US 20200219727A1

(19) **United States**

(12) **Patent Application Publication**

(10) **Pub. No.: US 2020/0219727 A1**

(43) **Pub. Date: Jul. 9, 2020**

DEGAI et al.

(54) **METHOD OF MANUFACTURING SEMICONDUCTOR DEVICE, SUBSTRATE PROCESSING APPARATUS, AND RECORDING MEDIUM**

(71) Applicant: **KOKUSAI ELECTRIC CORPORATION**, Tokyo (JP)

(72) Inventors: **Motomu DEGAI**, Toyama (JP); **Hiroshi ASHIHARA**, Toyama (JP)

(73) Assignee: **KOKUSAI ELECTRIC CORPORATION**, Tokyo (JP)

(21) Appl. No.: **16/818,865**

(22) Filed: **Mar. 13, 2020**

Related U.S. Application Data

(63) Continuation of application No. PCT/JP2017/035242, filed on Sep. 28, 2017.

Publication Classification

(51) **Int. Cl.**

H01L 21/223 (2006.01)
H01L 21/285 (2006.01)
H01L 21/02 (2006.01)

(52) **U.S. Cl.**

CPC ***H01L 21/223*** (2013.01); ***H01L 21/28562*** (2013.01); ***H01L 21/02153*** (2013.01); ***H01L 21/0217*** (2013.01); ***H01L 21/0215*** (2013.01); ***H01L 21/02129*** (2013.01)

(57) **ABSTRACT**

There is provided a technique that includes selectively doping a metal film with a dopant by performing: supplying a dopant-containing gas containing the dopant to a substrate in which the metal film and a film other than the metal film are formed on a film in which the dopant is doped; and removing the dopant-containing gas from above the substrate.

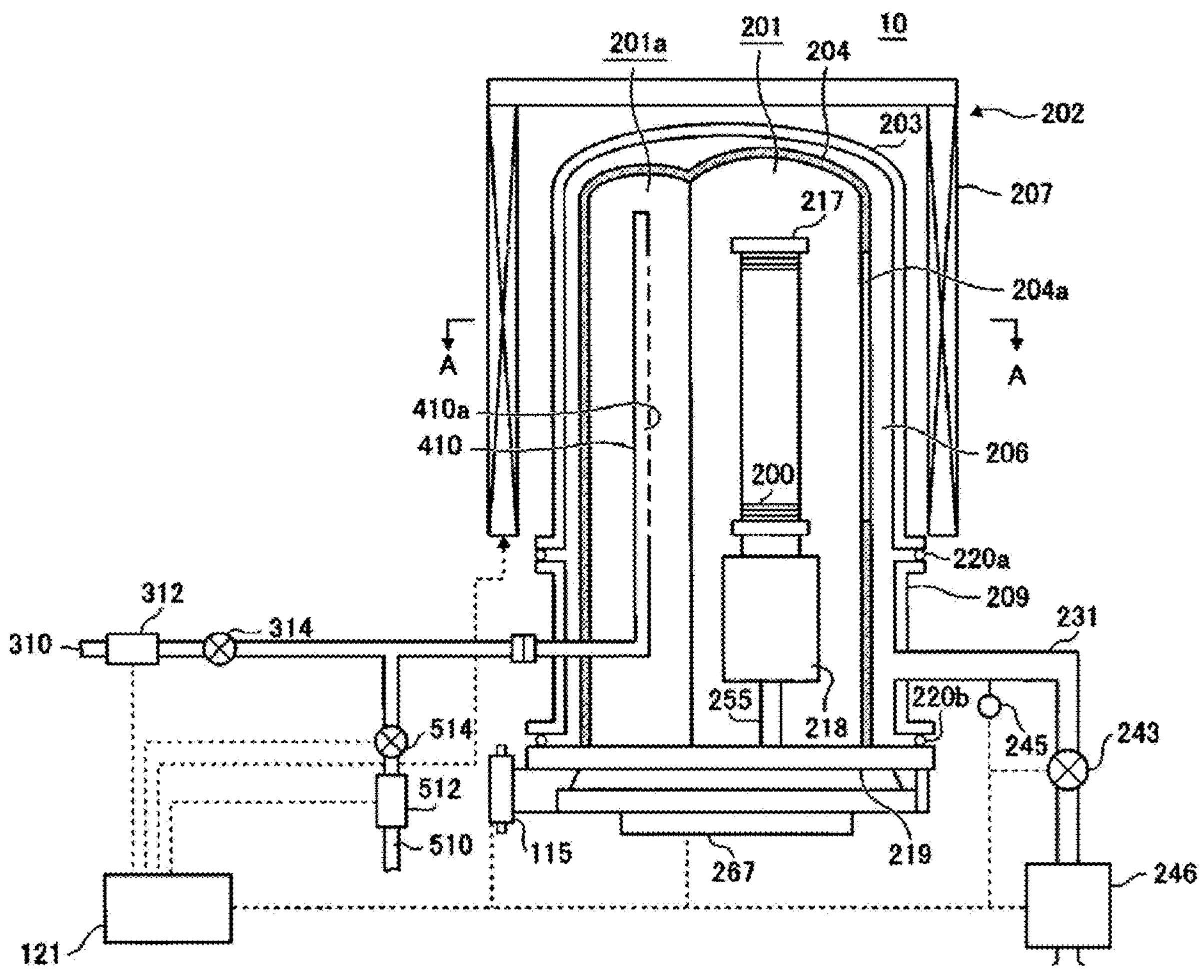


FIG. 1

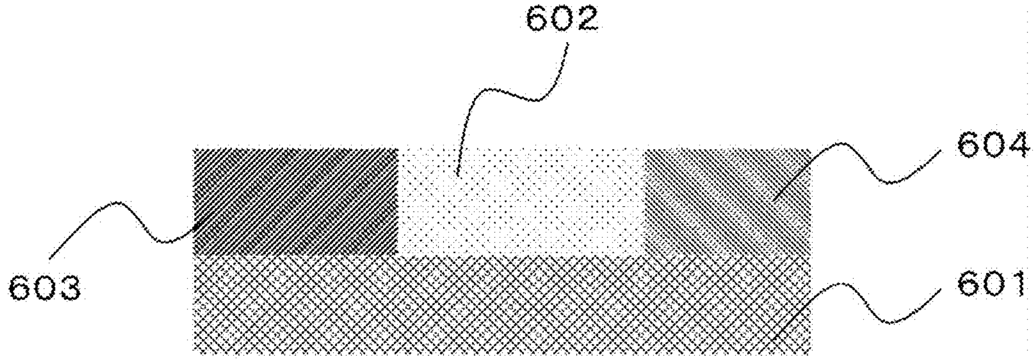


FIG. 2

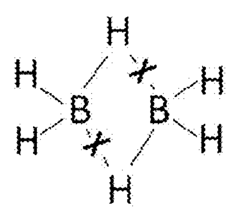


FIG. 3

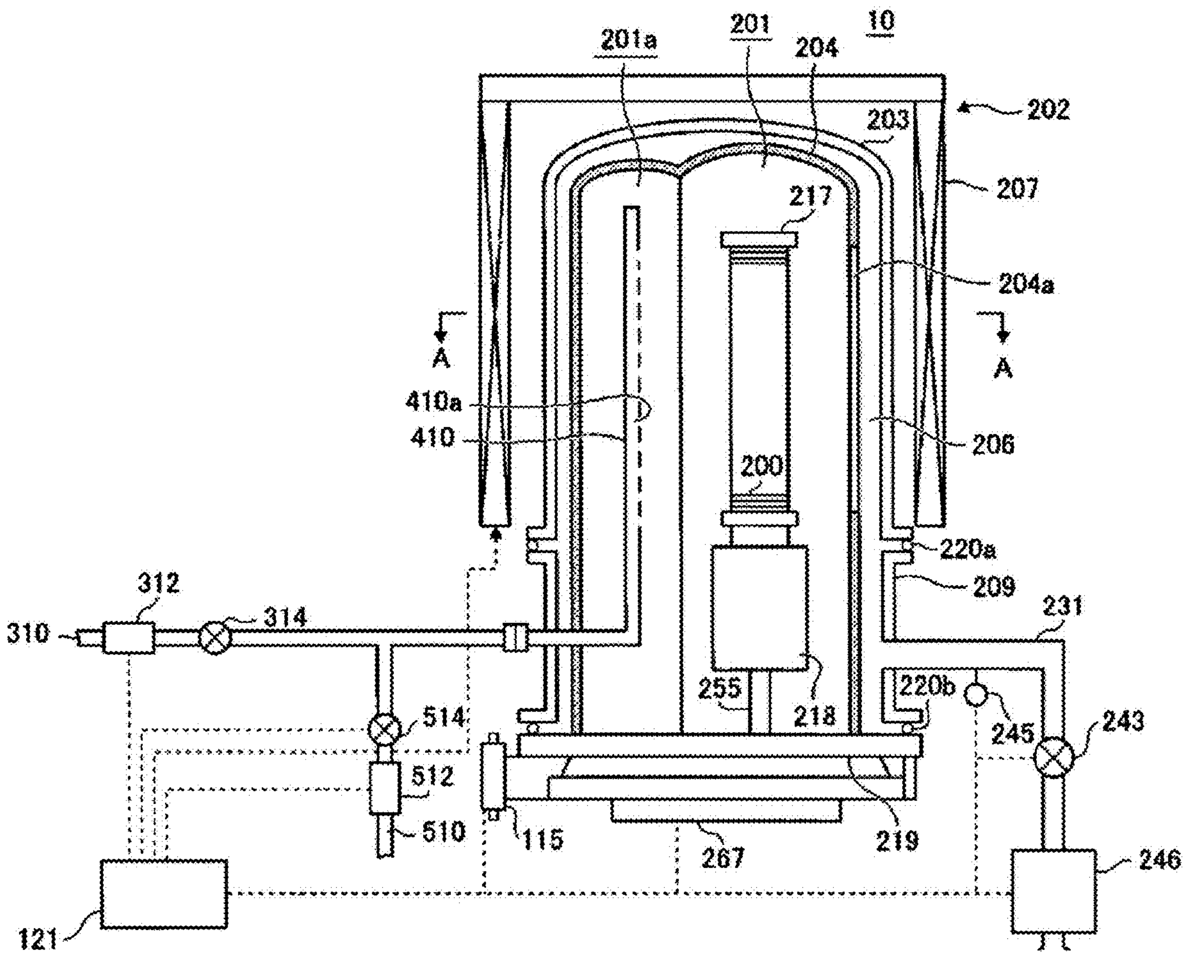

201a
201
204
10
202
203
207
217
204a
A
A
410a
410
206
200
220a
209
312
314
310
231
220b
255
218
514
245
243
512
510
115
267
219
246
121

FIG. 4

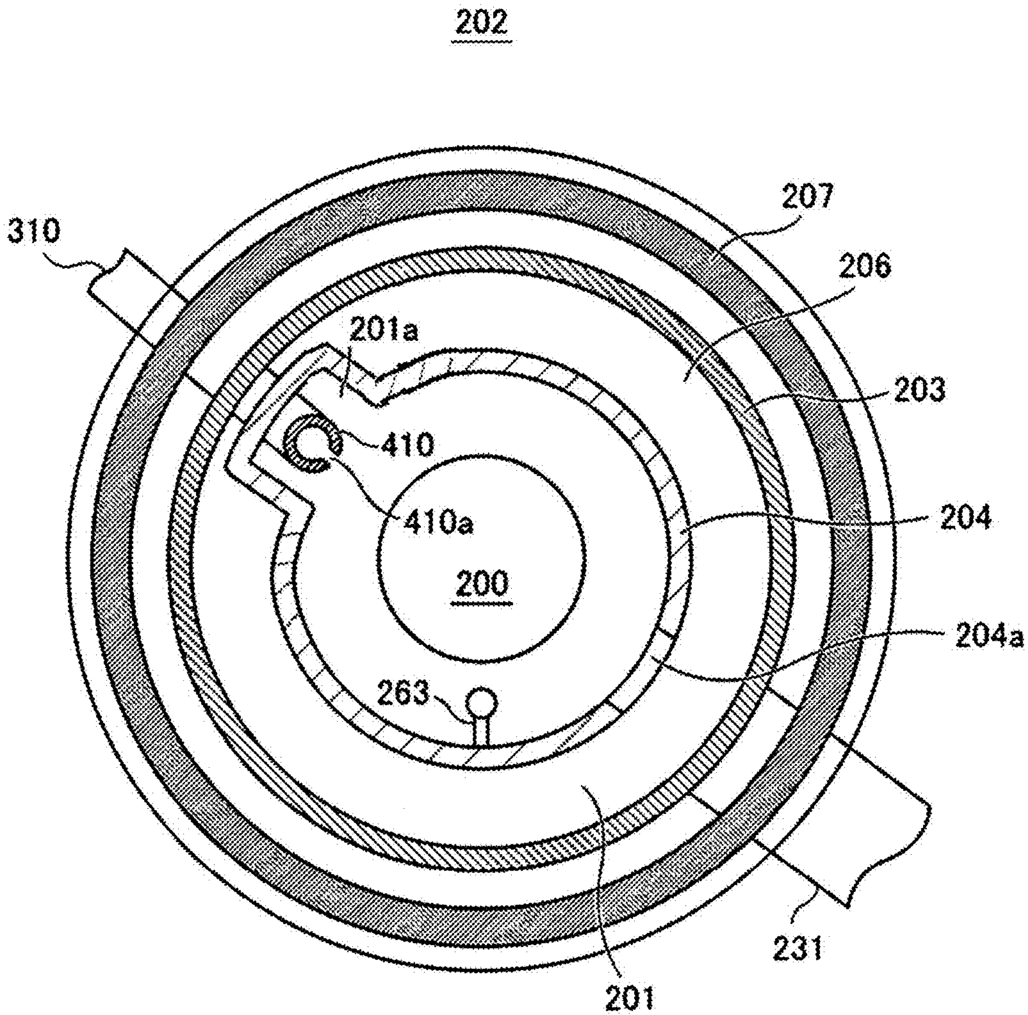


FIG. 5

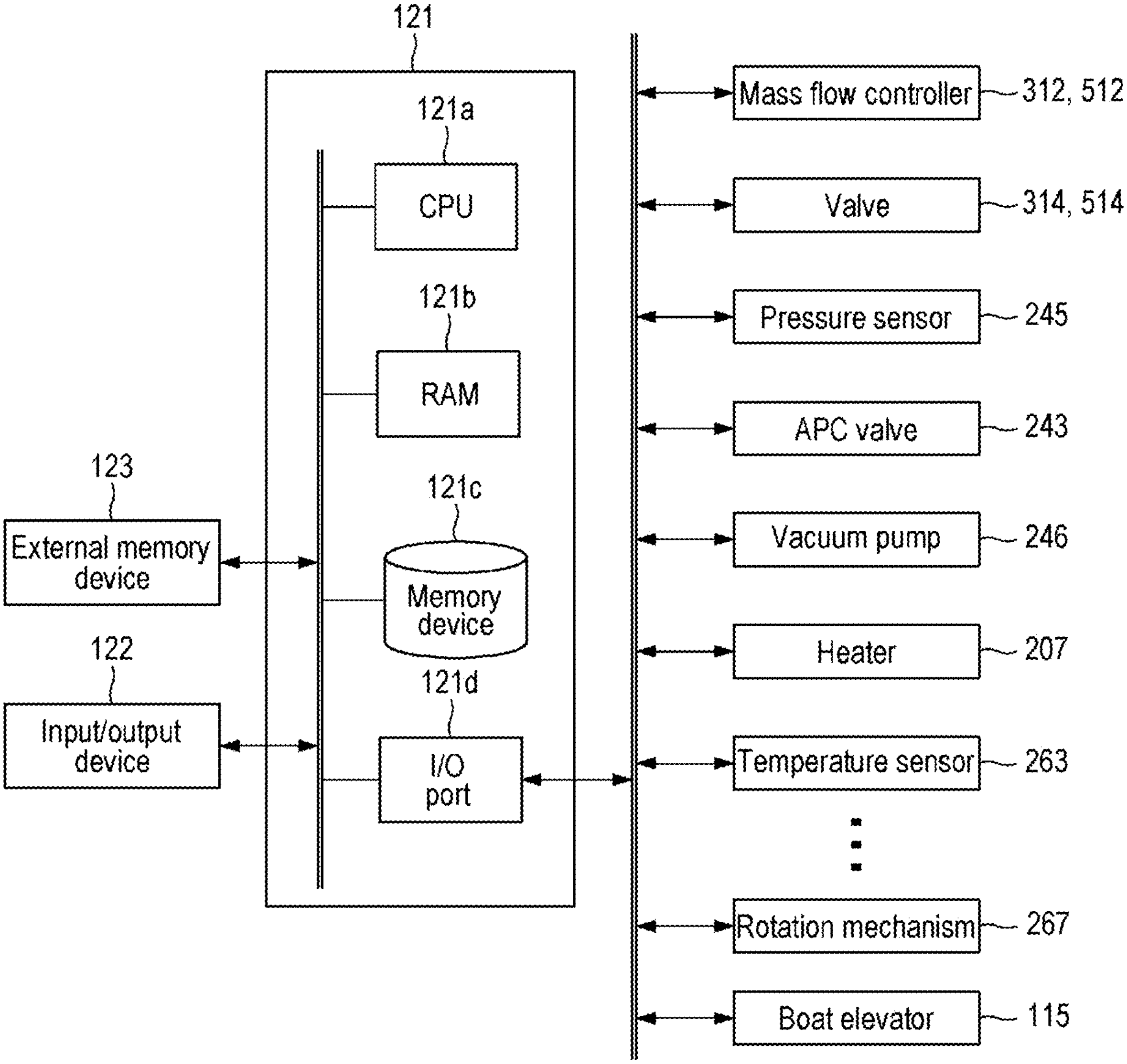

121
121a
CPU
121b
RAM
121c
Memory device
121d
I/O port
123
External memory device
122
Input/output device
Mass flow controller
312, 512
Valve
314, 514
Pressure sensor
245
APC valve
243
Vacuum pump
246
Heater
207
Temperature sensor
263
Rotation mechanism
267
Boat elevator
115

FIG. 6

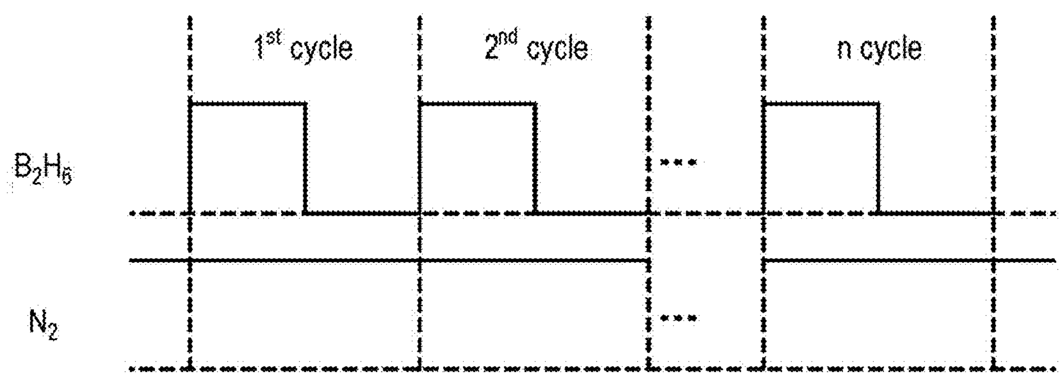

1st cycle
2nd cycle
n cycle
B_2H_6
N_2

FIG. 7

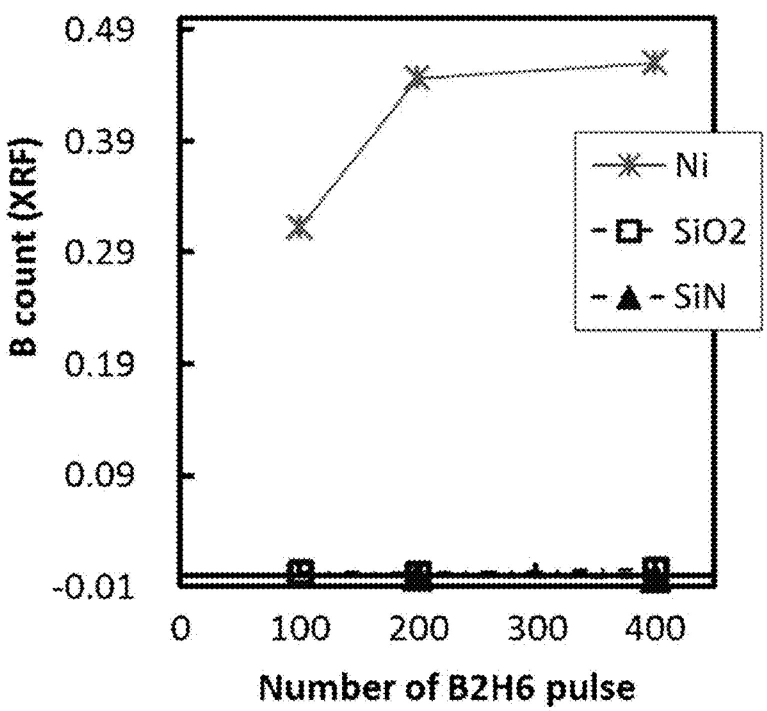

0.49
0.39
0.29
0.19
0.09
-0.01
B count (XRF)
0
100
200
300
400
Number of B2H6 pulse
Ni
SiO2
SiN

FIG. 8A

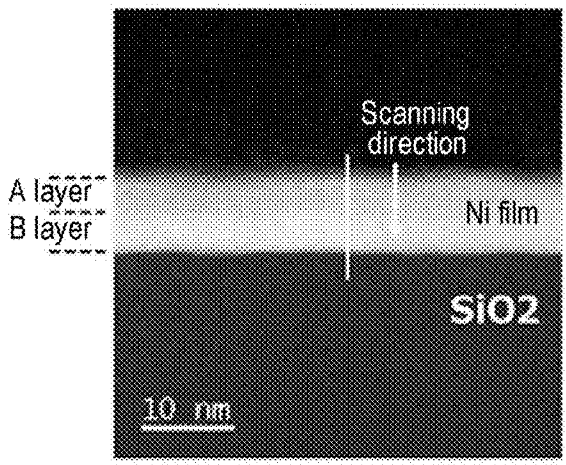

Scanning
direction
A layer
B layer
Ni film
SiO2
10 nm

FIG. 8B

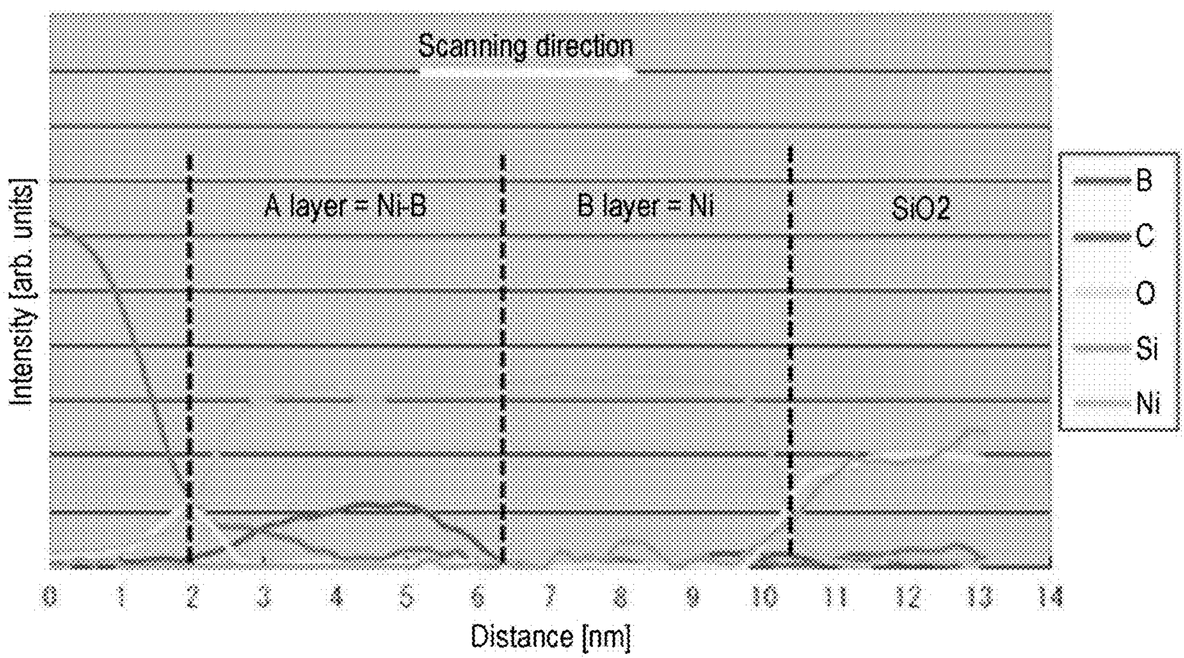
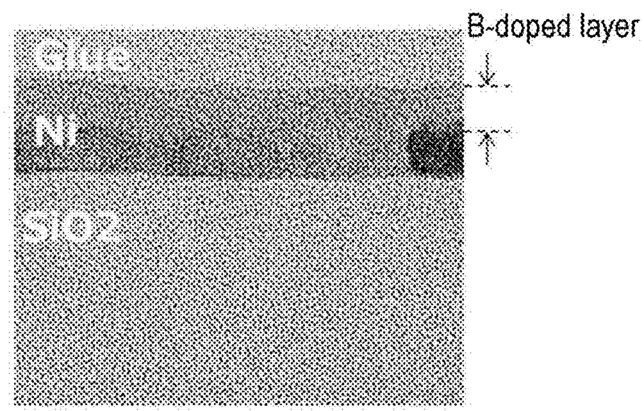

Scanning direction
A layer = Ni-B
B layer = Ni
SiO2
Intensity [arb. units]
B
C
O
Si
Ni
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
Distance [nm]

FIG. 9



METHOD OF MANUFACTURING SEMICONDUCTOR DEVICE, SUBSTRATE PROCESSING APPARATUS, AND RECORDING MEDIUM

CROSS-REFERENCE TO RELATED APPLICATION(S)

[0001] This application is a Bypass Continuation Application of PCT International Application No. PCT/JP2017/035242, filed on Sep. 28, 2017, the entire contents of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to a method of manufacturing a semiconductor device, a substrate processing apparatus, and a recording medium.

BACKGROUND

[0003] With the high integration and high performance of MOSFET (Metal Oxide Semiconductor Field Effect Transistor), various kinds of films are used for manufacture of MOSFETs.

[0004] For example, for a gate electrode of a MOSFET, there is a case where a metal film is formed on a silicon film in which impurities (dopants) are doped, and is annealed (thermally-treated), and the annealed metal film is used as metal silicide. In this case, out-diffusion of the impurities into the metal film from the silicon film doped with the impurities may occur, which may decrease the impurity concentration in the silicon film doped with the impurities.

SUMMARY

[0005] Some embodiments of the present disclosure provide a technique capable of suppressing diffusion of impurities from a silicon film doped with the impurities to a metal film formed on the silicon film.

[0006] According to one or more embodiments of the present disclosure, there is provided a technique that includes selectively doping a metal film with a dopant by performing: supplying a dopant-containing gas containing the dopant to a substrate in which the metal film and a film other than the metal film are formed on a film in which the dopant is doped; and removing the dopant-containing gas from above the substrate.

BRIEF DESCRIPTION OF DRAWINGS

[0007] FIG. **1** illustrates an example of a structure to which the present disclosure is applied.

[0008] FIG. **2** is a view for explaining decomposition of a B_2H_6 gas according to the present disclosure using a structural formula.

[0009] FIG. **3** is a schematic longitudinal sectional view illustrating a vertical process furnace of a substrate processing apparatus according to first embodiments of the present disclosure.

[0010] FIG. **4** is a schematic cross-sectional view taken along line A-A in FIG. **1**.

[0011] FIG. **5** is a schematic configuration diagram of a controller of the substrate processing apparatus according to the first embodiments of the present disclosure, in which a control system of the controller is illustrated in a block diagram.

[0012] FIG. **6** is a diagram showing gas supply timings according to the first embodiments of the present disclosure.

[0013] FIG. **7** is a graph showing a change in the amount ofB in each film with respect to the number of pulses of B_2H_6 gas according to the first embodiments of the present disclosure.

[0014] FIGS. **8**A and **8**B show an experimental result of TEM-EELS according to the first embodiments of the present disclosure, FIG. **8**A is a cross-sectional view, and FIG. **8**B is a view showing a result of analysis on a depth direction.

[0015] FIG. **9** is a sectional TEM image of a Ni film according to the first embodiments of the present disclosure.

DETAILED DESCRIPTION

[0016] There is a case where a metal film, for example, a nickel (Ni) film, is formed on a B-doped Si film added (doped) with an impurity, for example, boron (B) and is annealed, and the annealed metal film is used as metal silicide such as nickel silicide (NiSi). In this case, B may diffuse from the B-doped Si film into the Ni film, which may decrease the B concentration in the B-doped Si film. For the purpose of preventing this diffusion, it is conceivable to dope the Ni film with B in advance.

[0017] However, when B is doped into the Ni film, ifB is doped into other peripheral films, the film quality is deteriorated (in the case of an insulating film, the insulating property is reduced). For example, as illustrated in FIG. **1**, in a case where a Ni film **602** is formed on a B-doped Si film **601**, and a silicon nitride film (SiN film) **603** and a silicon oxide film (SiO film) **604** are formed at a periphery of the Ni film **602**, when the Ni film **602** is doped with B, the SiN film **603** and the SiO film **604** are also doped with B. Therefore, it is conceivable to prevent unwanted B doping by masking films other than the Ni film **602**. However, forming a mask increases the number of steps.

[0018] As a result of intensive studies, the present inventors have found that selectively (preferentially) doping B (selective doping, selective dope or selective addition of B) only into the Ni film can suppress B-doping into a film other than the Ni film **602** without using a mask. Specifically, when the Ni film is irradiated (supplied) with a B-containing gas, for example, a diborane (B_2H_6) gas, Ni acts as a catalyst to decompose the B_2H_6 gas. That is, the electron donating property of the metal Ni promotes the decomposition of the B_2H_6 gas. Then, as illustrated in FIG. **2**, a B—H bond is broken to form BH_3. Since BH_3 is unstable and highly reactive, B diffuses into Ni. In addition, since the coefficient of diffusion of B into Ni is large, B is easily introduced into Ni. On the other hand, since the SiN film and the SiO film are insulating films and have poor electron donating properties, there is no catalytic action of the metal Ni. Further, since the coefficient of diffusion of B into SiN or SiO is small, B is hardly introduced into SiN or SiO. Furthermore, for the SiO film, crystalline boron has acid resistance, and therefore, it may not be easily bonded to O. Therefore, B can be selectively added only to the Ni film. That is, it is possible to expose a gas containing B to a substrate on which Ni and other films are exposed, and dope only Ni with B. Details thereof will be described below.

First Embodiments of the Present Disclosure

[0019] First embodiments of the present disclosure will now be described with reference to FIGS. **3** to **5**. A substrate processing apparatus **10** is an example of an apparatus used for a semiconductor-device-manufacturing process.

(1) Configuration of Substrate Processing Apparatus

[0020] The substrate processing apparatus **10** includes a process furnace **202** provided with a heater **207** as a heating means (a heating mechanism or a heating system). The heater **207** has a cylindrical shape and is supported by a heat base (not shown) serving as a support plate so as to be vertically installed.

[0021] An outer tube **203** forming a reaction vessel (a process vessel) is disposed inside the heater **207** to be concentric with the heater **207**. The outer tube **203** is made of, for example, a heat resistant material such as quartz (SiO_2), silicon carbide (SiC), or the like, and has a cylindrical shape with its upper end closed and its lower end opened. A manifold (inlet flange) **209** is disposed to be concentric with the outer tube **203** under the outer tube **203**. The manifold **209** is made of, for example, a metal material such as stainless steel (SUS: Steel Use Stainless) or the like, and has a cylindrical shape with both of its upper and lower ends opened. An O-ring **220***a* serving as a seal member is installed between the upper end of the manifold **209** and the outer tube **203**. As the manifold **209** is supported by the heater base, the outer tube **203** is in a state of being vertically installed.

[0022] An inner tube **204** forming the reaction vessel is disposed inside the outer tube **203**. The inner tube **204** is made of, for example, a heat resistant material such as quartz (SiO_2), silicon carbide (SiC), or the like, and has a cylindrical shape with its upper end closed and its lower end opened. The process vessel (reaction vessel) mainly includes the outer tube **203**, the inner tube **204**, and the manifold **209**. A process chamber **201** is formed in a hollow cylindrical portion (the inside of the inner tube **204**) of the process vessel.

[0023] The process chamber **201** is configured to accommodate wafers **200** as substrates in a state where the wafers **200** are arranged in a horizontal posture and in multiple stages along a vertical direction by a boat **217** to be described below.

[0024] A nozzle **410** is installed in the process chamber **201** so as to penetrate through a sidewall of the manifold **209** and the inner tube **204**. A gas supply pipe **310** as a gas supply line is connected to the nozzle **410**. In this way, one nozzle **410** and one gas supply pipe **310** are installed at the substrate processing apparatus **10**, thereby allowing a gas to be supplied into the process chamber **201**. However, the process furnace **202** of the present embodiments is not limited to the above-described form.

[0025] A mass flow controller (MFC) **312**, which is a flow rate controller (a flow rate control part), and a valve **314**, which is an opening/closing valve, are installed to the gas supply pipe **310** sequentially from the upstream side. A gas supply pipe **510** for supplying an inert gas is connected to the gas supply pipe **310** at the downstream side of the valve **314**. An MFC **512** which is a flow rate controller (a flow rate control part), and a valve **514**, which is an opening/closing valve, are installed to the gas supply pipe **510** sequentially from the upstream side.

[0026] The nozzle **410** is connected to the leading end of the gas supply pipe **310**. The nozzle **410** is configured as an L-shaped nozzle and its horizontal portion is installed to pass through the sidewall of the manifold **209** and the inner tube **204**. The vertical portion of the nozzle **410** is installed inside a channel-shaped (groove-shaped) pre-chamber **201***a* formed to protrude radially outward of the inner tube **204** and extend in the vertical direction. The vertical portion of the nozzle **410** is installed upward (upward in the arrangement direction of the wafers **200**) along the inner wall of the inner tube **204** in the pre-chamber **201***a*.

[0027] The nozzle **410** is installed so as to extend from a lower region of the process chamber **201** to an upper region of the process chamber **201**, and a plurality of gas supply holes **410***a* are each formed at positions facing the wafers **200**. Thus, a process gas is supplied to the wafers **200** from each of the gas supply holes **410***a* of the nozzle **410**. The gas supply holes **410***a* are formed from a lower portion of the inner tube **204** to an upper portion thereof to have the same aperture area at the same aperture pitch. However, the gas supply holes **410***a* are not limited to the above-described form. For example, the aperture area may be gradually increased from the lower portion of the inner tube **204** to the upper portion thereof. This can make the flow rate of the gas supplied from the gas supply holes **410***a* more uniform.

[0028] The gas supply holes **410***a* of the nozzle **410** are installed at a position of the height from a lower portion of the boat **217** (which will be described below) to an upper portion thereof. Therefore, the process gas supplied into the process chamber **201** from the gas supply holes **410***a* of the nozzle **410** is supplied to the entire area of the wafers **200** accommodated from the lower portion of the boat **217** to the upper portion thereof, that is, the wafers **200** accommodated in the boat **217**. The nozzle **410** may be installed so as to extend from the lower region of the process chamber **201** to the upper region thereof, but may be installed so as to extend near the ceiling of the boat **217**.

[0029] A process gas, for example, a dopant-containing gas containing a dopant which is an impurity element, is supplied from the gas supply pipe **310** into the process chamber **201** via the MFC **312**, the valve **314**, and the nozzle **410**. An example of the dopant-containing gas may include a B-containing gas containing boron (B, boron) as a dopant, specifically for example, a diborane (B_2H_6) gas (5%, diluted with N_2).

[0030] An inert gas, for example, a nitrogen (N_2) gas, is supplied from the gas supply pipe **510** into the process chamber **201** via the MFC **512**, the valve **514**, and the nozzle **410**. In the following, an example in which the N_2 gas is used as the inert gas will be described. However, as the inert gas, in addition to the N_2 gas, it may be possible to use, e.g., a rare gas such as an argon (Ar) gas, a helium (He) gas, a neon (Ne) gas, a xenon (Xe) gas, or the like.

[0031] A process gas supply system mainly includes the gas supply pipe **310**, the MFC **312**, the valve **314**, and the nozzle **410**. However, the process gas supply system may include only the nozzle **410**. The process gas supply system may be simply referred to as a gas supply system. When the dopant-containing gas is flowed from the gas supply pipe **310**, a dopant-containing gas supply system mainly includes the gas supply pipe **310**, the MFC **312**, and the valve **314**. However the dopant-containing gas supply system may include the nozzle **410**. When the B-containing gas is used as the dopant-containing gas, the dopant-containing gas supply system may be referred to as a B-containing gas supply system. When the B_2H_6 gas is used as the B-containing gas, the B-containing gas supply system may be referred to as a B_2H_6 gas supply system. An inert gas supply system mainly includes the gas supply pipe **510**, the MFC **512**, and the valve **514**. The inert gas supply system may be referred to as a purge gas supply system, a dilution gas supply system, or a carrier gas supply system.

[0032] A gas-supplying method according to the present embodiments is to transfer a gas via the nozzle **410** disposed in the pre-chamber **201***a* in an elongated annular space defined by the inner wall of the inner tube **204** and the ends of the plurality of wafers **200**, that is, in a cylindrical space. Then, the gas is ejected into the inner tube **204** from the plurality of gas supply holes **410***a* installed at positions of the nozzle **410** facing the wafers. More specifically, the dopant-containing gas or the like is ejected through the gas supply holes **410***a* of the nozzle **410** in a direction parallel to the surfaces of the wafers **200**, that is, in a horizontal direction.

[0033] An exhaust hole (an exhaust port) **204***a* is a through-hole formed at a position facing the nozzle **410** on the side wall of the inner tube **204**, that is, at a position 180 degrees opposite to the pre-chamber **201***a*. The exhaust hole **204***a* is, for example, a slit-shaped through-hole elongated in the vertical direction. Therefore, a gas supplied into the process chamber **201** from the gas supply holes **410***a* of the nozzle **410** and flowing on the surfaces of the wafers **200**, that is, a remaining gas (a residual gas), flows into an exhaust path **206** formed by a gap formed between the inner tube **204** and the outer tube **203** through the exhaust hole **204***a*. Then, the gas flowing into the exhaust path **206** flows into an exhaust pipe **231** and is discharged out of the process furnace **202**.

[0034] The exhaust hole **204***a* is formed at a position facing the plurality of wafers **200** (preferably at a position facing the lower portion of the boat **217** from the upper portion thereof). Therefore, a gas supplied from the gas supply hole **410***a* to the vicinity of the wafers **200** in the process chamber **201** flows in a horizontal direction, that is, in a direction parallel to the surfaces of the wafers **200**, and then flows into the exhaust path **206** through the exhaust hole **204***a*. That is, the gas remaining in the process chamber **201** is exhausted in parallel with the main surfaces of the wafers **200** through the exhaust hole **204***a*. The exhaust hole **204***a* is not limited to the case where it is configured as a slit-shaped through-hole, but may be configured with a plurality of holes.

[0035] The exhaust pipe **231** for exhausting an internal atmosphere of the process chamber **201** is installed at the manifold **209**. A pressure sensor **245**, which is a pressure detector (pressure detecting part) for detecting an internal pressure of the process chamber **201**, an APC (auto pressure controller) valve **243** and a vacuum pump **246** as a vacuum-exhausting device are connected to the exhaust pipe **231** sequentially from the upstream side. The APC valve **243** is configured to perform or stop a vacuum-exhausting operation in the process chamber **201** by opening or closing the valve while the vacuum pump **246** is actuated, and is also configured to adjust the internal pressure of the process chamber **201** by adjusting an opening degree of the valve while the vacuum pump **246** is actuated. An exhaust system or an exhaust line mainly includes the exhaust hole **204***a*, the exhaust path **206**, the exhaust pipe **231**, the APC valve **243**, and the pressure sensor **245**. The exhaust system may include the vacuum pump **246**.

[0036] A seal cap **219**, which serves as a furnace opening cover configured to hermetically seal a lower end opening of the manifold **209**, is installed under the manifold **209**. The seal cap **219** is configured to contact the lower end of the manifold **209** from the lower side in the vertical direction. The seal cap **219** is made of, for example, a metal material such as stainless steel (SUS) or the like, and is formed in a disc shape. An O-ring **220***b*, which is a seal member making contact with the lower end of the manifold **209**, is installed at an upper surface of the seal cap **219**. A rotation mechanism **267** configured to rotate the boat **217** that accommodates wafers **200** is installed at the opposite side of the seal cap **219** from the process chamber **201**. A rotary shaft **255** of the rotation mechanism **267**, which penetrates through the seal cap **219**, is connected to the boat **217**. The rotation mechanism **267** is configured to rotate the wafers **200** by rotating the boat **217**. The seal cap **219** is configured to be vertically moved up and down by a boat elevator **115** which is an elevating mechanism vertically installed outside the outer tube **203**. The boat elevator **115** is configured so as to load/unload the boat **217** into/out of the process chamber **201** by moving the seal cap **219** up and down. The boat elevator **115** is configured as a transfer device (transfer mechanism) which transfers the boat **217** and the wafers **200** accommodated in the boat **217**, into/out of the process chamber **201**.

[0037] The boat **217** serving as a substrate support is configured to support a plurality of wafers **200**, for example, 25 to 200 wafers, in such a state that the wafers **200** 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. As such, the boat **217** is configured to arrange the wafers **200** to be spaced apart from each other. The boat **217** is made of a heat resistant material such as quartz or SiC. Heat-insulating plates **218** made of a heat resistant material such as quartz or SiC are supported in a horizontal posture and in multiple stages (not shown) below the boat **217**. This configuration makes it difficult for heat from the heater **207** to be transferred to the seal cap **219**. However, the present embodiments are not limited to the above-described form. For example, instead of installing the heat-insulating plates **218** below the boat **217**, a heat-insulating tube configured as a cylindrical member made of a heat resistant material such as quartz or SiC may be installed.

[0038] As illustrated in FIG. **4**, a temperature sensor **263** serving as a temperature detector is installed in the inner tube **204**. Based on temperature information detected by the temperature sensor **263**, a state of supplying electric power to the heater **207** is adjusted such that the interior of the process chamber **201** has a desired temperature distribution. The temperature sensor **263** has an L-shape and is installed along the inner wall of the inner tube **204** in the same manner as the nozzle **410**.

[0039] As illustrated in FIG. **5**, a controller **121**, which is a control part (control means), may be configured as a computer including a CPU (central processing unit) **121***a*, a RAM (random access memory) **121***b*, a memory device **121***c*, and an I/O port **121***d*. The RAM **121***b*, the memory device **121***c*, and the I/O port **121***d* are configured to exchange data with the CPU **121***a* via an internal bus. An input/output device **122** formed of, e.g., a touch panel or the like, is connected to the controller **121**.

[0040] The memory device **121***c* is configured by, for example, a flash memory, a HDD (hard disk drive), or the like. A control program for controlling operations of a substrate processing apparatus and a process recipe, in which sequences and conditions of a semiconductor-device-manufacturing method to be described below are written, are readably stored in the memory device **121***c*. The process recipe functions as a program for causing the controller **121** to execute various steps in the semiconductor-device-manufacturing method to be described below, to obtain an expected result. Hereinafter, the process recipe and the control program may be generally and simply referred to as a "program." When the term "program" is used herein, it may indicate a case of including the process recipe only, a case of including the control program only, or a case of including both the process recipe and the control program. The RAM **121***b* is configured as a memory area (work area) in which a program or data read by the CPU **121***a* is temporarily stored.

[0041] The I/O port **121***d* is connected to the MFCs **312** and **512**, the valves **314** and **514**, the pressure sensor **245**, the APC valve **243**, the vacuum pump **246**, the heater **207**, the temperature sensor **263**, the rotation mechanism **267**, the boat elevator **115**, and so on.

[0042] The CPU **121***a* is configured to read and execute the control program from the memory device **121***c*. The CPU **121***a* is also configured to read the recipe from the memory device **121***c* according to an input of an operation command from the input/output device **122**. The CPU **121***a* is configured to control the flow-rate-adjusting operation of various kinds of gases by the MFCs **312** and **512**, the opening/closing operation of the valves **314** and **514**, the opening/closing operation of the APC valve **243**, the pressure-adjusting operation performed by the APC valve **243** based on the pressure sensor **245**, the temperature-adjusting operation of heater **207** based on the temperature sensor **263**, the actuating and stopping of the vacuum pump **246**, the rotation and rotation-speed-adjusting operation of the boat **217** by the rotation mechanism **267**, the moving up/down operation of the boat **217** by the boat elevator **115**, the accommodating operation of the wafers **200** in the boat **217**, and the like, according to contents of the read recipe.

[0043] The controller **121** may be configured by installing, on the computer, the aforementioned program stored in an external memory device **123** (for example, a magnetic tape, a magnetic disk such as a flexible disk or a hard disk, an optical disc such as a CD or a DVD, a magneto-optical disc such as a MO, a semiconductor memory such as a USB memory or a memory card, etc.). The memory device **121***c* or the external memory device **123** is configured as a non-transitory computer-readable recording medium. Hereinafter, the memory device **121***c* and the external memory device **123** may be generally and simply referred to as a "recording medium." When the term "recording medium" is used herein, it may indicate a case of including the memory device **121***c* only, a case of including the external memory device **123** only, or a case of including both the memory device **121***c* and the external memory device **123**. Furthermore, the program may be provided to the computer using a communication means such as the Internet or a dedicated line, instead of using the external memory device **123**.

(2) Substrate-Processing Process (Film-Forming Step)

[0044] As one step of a process of manufacturing a semiconductor device, an example of a step of selectively doping a Ni film of a wafer **200** with B in which the Ni film and a film (for example, a SiN film or a SiO film) other than the Ni film are formed on a film in which B is doped (a B-doped Si film) will be described with reference to FIG. **6**. The step of selectively doping the Ni film with B is performed using the process furnace **202** of the above-described substrate processing apparatus **10**. In the following description, the operations of various parts constituting the substrate processing apparatus **10** are controlled by the controller **121**.

[0045] A substrate-processing process (a semiconductor-device-manufacturing process) according to the present embodiments includes selectively doping a metal film (Ni film) with a dopant (B) by performing: a step of supplying a dopant-containing gas (B_2H_6 gas) containing the dopant (B) to a wafer **200** in which the metal film (Ni film) and a film (for example, SiN film or SiO film) other than the metal film (Ni film) are formed on a film in which the dopant (B) is doped (B-doped Si film); and a step of removing the dopant-containing gas (B_2H_6 gas) from above the wafer **200**.

[0046] When the term "wafer" is used in the present disclosure, it may refer to "a wafer itself" or "a wafer and a laminated body (aggregated body) of certain layers or films formed on a surface of the wafer." (In other words, the term "wafer" may be referred to including a certain layer or film formed on the surface of the wafer.) When the phrase "a surface of a wafer" is used in the present disclosure, it may refer to "a surface (exposed surface) of a wafer itself" or "a surface of a certain layer or film formed on a wafer, that is, the outermost surface of the wafer as a laminated body". When the term "substrate" is used in the present disclosure, it may be synonymous with the term "wafer."

(Wafer Loading)

[0047] When a plurality of wafers **200** in each of which a Ni film and a film (for example, a SiN film or a SiO film) other than the Ni film are formed on a B-doped Si film are charged on the boat **217** (wafer charging), the boat **217** supporting the plurality of wafers **200** is lifted up by the boat elevator **115** to be loaded into the process chamber **201** (boat loading). In this state, the seal cap **219** seals the lower end opening of the outer tube **203** via the O-ring **220**.

(Pressure Adjustment and Temperature Adjustment)

[0048] The interior of the process chamber **201** is vacuum-exhausted by the vacuum pump **246** so as to reach a desired pressure (degree of vacuum). In this operation, the internal pressure of the process chamber **201** is measured by the pressure sensor **245**. The APC valve **243** is feedback-controlled based on the measured pressure information (pressure adjustment). The vacuum pump **246** keeps operating at all times at least until a process to the wafers **200** is completed. In addition, the interior of the process chamber **201** is heated by the heater **207** to a desired temperature. In this operation, the state of supplying electric power to the heater **207** is feedback-controlled based on the temperature information detected by the temperature sensor **263** (temperature adjustment) such that the interior of the process chamber **201** has a desired temperature distribution. The heating of the interior of the process chamber **201** by the heater **207** is continuously performed at least until the process to the wafer **200** is completed.

[0049] Subsequently, a step of selectively doping the Ni film of the wafer **200** with B is performed. Hereinafter, a B_2H_6 gas is intermittently (pulsingly) supplied to the wafer **200** (pulse supply).

(B_2H_6-Gas-Supplying Step)

[0050] The valve **314** is opened to allow a B_2H_6 gas, which is a dopant-containing gas, to flow into the gas supply pipe **310**. A flow rate of the B_2H_6 gas is adjusted by the MFC **312**, and then the B_2H_6 gas is supplied from the gas supply holes **410***a* the nozzle **410** into the process chamber **201** and is exhausted through the exhaust pipe **231**. In this operation, the B_2H_6 gas is supplied to the wafer **200**. At the same time, the valve **514** may be opened to allow an inert gas such as a N_2 gas to flow into the gas supply pipe **510**. A flow rate of the N_2 gas that is flowed into the gas supply pipe **510** is adjusted by the MFC **512**, and the N_2 gas is supplied into the process chamber **201** together with the B_2H_6 gas and is exhausted through the exhaust pipe **231**.

[0051] At this time, the APC valve **243** is adjusted so that the internal pressure of the process chamber **201** falls within a range of, for example, 40 to 1,000 Pa. If the internal pressure is lower than 40 Pa, the concentration of B, which is deposited on the surface of the wafer **200** as the B_2H_6 gas is decomposed, decreases. Although the penetration of B into Ni is due to a diffusion effect, a diffusion speed is proportional to a concentration gradient. Therefore, if the B concentration is low, a speed at which B penetrates into Ni may be significantly reduced. If the internal pressure is higher than 1,000 Pa, collision between B_2H_6 gas molecules in the gas phase frequently occurs, thereby decomposing the B_2H_6 gas. However, the selectivity of B doping is caused by the fact that the B_2H_6 gas is decomposed on the Ni surface but is not decomposed on the SiO or SiN surface. Therefore, when the B_2H_6 gas is decomposed in the gas phase reaction, BH_3, which is a decomposition product, is supplied to any of the Ni, SiO, SiN, and the like, which may deteriorate the selectivity.

[0052] A supply flow rate of the B_2H_6 gas, which is controlled by the MFC **312**, is set to fall within a range of, e.g., 0.3 to 1.0 slm. When the flow rate is smaller than 0.3 slm, a flow velocity of the B_2H_6 gas becomes low, and accordingly the B_2H_6 gas easily stays on the surface and is easily physically adsorbed on the surface. When the physical adsorption density increases, the B_2H_6 gas is easily thermally decomposed. Since this decomposition occurs regardless of the type of a film, it can also occur on the surface of the SiO film or SiN film, which may deteriorate the selectivity of B doping. The time for which the B_2H_6 gas is supplied to the wafer **200** is set to fall within a range of, e.g., 8 to 12 seconds.

[0053] At this time, the temperature of the heater **207** is set such that the temperature of the wafer **200** falls within a range of, e.g., 100 to 300 degrees C., specifically 160 to 220 degrees C. If the temperature is lower than 100 degrees C., the decomposition reaction of the B_2H_6 gas by the catalytic action of Ni requires activation energy and accordingly may not occur. In addition, if the temperature is lower than 100 degrees C., since the diffusion of B in Ni becomes slow or hardly occurs, B may not penetrate into Ni or it may take a very long time for B to penetrate into Ni. If the temperature is higher than 300 degrees C., since the B_2H_6 gas is self-(thermally) decomposed, the selectivity may be broken and B may penetrate into or be deposited on the SiN film or the SiO film. At this time, only the B_2H_6 gas and the N_2 gas are flowed into the process chamber **201** and B is added to the Ni film formed on the surface of the wafer **200** by the supply of the B_2H_6 gas.

(Residual-Gas-Removing Step)

[0054] After B is added to the Ni film, the valve **314** is closed to stop the supply of the B_2H_6 gas. At this time, with the APC valve **243** of the exhaust pipe **231** kept open, the interior of the process chamber **201** is vacuum-exhausted by the vacuum pump **246** to remove the unreacted B_2H_6 gas remaining in the process chamber **201** or the B_2H_6 gas contributed to the addition of B, from the process chamber **201**. At this time, with the valve **514** kept open, the supply of the N_2 gas into the process chamber **201** is maintained. The N_2 gas can act as a purge gas to enhance the effect of removing the unreacted B_2H_6 gas remaining in the process chamber **201** or the B_2H_6 gas contributed to the addition of B, from the process chamber **201**.

(Performing Predetermined Number of Times)

[0055] When a cycle that performs the above-described B_2H_6-gas-supplying step and residual-gas-removing step sequentially is performed once or more (a predetermined number of times (n times)), B is added up to a predetermined depth (for example, 4 to 5 nm) in the Ni film on the wafer **200** to form a B-doped Ni film. The addition of B is the diffusion of B into the Ni film, which is saturated up to the above-mentioned depth and is not added to a further depth. The above cycle is preferably repeated multiple times.

(After-Purge and Returning to Atmospheric Pressure)

[0056] A N_2 gas is supplied into the process chamber **201** from the gas supply pipe **510** and is exhausted through the exhaust pipe **231**. The N_2 gas acts as a purge gas, whereby the interior of the process chamber **201** is purged with an inert gas, and gases and by-products remaining in the process chamber **201** are removed from the interior of the process chamber **201** (after-purge). Thereafter, the internal atmosphere of the process chamber **201** is substituted with an inert gas (inert gas substitution), and the internal pressure of the process chamber **201** is returned to the normal pressure (returning to atmospheric pressure).

(Wafer Unloading)

[0057] Thereafter, the seal cap **219** is moved down by the boat elevator **115** to open the lower end of the outer tube **203**. Then, the processed wafers **200** supported by the boat **217** are unloaded from the lower end of the outer tube **203** to the outside of the outer tube **203** (boat unloading). Thereafter, the processed wafers **200** are discharged from the boat **217** (wafer discharging).

[0058] FIG. **7** shows a XPF (X-ray Photoelectron Spectroscopy) spectrum when the above-described B_2H_6-gas-supplying step and residual-gas-removing step are sequentially repeated 400 times (n=400). FIG. **7** shows the amount of B (B count (XRF)) in each film with respect to the number of pulses of B_2H_6 gas (Number of B_2H_6 pulse). It can be seen from FIG. **7** that B is added to the Ni film, whereas B is not added to the SiO film (SiO_2 film) and the SiN film. It can also be seen that the amount of B added to the Ni film decreases and become saturated as the number of B_2H_6 pulses increases.

[0059] FIGS. **8**A and **8**B show the results of analysis on elements contained in the Ni film by TEM (Transmission Electron Microscope)-EELS (Electron Energy-Loss Spectroscopy). It can be seen from FIGS. **8**A and **8**B that, along a scanning direction shown in FIG. **8**A, a Ni—B layer (A layer) containing B is formed at a depth of about 2 to 6.3 nm from the surface of the Ni film, a Ni layer (B layer) containing substantially no B is formed at a depth of about 6.3 to 10.4 nm, and a deeper SiO layer (SiO_2 layer) also contains substantially no B, as shown in FIG. **8**B. In the A layer, B is particularly remarkably added up to a depth of about 4 to 5 nm.

[0060] It can also be seen from a TEM image of the section of the Ni film shown in FIG. **9** that the Ni film is divided into two upper and lower layers. In the Ni film, crystal grains are observed in the lower layer to which B is not added, whereas crystal grains disappear in the upper layer to which B is added. It is, therefore, confirmed that the crystallinity of the Ni film is changed by the addition of B.

[0061] One of the reasons why the Ni film is annealed in a later step to form NiSi may be to put Si into the Ni film to form NiSi in order to eliminate a Schottky junction (since electric conduction occurs via a trap, the Schottky junction is eliminated). At this time, by previously putting B into the Ni film, the impurity concentration in NiSi may increase to thereby increase the ohmic conduction. That is, it is as if the work function has disappeared.

(3) Effects According to the Present Embodiments

[0062] According to the present embodiments, one or more effects set forth below may be achieved.

[0063] (a) By supplying a B-containing gas to a substrate in which a Ni film and a film other than the Ni film are formed on a film in which B is doped (B-doped Si film), at a temperature that does not cause self-decomposition, the Ni film can be selectively doped with B without using a mask.

[0064] (b) By supplying the B-containing gas in pulses, the uniformity of amount of B added to the Ni film can be improved.

[0065] (c) By doping the Ni film with B, the crystallinity of the Ni film is changed so that the Ni film can have a crystalline structure having a property of improving etching resistance.

[0066] (d) By previously doping the Ni film with B, the impurity concentration in NiSi (that is, B-doped NiSi) formed in a later step can be increased so that the ohmic conduction can be increased.

Second Embodiments of the Present Disclosure

[0067] Next, second embodiments of the present disclosure will be described. Parts different from the first embodiments will be mainly described, and explanation about the same parts as in the first embodiments will be omitted. The second embodiments are different from the first embodiments in that the B_2H_6-gas-supplying step is performed only once (n=1). That is, the B_2H_6 gas is supplied not in pulses but continuously (continuous supply).

[0068] According to the second embodiments, one or more of the above-described effects can be achieved, and the following effects can further be achieved.

[0069] (e) The processing time can be reduced by continuously supplying the B_2H_6 gas (throughput improvement).

Third Embodiments of the Present Disclosure

[0070] Next, third embodiments of the present disclosure will be described. Parts different from the first embodiments will be mainly described, and explanation about the same parts as in the first embodiments will be omitted. Two types of gases are used as the B-containing gas. For example, a B_2H_6 gas (first dopant-containing gas) and a BCl_3 gas (second dopant gas) are used as the B-containing gas. A BCl_3-gas-supplying step of supplying the BCl_3 gas to the wafer **200** is first performed in the same procedure as the B_2H_6-gas-supplying step of the first embodiments, a residual-gas-removing step is performed in the same procedure as in the first embodiments, and the B_2H_6-gas-supplying step and the residual-gas-removing step are then performed in the same procedure as in the first embodiments. This cycle is performed n times. That is, the BCl_3 gas and the B_2H_6 gas are alternately supplied to the wafer **200** so as not to be mixed with each other (alternate supply).

[0071] According to the third embodiments, one or more of the above-described effects can be achieved, and the following effects can further be achieved.

[0072] (f) By alternately supplying the BCl_3 gas and the B_2H_6 gas, mutual ligands bonded to B penetrated into the Ni film can react with each other, thereby suppressing unintended impurities (Cl and H) from leaving in the Ni film. That is, Cl in the BCl_3 gas reacts with H in the B_2H_6 gas to form HCl, which is removed from the Ni film, preferentially leaving B in the Ni film.

[0073] (g) By flowing the BCl_3 gas before the B_2H_6 gas, it is possible to prevent HCl formed by the reaction of the mutual ligands from being introduced into the Ni film.

[0074] An example in which B is added after the Ni film is formed has been described above. However, the present disclosure is not limited thereto. For example, a B-doped Ni film may be formed by alternately repeating the formation of the Ni film and the addition of B. By forming the B-doped Ni film by alternately repeating the formation of the Ni film and the addition of B, the uniformity of amount of B added to the Ni film can be improved. In this case, the formation of the Ni film and the addition of B may be performed in the same process chamber (in-situ).

[0075] Further, in the above description, a double-tube reaction vessel including the outer tube **203** and the inner tube **204** is used as the reaction vessel of the substrate processing apparatus. However, the present disclosure is not limited thereto. For example, a single-tube reaction vessel including only one tube may be used.

[0076] Further, an example in which the B_2H_6 gas or the BCl_3 gas is used as the B-containing gas has been described above. However, the present disclosure is not limited thereto. For example, diborane, boron trichloride, triethylboron, trisdimethylaminoboron, trisdiethylaminoboron, triethoxyboron, trimethoxyboron, or the like may be used as the B-containing gas.

[0077] Further, an example in which the Ni film is used as a film to be preferentially selectively doped has been described above. However, the present disclosure is not limited thereto. For example, a metal film such as a cobalt (Co) film, or a silicon (Si) film may be used as the film to be preferentially selectively doped.

[0078] Further, an example in which the SiN film or the SiO film is used as a film (non-selectively doped film) different from the film to be selectively doped has been described above. However, the present disclosure is not limited thereto. For example, a silicon film, a tantalum film (Ta film), a tantalum nitride film (TaN film), a titanium film

(Ti film), a titanium nitride film (TiN film), a tungsten film (W film), or the like may be used as the non-selectively doped film.

[0079] Furthermore, an example in which the present disclosure is used for an electrode of a MOSFET has been described in the above-described experimental example. However, the present disclosure is not limited thereto. For example, the present disclosure can be applied to a source, a drain, or the like of the MOSFET.

[0080] While various typical embodiments and examples of the present disclosure have been described above, the present disclosure is not limited to these embodiments and examples, but may be used in proper combinations thereof.

INDUSTRIAL APPLICABILITY

[0081] According to the present disclosure, it is possible to suppress diffusion of impurities from a silicon film doped with the impurities to a metal film formed on the silicon film.

[0082] While certain embodiments have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the disclosures. Indeed, the embodiments described herein may be embodied in a variety of other forms. Furthermore, various omissions, substitutions and changes in the form of the embodiments described herein may be made without departing from the spirit of the disclosures. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the disclosures.

What is claimed is:

1. A method of manufacturing a semiconductor device, comprising:
- selectively doping a metal film with a dopant by performing:
  - supplying a dopant-containing gas containing the dopant to a substrate in which the metal film and a film other than the metal film are formed on a film in which the dopant is doped; and
  - removing the dopant-containing gas from above the substrate.

2. The method according to claim **1**, wherein the dopant is boron.

3. The method according to claim **2**, wherein the dopant-containing gas is diborane, boron trichloride, triethylboron, trisdimethylaminoboron, trisdiethylaminoboron, triethoxyboron, or trimethoxyboron.

4. The method according to claim **1**, wherein the metal film is a nickel film.

5. The method according to claim **1**, wherein the film other than the metal film is a silicon film, a silicon oxide film, a silicon nitride film, a tantalum film, a tantalum nitride film, a titanium film, a titanium nitride film, or a tungsten film.

6. The method according to claim **1**, wherein the act of supplying the dopant-containing gas and the act of removing the dopant-containing gas are alternately repeated multiple times.

7. The method according to claim **6**, wherein the dopant-containing gas is diborane.

8. The method according to claim **1**, wherein the act of supplying the dopant-containing gas and the act of removing the dopant-containing gas are each performed once.

9. A method of manufacturing a semiconductor device, comprising:
- selectively doping a metal film with a dopant by sequentially repeating, multiple times:
  - supplying a first dopant-containing gas containing the dopant to a substrate in which the metal film and a film other than the metal film are formed on a film in which the dopant is doped;
  - removing the first dopant-containing gas from above the substrate;
  - supplying a second dopant-containing gas containing the dopant to above the substrate; and
  - removing the second dopant-containing gas from above the substrate.

10. The method according to claim **9**, wherein the dopant is boron, one of the first dopant-containing gas and the second dopant-containing gas is diborane, and the other of the first dopant-containing gas and the second dopant-containing gas is boron trichloride.

11. A substrate processing apparatus comprising:
- a process chamber that accommodates a substrate;
- a gas supply system configured to supply a dopant-containing gas containing a dopant to the substrate in the process chamber;
- an exhaust system configured to exhaust an interior of the process chamber; and
- a controller configured to control the gas supply system and the exhaust system so as to perform a process including:
  - selectively doping a metal film with the dopant by performing:
    - supplying the dopant-containing gas to the substrate, which is accommodated in the process chamber, in which the metal film and a film other than the metal film are formed on a film in which the dopant is doped; and
    - exhausting the dopant-containing gas from the process chamber.

12. A substrate processing apparatus comprising:
- a process chamber that accommodates a substrate;
- a gas supply system configured to supply a first dopant-containing gas containing a dopant and a second dopant-containing gas, which is different from the first dopant-containing gas, containing the dopant to the substrate in the process chamber;
- an exhaust system configured to exhaust an interior of the process chamber; and
- a controller configured to control the gas supply system and the exhaust system so as to perform a process including:
  - selectively doping a metal film with the dopant by sequentially repeating, multiple times:
    - supplying the first dopant-containing gas to the substrate, which is accommodated in the process chamber, in which the metal film and a film other than the metal film are formed on a film in which the dopant is doped;
    - exhausting the first dopant-containing gas from the process chamber;
    - supplying the second dopant-containing gas to the substrate which is accommodated in the process chamber; and
    - exhausting the second dopant-containing gas from the process chamber.

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

selectively doping a metal film with a dopant by performing:

supplying a dopant-containing gas containing the dopant to a substrate, which is accommodated in a process chamber of the substrate processing apparatus, in which the metal film and a film other than the metal film are formed on a film in which the dopant is doped; and

removing the dopant-containing gas from above the substrate.

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

selectively doping a metal film with a dopant by sequentially repeating, multiple times:

supplying a first dopant-containing gas containing the dopant to a substrate, which is accommodated in a process chamber of the substrate processing apparatus, in which the metal film and a film other than the metal film are formed on a film in which the dopant is doped;

removing the first dopant-containing gas from above the substrate;

supplying a second dopant-containing gas containing the dopant to above the substrate; and

removing the second dopant-containing gas from above the substrate.

* * * * *