipe may be appropriately selected from among a plurality of process recipes according to the details of the substrate processing. Specifically, a plurality of process recipes prepared individually according to the details of the substrate processing may be stored (installed) in advance in the memory 121c included in the substrate processing apparatus via a telecommunication line or a recording medium (e.g., external memory 123) on which the process recipes are recorded. When starting substrate processing, the CPU 121a included in the substrate processing apparatus may appropriately select a suitable process recipe from among the plurality of process recipes stored in the memory 121c according to the details of the substrate processing. With this configuration, a single substrate processing apparatus can form thin films of various film types, composition ratios, film qualities, and film thicknesses in a versatile manner and with good reproducibility. An operational burden on the operator (e.g., a burden of inputting processing procedures, processing conditions, and the like) can be reduced, and substrate processing can be started promptly while avoiding operational errors by the operator.

[0090] The present disclosure can also be realized, for example, by modifying a process recipe of an existing substrate processing apparatus. When modifying the process recipe, it is also possible to install the process recipe according to the present disclosure into an existing substrate processing apparatus via a telecommunication line or a recording medium on which the process recipe is recorded, or to operate an input/output device of the existing substrate processing

apparatus to modify the process recipe itself to a process recipe according to the present disclosure.

[0091] The above-described embodiment and modifications may be used in appropriate combinations. In such a case, the processing procedures and processing conditions may be, for example, the same as the processing conditions of the above-described embodiment and modifications.

[0092] The embodiment of the present disclosure is 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.

[0093] The disclosure of Japanese Patent Application No. 2024-052683 filed on March 28, 2024 is incorporated herein in its entirety by reference.

All publications, patent applications, and technical standards described in the present specification are incorporated herein by reference to the same extent as when each individual publication, patent application, or technical standard is specifically and individually indicated to be incorporated by reference.

WHAT IS CLAIMED IS:

1. A method of processing a substrate, comprising:

(a) supplying a first material containing a first element constituting a film to the substrate;

(b) supplying a second material containing a second element constituting the film to the substrate;

(c) supplying a third material containing a third element to be added to the film to the substrate; and

(d) performing (a), (b), and (c) a predetermined number of times to form the film containing the first element, the second element, and the third element,

wherein a difference between an electronegativity of the third element and an electronegativity of the second element is greater than a difference between an electronegativity of the first element and the electronegativity of the second element.

2. The method of Claim 1, wherein the electronegativity of the third element is lower than the electronegativity of the second element or the electronegativity of the first element.

3. The method of Claim 1 or 2, wherein an atomic size of the third element is larger than an atomic size of the first element or an atomic size of the second element, and closer to the atomic size of the first element than the atomic size of the second element.

4. The method of any one of Claims 1 to 3, wherein the third element is an element capable of taking a tricoordinate or tetracoordinate configuration.

5. The method of any one of Claims 1 to 8, wherein the third element is a metal element.

6. The method of any one of Claims 1 to 8, wherein the third element is a transition metal element.

7. The method of any one of Claims 1 to 8, wherein the third element is a non-transition metal element.

8. The method of any one of Claims 1 to 8, wherein the third element is at least one selected from the group of elements in Period 3, Period 4, and Period 5 of a periodic table.

9. The method of any one of Claims 1 to 8, wherein the third element is at least one selected from the group of Al, Zn, Ga, and In.

10. The method of any one of Claims 1 to 8, wherein the third element is at least one selected from the group of Zn, Ga, and In.

11. The method of any one of Claims 1 to 10, wherein the first element is a Group 14 element.

12. The method of any one of Claims 1 to 11, wherein the second element is a Group 15 element.

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

(a) supplying a first material containing a first element constituting a film to the substrate;

(b) supplying a second material containing a second element constituting the film to the substrate;

(c) supplying a third material containing a third element to be added to the film to the substrate; and

(d) performing (a), (b), and (c) a predetermined number of times to form the film containing the first element, the second element, and the third element,

wherein a difference between an electronegativity of the third element and an electronegativity of the second element is greater than a difference between an electronegativity of the first element and the electronegativity of the second element.

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

(a) supplying a first material containing a first element constituting a film to a substrate;

(b) supplying a second material containing a second element constituting the film to the substrate;

(c) supplying a third material containing a third element to be added to the film to the substrate, wherein a difference between an electronegativity of the third element and an electronegativity of the second element is greater than a difference between an electronegativity of the first element and the electronegativity of the second element; and

(d) performing (a), (b), and (c) a predetermined number of times to form the film containing the first element, the second element, and the third element.

15. A substrate processing apparatus comprising:

a first supplier configured to supply a first material containing a first element constituting a film to a substrate;

a second supplier configured to supply a second material containing a second element constituting the film to the substrate;

a third supplier configured to supply a third material containing a third element to be added to the film to the substrate; and

a controller configured to be capable of controlling the first supplier, the second supplier, and the third supplier so as to perform a predetermined process;

wherein a difference between an electronegativity of the third element and an electronegativity of the second element is greater than a difference between an electronegativity of the first element and the electronegativity of the second element, and

wherein the predetermined process includes:

(a) supplying the first material to the substrate;

(b) supplying the second material to the substrate;

(c) supplying the third material to the substrate; and

(d) performing (a), (b), and (c) a predetermined number of times to form the film containing the first element, the second element, and the third element.