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(54) **FILM FORMATION METHOD AND APPARATUS FOR SEMICONDUCTOR PROCESS**

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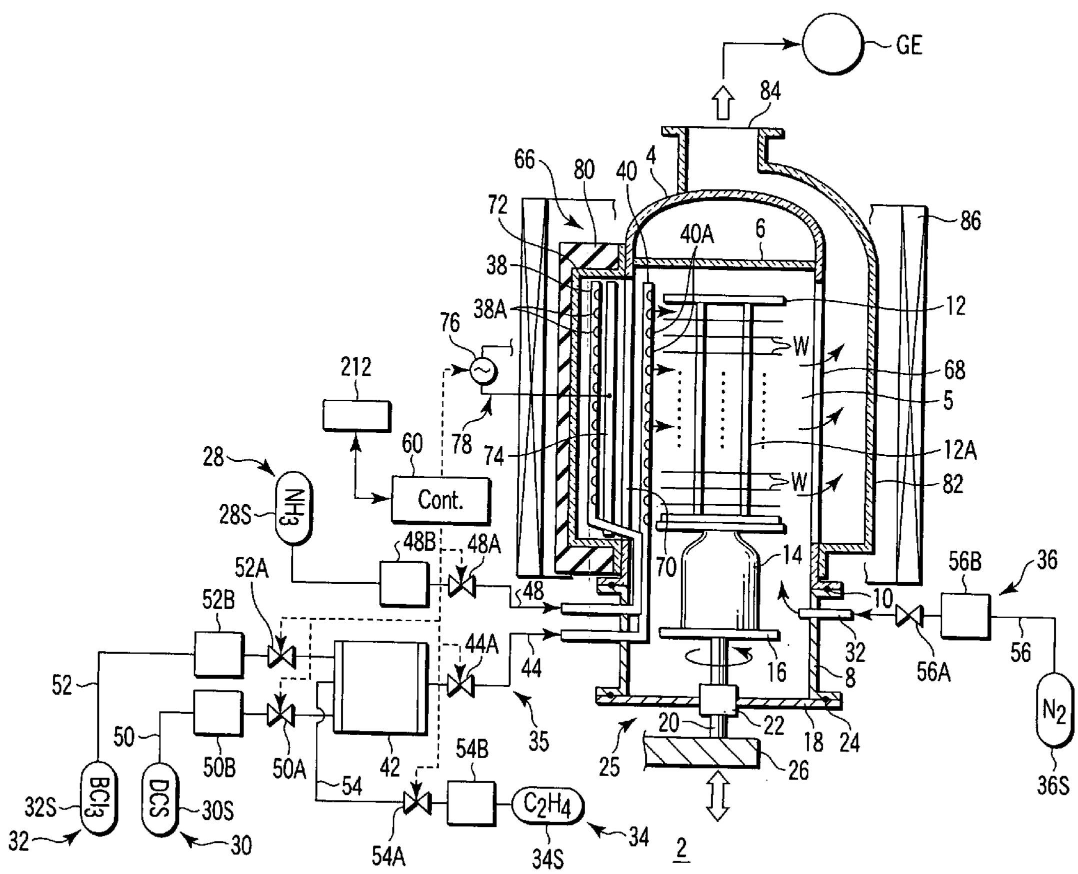
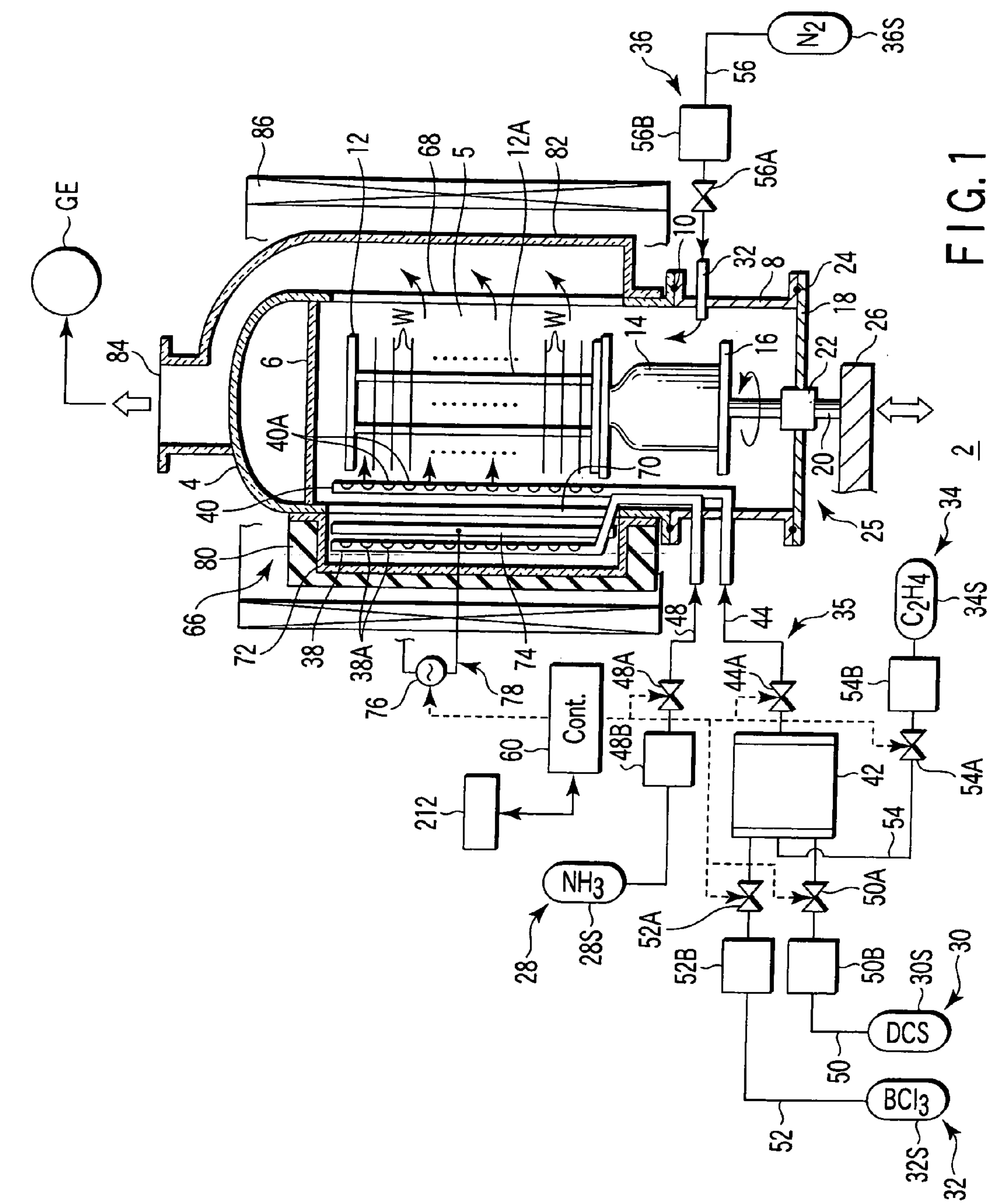
(57) **ABSTRACT**

A film formation apparatus for a semiconductor process includes a process gas supply system configured to supply process gases. The process gas supply system includes a gas mixture tank configured to mix first and third process gases to form a mixture gas, a mixture gas supply line configured to supply the mixture gas from the gas mixture tank to a process field, a second process gas supply circuit having a second process gas supply line configured to supply a second process gas to the process field without passing through the gas mixture tank, and first and second switching valves disposed on the mixture gas supply line and the second process gas supply line, respectively. A control section controls the first and second switching valves to be opened and closed so as to alternately and pulse-wise supply the mixture gas and the second process gas to the process field.




GE
84
86
12
68
5
12A
82
36
56
N_2
36S
56B
56A
10
32
8
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18
26
22
16
14
6
4
40A
W
70
20
2
40
80
66
72
38
38A
74
48
44
35
34
C_2H_4
34S
54B
48A
44A
76
78
Cont.
60
48B
42
54A
54
212
NH_3
28S
28
52A
50A
52B
50B
30S
30
DCS
50
BCl_3
52
32S
32

FIG. 1

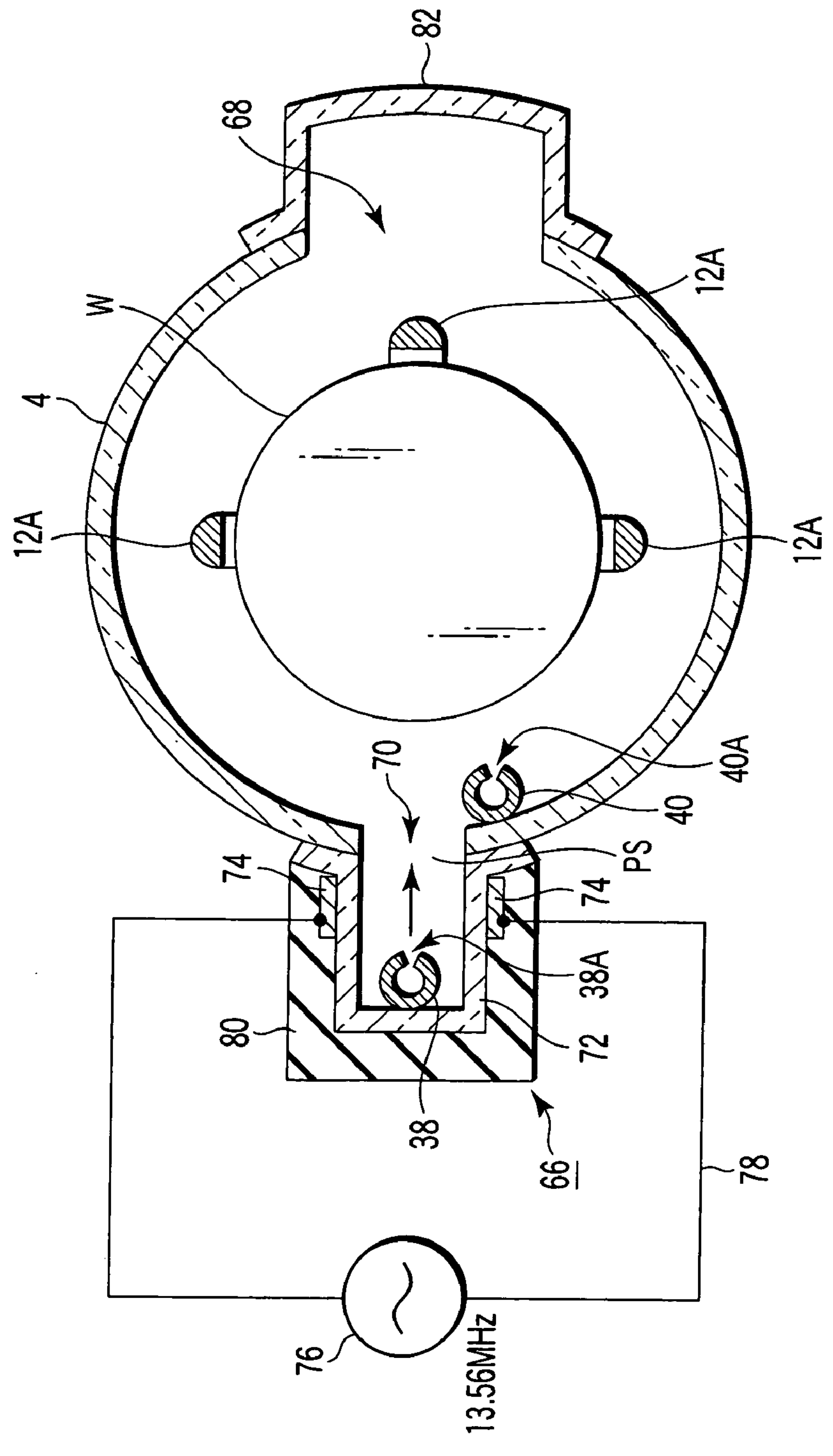

82
68
W
4
12A
12A
12A
70
40A
40
PS
74
74
38A
72
80
38
66
78
76
13.56MHz

FIG. 2

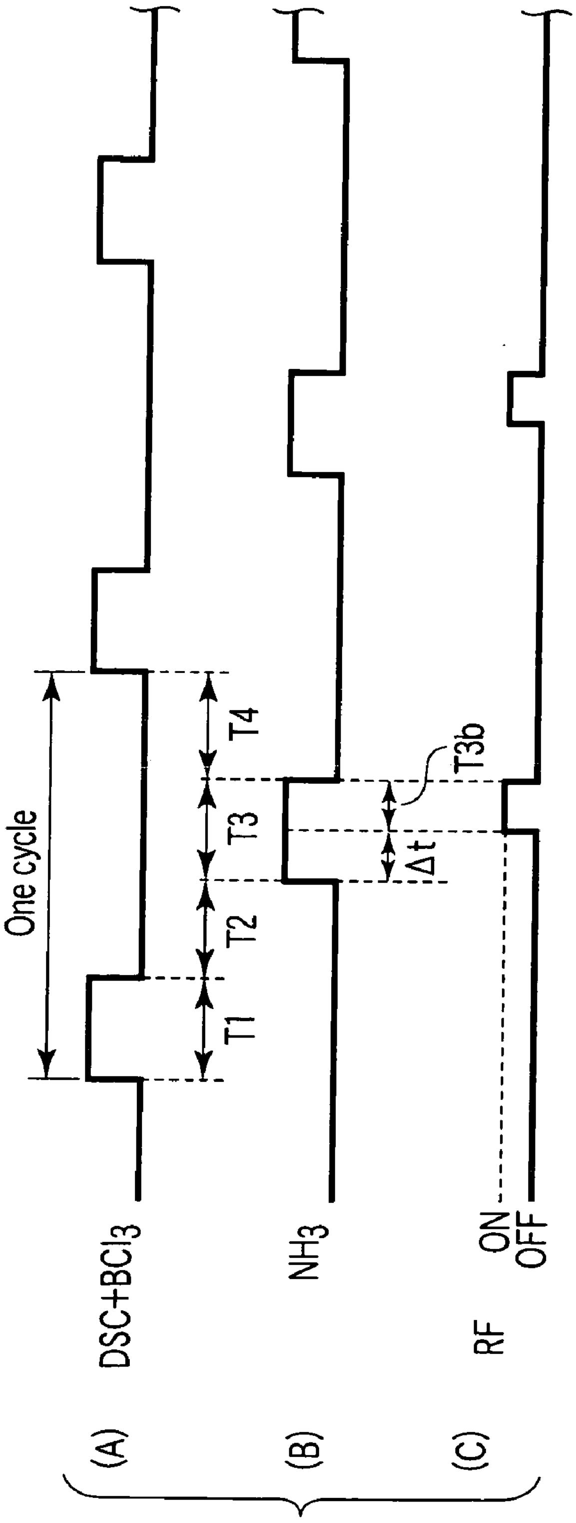


FIG. 3

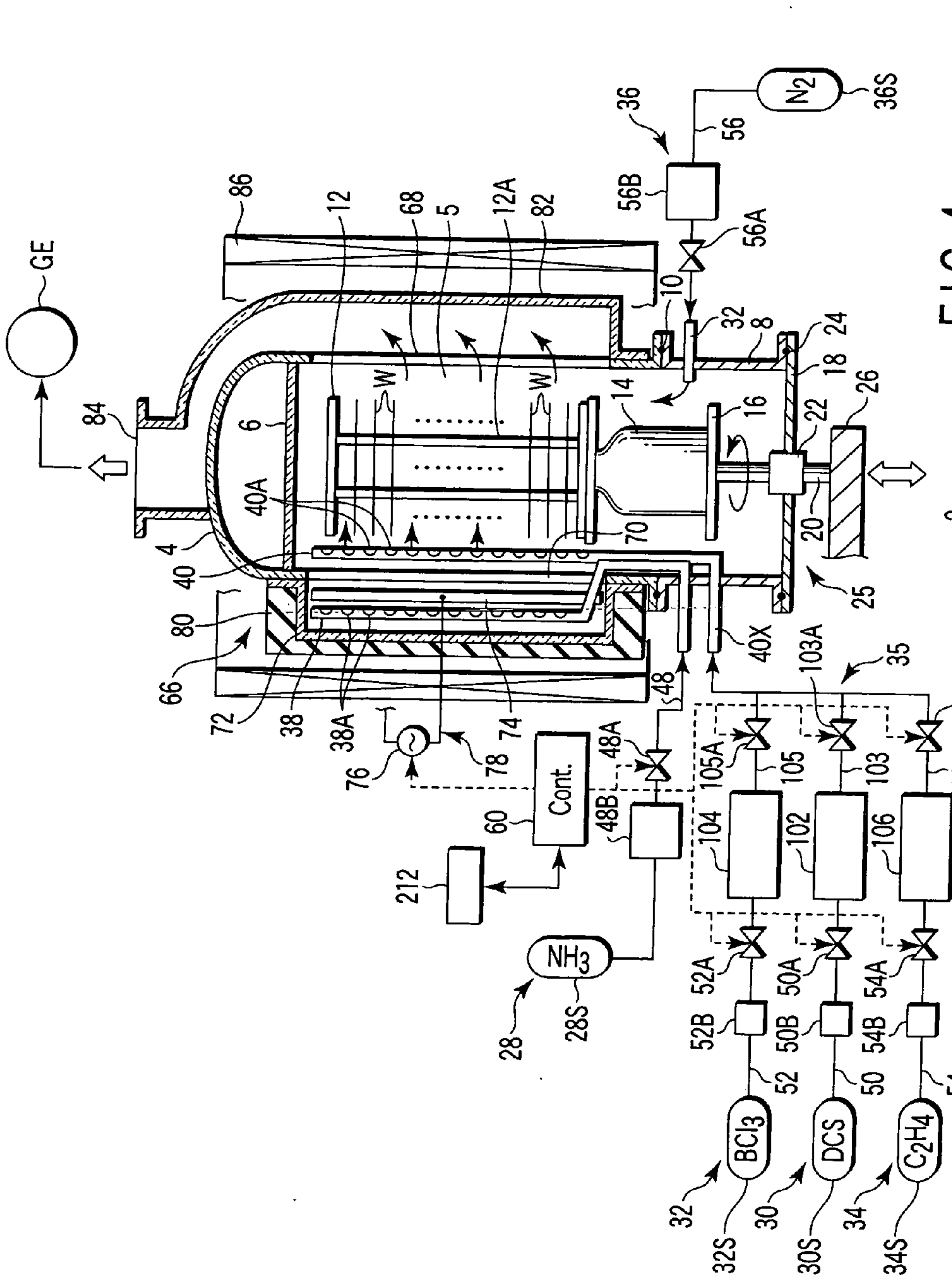
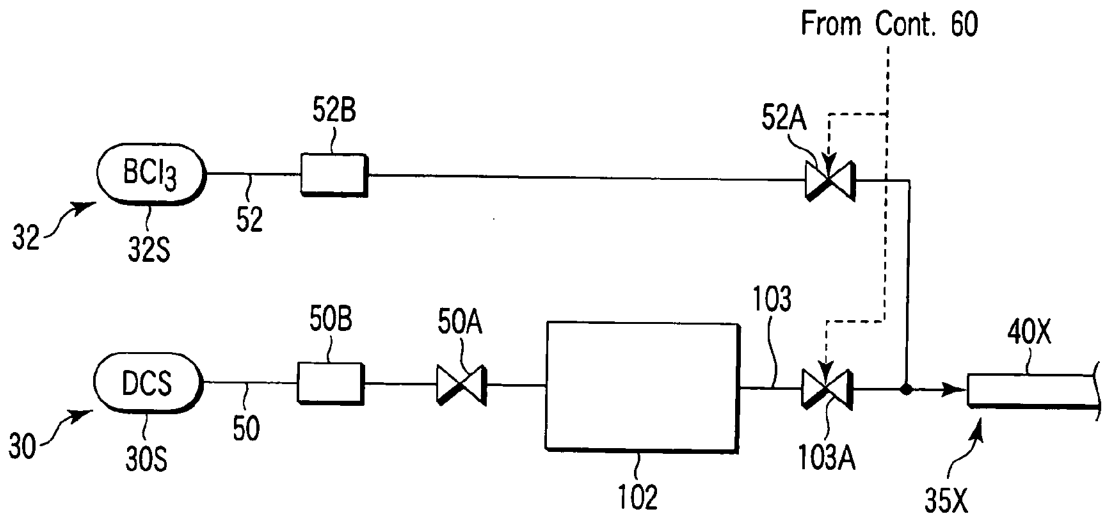
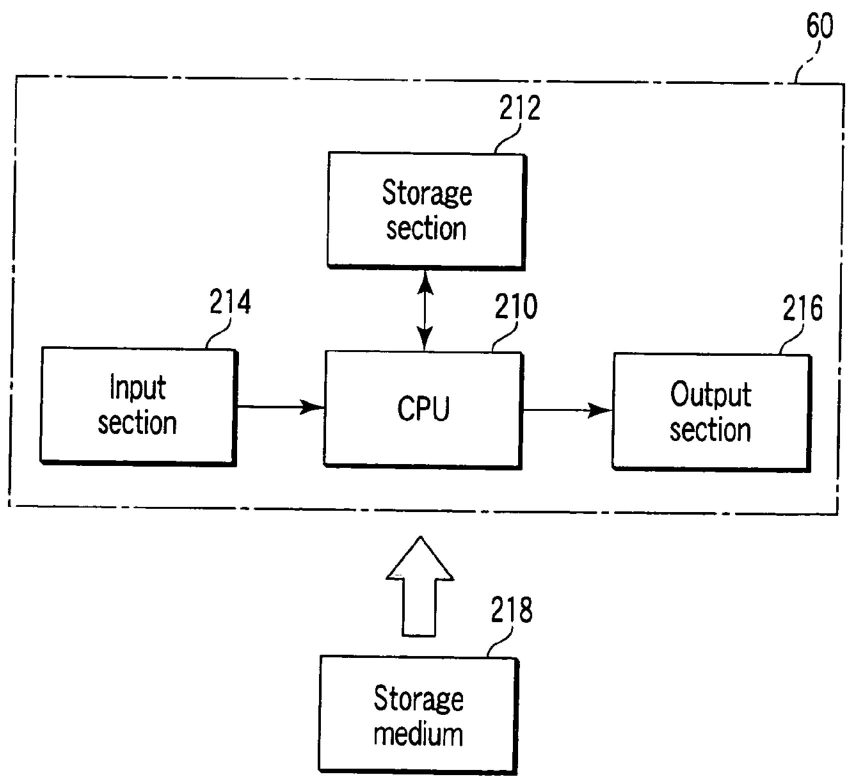


FIG. 4


From Cont. 60
52B
52A
BCl3
32
32S
52
50B
50A
103
40X
DCS
30
30S
50
103A
102
35X

F I G. 5


60
212
Storage section
214
210
216
Input section
CPU
Output section
218
Storage medium

F I G. 6

FILM FORMATION METHOD AND APPARATUS FOR SEMICONDUCTOR PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is based upon and claims the benefit of priority from prior Japanese Patent Applications No. 2005-070034, filed Mar. 11, 2005; and No. 2006-004192, filed Jan. 11, 2006, the entire contents of both of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a film formation apparatus and method for a semiconductor process for forming a thin film on a target substrate, such as a semiconductor wafer. The term "semiconductor process" used herein includes various kinds of processes which are performed to manufacture a semiconductor device or a structure having wiring layers, electrodes, and the like to be connected to a semiconductor device, on a target substrate, such as a semiconductor wafer or a glass substrate used for an LCD (Liquid Crystal Display) or FPD (Flat Panel Display), by forming semiconductor layers, insulating layers, and conductive layers in predetermined patterns on the target substrate.

[0004] 2. Description of the Related Art

[0005] In manufacturing semiconductor devices for constituting semiconductor integrated circuits, a target substrate, such as a semiconductor wafer, is subjected to various processes, such as film formation, etching, oxidation, diffusion, reformation, annealing, and natural oxide film removal. Jpn. Pat. Appln. KOKAI Publication No. 6-34974 discloses a semiconductor processing method of this kind performed in a vertical heat-processing apparatus (of the so-called batch type). According to this method, semiconductor wafers are first transferred from a wafer cassette onto a vertical wafer boat and supported thereon at intervals in the vertical direction. The wafer cassette can store, e.g., 25 wafers, while the wafer boat can support 30 to 150 wafers. Then, the wafer boat is loaded into a process container from below, and the process container is airtightly closed. Then, a predetermined heat process is performed, while the process conditions, such as process gas flow rate, process pressure, and process temperature, are controlled.

[0006] Conventionally, silicon oxide films (SiO_2 films) are mainly used as insulating films for semiconductor devices. However, in recent years, owing to the demands of increased integration and miniaturization of semiconductor integrated circuits, silicon nitride films (Si_3N_4 films) are used in place of silicon oxide films, as needed (Jpn. Pat. Appln. KOKAI Publication No. 6-34974). For example, silicon nitride films are disposed as films resistant to oxidation, films for preventing impurity diffusion, and sidewall films of gate electrode structures. Since silicon nitride films provide a low coefficient of impurity diffusion and a good barrier property against oxidation, they are very suitable as insulating films for the purpose described above. Further, boron nitride films (BN films) have also attracted attention for the same reasons.

[0007] For example, where dichlorosilane (DCS) and NH_3 are supplied as a silane family gas and a nitriding gas, respectively, to form a silicon nitride film (SiN), the process is performed, as follows. Specifically, DCS and NH_3 gas are alternately and intermittently supplied into a process container with purge periods interposed therebetween. When NH_3 gas is supplied, an RF (radio frequency) is applied to generate plasma within the process container so as to promote a nitridation reaction. More specifically, when DCS is supplied into the process container, a layer with a thickness of one molecule or more of DCS is adsorbed onto the surface of wafers. The superfluous DCS is removed during the purge period. Then, NH_3 is supplied and plasma is generated, thereby performing low temperature nitridation to form a silicon nitride film. These sequential steps are repeated to complete a film having a predetermined thickness.

[0008] On the other hand, in recent years, increasing the operation speed of semiconductor devices is also an important factor. In this respect, silicon nitride films have a relatively high dielectric constant, which increases parasitic capacitance and thus is problematic. Specifically, with an increase in parasitic capacitance, the mobility of electrons is suppressed, so the device operation speed decreases. Further, where a silicon nitride film is used for a sensor of the charge storage type, there is a problem in that parasitic capacitance increases a background level.

[0009] Under the circumstances, it has been proposed to dope a silicon nitride film with an impurity, so as to decrease the dielectric constant while maintaining the impurity diffusion coefficient and oxidation barrier property. Jpn. Pat. Appln. KOKAI Publication No. 2004-6801 discloses a method of forming a silicon nitride film doped with boron (B) as an impurity, by CVD (Chemical Vapor Deposition). Silicon nitride films doped with boron (SiBN) have not only a low coefficient of impurity diffusion and a good barrier property against oxidation, but also a very low dielectric constant, so they are very useful as insulating films.

[0010] However, as described later, the present inventors have found that, where a process gas in a small amount, such as a doping gas, is used in conventional vertical heat-processing apparatuses (of the so-called batch type), the inter-substrate uniformity in the composition of deposited films tends to be deteriorated.

BRIEF SUMMARY OF THE INVENTION

[0011] An object of the present invention is to provide an apparatus and method for a semiconductor process, which can uniformly supply a process gas in a small amount, such as a doping gas, into a process container in the vertical direction, thereby improving the inter-substrate uniformity in the composition of deposited films.

[0012] According to a first aspect of the present invention, there is provided a film formation apparatus for a semiconductor process, comprising:

[0013] a process container having a process field configured to accommodate a plurality of target substrates stacked at intervals;

[0014] a support member configured to support the target substrates inside the process field;

[0015] a heater configured to heat the target substrates inside the process field;

[0016] an exhaust system configured to exhaust gas inside the process field;

[0017] a process gas supply system configured to supply process gases to the process field so as to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film;

[0018] a control section configured to control an operation of the apparatus including the process gas supply system,

[0019] wherein the process gas supply system comprises

[0020] a gas mixture tank disposed outside the process container and configured to mix the first and third process gases to form a mixture gas,

[0021] a mixture gas supply line configured to supply the mixture gas from the gas mixture tank to the process field,

[0022] first and third process gas supply circuits configured to supply the first and third process gases to the gas mixture tank, respectively,

[0023] a second process gas supply circuit having a second process gas supply line configured to supply the second process gas to the process field without passing through the gas mixture tank,

[0024] first and second switching valves disposed on the mixture gas supply line and the second process gas supply line, respectively, and

[0025] wherein the control section controls the first and second switching valves to be opened and closed so as to alternately and pulse-wise supply the mixture gas from the gas mixture tank and the second process gas from the second process gas supply circuit to the process field.

[0026] According to a second aspect of the present invention, there is provided a film formation apparatus for a semiconductor process, comprising:

[0027] a process container having a process field configured to accommodate a plurality of target substrates stacked at intervals;

[0028] a support member configured to support the target substrates inside the process field;

[0029] a heater configured to heat the target substrates inside the process field;

[0030] an exhaust system configured to exhaust gas inside the process field;

[0031] a process gas supply system configured to supply process gases to the process field so as to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film, and the third process gas is supplied to the process field in an amount smaller than that of the first process gas;

[0032] a control section configured to control an operation of the apparatus including the process gas supply system,

[0033] wherein the process gas supply system comprises

[0034] a mixture gas supply line configured to mix the first and third process gases to form a mixture gas and supply the mixture gas to the process field,

[0035] first and third process gas supply circuits having first and third process gas supply lines configured to supply the first and third process gases to the mixture gas supply line, respectively,

[0036] a second process gas supply circuit having a second process gas supply line configured to supply the second process gas to the process field without passing through the mixture gas supply line,

[0037] first, second, and third switching valves disposed on the first, second, and third process gas supply lines, respectively,

[0038] a first tank disposed on the first process gas supply line immediately before the first switching valve to temporarily store the first process gas, and

[0039] wherein the control section controls the first, second, and third switching valves to be opened and closed so as to alternately and pulse-wise supply the mixture gas from the mixture gas supply line and the second process gas from the second process gas supply circuit to the process field.

[0040] According to a third aspect of the present invention, there is provided a film formation method for a semiconductor process, comprising:

[0041] heating a plurality of target substrates stacked at intervals within a process field in a process container; and

[0042] supplying process gases to the process field to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film,

[0043] wherein said supplying the process gases comprises

[0044] supplying the first and third process gases to a gas mixture tank disposed outside the process container to form a mixture gas,

[0045] supplying the mixture gas from the gas mixture tank to the process field, and

[0046] supplying the second process gas to the process field without passing through the gas mixture tank,

[0047] so as to alternately and pulse-wise supply the mixture gas and the second process gas to the process field.

[0048] According to a fourth aspect of the present invention, there is provided a film formation method for a semiconductor process, comprising:

[0049] heating a plurality of target substrates stacked at intervals within a process field in a process container; and

[0050] supplying process gases to the process field to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film, and the third process gas is supplied to the process field in an amount smaller than that of the first process gas,

[0051] wherein said supplying the process gases comprises

[0052] supplying the first and third process gases to a mixture gas supply line to form a mixture gas and supply the mixture gas to the process field, while temporarily storing the first process gas in a first tank disposed immediately before the mixture gas supply line, and

[0053] supplying the second process gas to the process field without passing through the mixture gas supply line,

[0054] so as to alternately and pulse-wise supply the mixture gas and the second process gas to the process field.

[0055] According to a fifth aspect of the present invention, there is provided a computer readable medium containing program instructions for execution on a processor, which, when executed by the processor, cause a film formation apparatus for a semiconductor process to execute

[0056] heating a plurality of target substrates stacked at intervals within a process field in a process container; and

[0057] supplying process gases to the process field to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film,

[0058] wherein said supplying the process gases comprises

[0059] supplying the first and third process gases to a gas mixture tank disposed outside the process container to form a mixture gas,

[0060] supplying the mixture gas from the gas mixture tank to the process field, and

[0061] supplying the second process gas to the process field without passing through the gas mixture tank,

[0062] so as to alternately and pulse-wise supply the mixture gas and the second process gas to the process field.

[0063] According to a sixth aspect of the present invention, there is provided a computer readable medium containing program instructions for execution on a processor, which, when executed by the processor, cause a film formation apparatus for a semiconductor process to execute

[0064] heating a plurality of target substrates stacked at intervals within a process field in a process container; and

[0065] supplying process gases to the process field to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film, and the third process gas is supplied to the process field in an amount smaller than that of the first process gas,

[0066] wherein said supplying the process gases comprises

[0067] supplying the first and third process gases to a mixture gas supply line to form a mixture gas and supply the mixture gas to the process field, while temporarily storing the first process gas in a first tank disposed immediately before the mixture gas supply line, and

[0068] supplying the second process gas to the process field without passing through the mixture gas supply line,

[0069] so as to alternately and pulse-wise supply the mixture gas and the second process gas to the process field.

[0070] Additional objects and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

[0071] The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate embodiments of the invention, and together with the general description given above and the detailed description of the embodiments given below, serve to explain the principles of the invention.

[0072] **FIG. 1** is a sectional view showing a film formation apparatus (vertical CVD apparatus) according to a first embodiment of the present invention;

[0073] **FIG. 2** is a sectional plan view showing part of the apparatus shown in **FIG. 1**;

[0074] **FIG. 3** is a timing chart of the gas supply and RF (radio frequency) application of a film formation method according to a first embodiment;

[0075] **FIG. 4** is a sectional view showing a film formation apparatus (vertical CVD apparatus) according to a second embodiment of the present invention;

[0076] **FIG. 5** is a view showing part of a gas supply system used in a film formation apparatus according to a modification of the second embodiment; and

[0077] **FIG. 6** is a block diagram schematically showing the structure of a main control section.

DETAILED DESCRIPTION OF THE INVENTION

[0078] In the process of developing the present invention, the inventors studied problems caused in conventional film formation apparatuses for a semiconductor process, where a plurality of source gases were used to perform a film formation process, such as a process for forming a thin film doped with an impurity. As a result, the inventors have arrived at the findings given below.

[0079] Specifically, where a plurality of source gases are used to perform a film formation process, it is important to control the ratio of film composition elements of to be a predetermined value, so as to attain high film quality. However, for example, where the source gases includes a main source gas containing a main component element of a deposition film and a doping gas, the supply amount of the doping gas is far smaller than the supply amount of the main source gas, in general. In this case, since the supply amount of the doping gas supplied into a vertical process container is small, a problem arises such that an element derived from the doping gas is taken into deposited films on wafers in varying amounts, depending on the wafer position in the vertical direction. Consequently, the inter-substrate uniformity in the composition of the deposited films tends to be lower. This problem is caused due to differences in the adsorptivity of the source gas relative to the wafer surface and in the flow rate of the source gases.

[0080] For this reason, where the supply amount of a gas, such as a doping gas, supplied into a vertical process container is small, countermeasures are required to supply the gas at a uniform supply amount in the vertical direction. For example, a gas nozzle having a number of gas spouting holes at predetermined intervals is disposed to extend in the longitudinal direction of the vertical process container, and the doping gas is delivered from the holes. Alternatively, the supply time of the doping gas is shortened to increase the flow rate of the gas per unit time. However, even with the former countermeasure, where a very small gas supply amount is handled, the flow rate from gas spouting holes at the upstream side tends to be higher than the flow rate from gas spouting holes at the downstream side. In this respect, it is not easy to optimize the dimensions and so forth of gas spouting holes, so as to uniformize the flow rate from the gas spouting holes, for a small gas supply amount.

[0081] Further, where the supply amount of a gas, such as a doping gas, is very small, the gas can be mixed with an inactive carrier gas to increase the total flow rate, as a countermeasure. In this case, however, due to the presence of the carrier gas, the partial pressure of the doping gas decreases and thus the adsorption rate of the doping gas decreases by that much.

[0082] Embodiments of the present invention achieved on the basis of the findings given above will now be described with reference to the accompanying drawings. In the following description, the constituent elements having substantially the same function and arrangement are denoted by the same reference numerals, and a repetitive description will be made only when necessary.

[0083] <First Embodiment>

[0084] **FIG. 1** is a sectional view showing a film formation apparatus (vertical CVD apparatus) according to a first embodiment of the present invention. **FIG. 2** is a sectional plan view showing part of the apparatus shown in **FIG. 1**. The film formation apparatus **2** has a process field configured to be selectively supplied with a first process gas containing dichlorosilane (DCS) gas as a silane family gas, a second process gas containing ammonia (NH_3) gas as a nitriding gas, and a third process gas containing BCl_3 gas as a boron-containing gas. The film formation apparatus **2** is configured to form an SIBN (boron doped silicon nitride) film on target substrates by CVD in the process field. Accordingly, the boron-containing gas is used as a doping gas. The process field is further configured to be selectively supplied with a fourth process gas containing C_2H_4 gas (ethylene gas) as a carbon hydride gas, as needed.

[0085] The apparatus **2** includes a process container **4** shaped as a cylindrical column with a ceiling and an opened bottom, in which a process field **5** is defined to accommodate and process a plurality of semiconductor wafers (target substrates) stacked at intervals in the vertical direction. The entirety of the process container **4** is made of, e.g., quartz. The top of the process container **4** is provided with a quartz ceiling plate **6** to airtightly seal the top. The bottom of the process container **4** is connected through a seal member **10**, such as an O-ring, to a cylindrical manifold **8**. The process container may be entirely formed of a cylindrical quartz column without a manifold **8** separately formed.

[0086] The manifold **8** is made of, e.g., stainless steel, and supports the bottom of the process container **4**. A wafer boat **12** made of quartz is moved up and down through the bottom port of the manifold **8**, so that the wafer boat **12** is loaded/unloaded into and from the process container **4**. A number of target substrates or semiconductor wafers W are stacked on a wafer boat **12**. For example, in this embodiment, the wafer boat **12** has struts **12**A that can support, e.g., about 50 to 100 wafers having a diameter of 300 mm at essentially regular intervals in the vertical direction.

[0087] The wafer boat **12** is placed on a table **16** through a heat-insulating cylinder **14** made of quartz. The table **16** is supported by a rotary shaft **20**, which penetrates a lid **18** made of, e.g., stainless steel, and is used for opening/closing the bottom port of the manifold **8**.

[0088] The portion of the lid **18** where the rotary shaft **20** penetrates is provided with, e.g., a magnetic-fluid seal **22**, so that the rotary shaft **20** is rotatably supported in an airtightly sealed state. A seal member **24**, such as an O-ring, is interposed between the periphery of the lid **18** and the bottom of the manifold **8**, so that the interior of the process container **4** can be kept sealed.

[0089] The rotary shaft **20** is attached at the distal end of an arm **26** supported by an elevating mechanism **25**, such as a boat elevator. The elevating mechanism **25** moves the wafer boat **12** and lid **18** up and down integratedly. The table **16** may be fixed to the lid **18**, so that wafers W are processed without rotation of the wafer boat **12**.

[0090] A gas supply system is connected to the side of the manifold **8** to supply predetermined process gases to the process field **5** within the process container **4**. Specifically, the gas supply system includes a second process gas supply circuit **28**, a first process gas supply circuit **30**, a third process gas supply circuit **32**, and a purge gas supply circuit **36**, and, as needed, a fourth process gas supply circuit **34**. The first process gas supply circuit **30** is arranged to supply a first process gas containing a silane family gas, such as DCS (dichlorosilane) gas. The second process gas supply circuit **28** is arranged to supply a second process gas containing a nitriding gas, such as ammonia (NH_3) gas. The third process gas supply circuit **32** is arranged to supply a third process gas containing a boron-containing gas (doping gas), such as BCl_3 gas. The fourth process gas supply circuit **34** is arranged to supply a fourth process gas containing a carbon hydride gas, such as C_2H_4 gas (ethylene gas). The purge gas supply circuit **36** is arranged to supply an inactive gas, such as N_2 gas, as a purge gas. Each of the first, second, and fourth process gases is mixed with a suitable amount of carrier gas, as needed. However, such a carrier gas will not be mentioned, hereinafter, for the sake of simplicity of explanation.

[0091] More specifically, the first, third, and fourth process gas supply circuits **30**, **32**, and **34** are connected to a common mixture gas supply circuit **35**. The mixture gas supply circuit **35** has a gas mixture tank configured to mix the first and third process gases, and further the fourth process gas in addition thereto, as needed. The gas mixture tank **42** is designed to have a volume for uniformly mixing the gases and temporarily store a sufficient supply amount of the mixture gas, such as a volume of, e.g., about four liters (to be changed depending on the gas flow rate). The gas mixture tank **52** is connected to a gas distribution nozzle **40** formed of a quartz pipe through a mixture gas supply line **44** provided with a switching valve **44**A. On the other hand, the second process gas supply circuit **28** is connected to a gas distribution nozzle **38** formed of a quartz pipe.

[**0092**] The gas distribution nozzles **38** and **40** penetrate the sidewall of the manifold **8** from the outside and then turn and extend upward. The gas distribution nozzles **38** and **40** respectively have a plurality of gas spouting holes **38**A and **40**A, each set of holes being formed at predetermined intervals in the longitudinal direction (the vertical direction) over all the wafers W on the wafer boat **12**. Each of the gas spouting holes **38**A and **40**A delivers the corresponding process gas almost uniformly in the horizontal direction, so as to form gas flows parallel with the wafers W on the wafer boat **12**. The purge gas supply circuit **36** includes a short gas nozzle **46**, which penetrates the sidewall of the manifold **8** from the outside.

[**0093**] The gas mixture tank **52** is connected to gas sources **30**S, **32**S, and **34**S of DCS gas, $BC1_3$ gas, and C_2H_4 gas, respectively, through gas supply lines (gas passages) **50**, **52**, and **54** of the first, third, and fourth process gas supply circuits **30**, **32**, and **34**, respectively. The gas distribution nozzle **38** of the second process gas supply circuit **28** is connected to a gas source **28**S of NH_3 gas through a gas supply line (gas passage) **48**. The nozzle **46** of the purge gas supply circuit **36** is connected to a gas source **36**S of N_2 gas through gas supply lines (gas passage) **56**. The gas supply lines **48**, **50**, **52**, **54**, and **56** are provided with switching valves **48**A, **50**A, **52**A, **54**A, and **56**A and flow rate controllers **48**B, **50**B, **52**B, **54**B, and **56**B, such as mass flow controllers, respectively. With this arrangement, NH_3 gas, DCS gas, BCl_3 gas, C_2H_4 gas, and N_2 gas can be supplied at controlled flow rates.

[**0094**] A gas exciting section **66** is formed at the sidewall of the process container **4** in the vertical direction. On the side of the process container **4** opposite to the gas exciting section **66**, a long and thin exhaust port **68** for vacuum-exhausting the inner atmosphere is formed by cutting the sidewall of the process container **4** in, e.g., the vertical direction.

[**0095**] Specifically, the gas exciting section **66** has a vertically long and thin opening **70** formed by cutting a predetermined width of the sidewall of the process container **4**, in the vertical direction. The opening **70** is covered with a quartz cover **72** airtightly connected to the outer surface of the process container **4** by welding. The cover **72** has a vertical long and thin shape with a concave cross-section, so that it projects outward from the process container **4**.

[**0096**] With this arrangement, the gas exciting section **66** is formed such that it projects outward from the sidewall of the process container **4** and is opened on the other side to the interior of the process container **4**. In other words, the inner space of the gas exciting section **66** communicates with the process field **5** within the process container **4**. The opening **70** has a vertical length sufficient to cover all the wafers W on the wafer boat **12** in the vertical direction.

[**0097**] A pair of long and thin electrodes **74** are disposed on the opposite outer surfaces of the cover **72**, and face each other along the longitudinal direction (the vertical direction). The electrodes **74** are connected to an RF (Radio Frequency) power supply **76** for plasma generation, through feed lines **78**. An RF voltage of, e.g., 13.56 MHz is applied to the electrodes **74** to form an RF electric field for exciting plasma between the electrodes **74**. The frequency of the RF voltage is not limited to 13.56 MHz, and it may be set at another frequency, e.g., 400 kHz.

[**0098**] The gas distribution nozzle **38** of the second process gas is bent outward in the radial direction of the process container **4**, at a position lower than the lowermost wafer W on the wafer boat **12**. Then, the gas distribution nozzle **38** vertically extends at the deepest position (the farthest position from the center of the process container **4**) in the gas exciting section **66**. As shown also in **FIG. 2**, the gas distribution nozzle **38** is separated outward from an area sandwiched between the pair of electrodes **74** (a position where the RF electric field is most intense), i.e., a plasma generation area PS where the main plasma is actually generated. The second process gas containing NH_3 gas is spouted from the gas spouting holes **38**A of the gas distribution nozzle **38** toward the plasma generation area PS. Then, the second process gas is excited (decomposed or activated) in the plasma generation area PS, and is supplied in this state onto the wafers W on the wafer boat **12**.

[**0099**] An insulating protection cover **80** made of, e.g., quartz is attached on and covers the outer surface of the cover **72**. A cooling mechanism (not shown) is disposed in the insulating protection cover **80** and comprises coolant passages respectively facing the electrodes **74**. The coolant passages are supplied with a coolant, such as cooled nitrogen gas, to cool the electrodes **74**. The insulating protection cover **80** is covered with a shield (not shown) disposed on the outer surface to prevent RF leakage.

[**0100**] At a position near and outside the opening **70** of the gas exciting section **66**, the gas distribution nozzle **40** of the mixture gas supply circuit **35** is disposed to vertically extend upward. The mixture gas (a mixture gas of the first and third process gases, and further the fourth process gas in addition thereto, as needed) is spouted from the gas spouting holes **40**A of the gas distribution nozzle **40** toward the center of the process container **4**.

[**0101**] On the other hand, the exhaust port **68**, which is formed opposite the gas exciting section **66**, is covered with an exhaust port cover member **82**. The exhaust port cover member **82** is made of quartz with a U-shape cross-section, and attached by welding. The exhaust cover member **82** extends upward along the sidewall of the process container **4**, and has a gas outlet **84** at the top of the process container **4**. The gas outlet **84** is connected to a vacuum-exhaust system GE including a vacuum pump and so forth.

[**0102**] The process container **4** is surrounded by a heater **86**, which is used for heating the atmosphere within the process container **4** and the wafers W. A thermocouple (not shown) is disposed near the exhaust port **68** in the process container **4** to control the heater **86**.

[0103] The film formation apparatus **2** further includes a main control section **60** formed of, e.g., a computer, to control the entire apparatus. The main control section **60** can control the film formation process described below in accordance with the process recipe of the film formation process concerning, e.g., the film thickness and composition of a film to be formed, stored in the memory **212** thereof in advance. In the memory **212**, the relationship between the process gas flow rates and the thickness and composition of the film is also stored as control data in advance. Accordingly, the main control section **60** can control the elevating mechanism **25**, gas supply circuits **28**, **30**, **32**, **34**, **35** and **36**, exhaust system GE, gas exciting section **66**, heater **86**, and so forth, based on the stored process recipe and control data.

[0104] Next, an explanation will be given of a film formation method (so called ALD (Atomic Layer Deposition) film formation) performed in the apparatus shown in **FIG. 1**. In this film formation method, an insulating film of SiBN is formed on semiconductor wafers by CVD. In order to achieve this, a first process gas containing dichlorosilane (DCS) gas as a silane family gas, a second process gas containing ammonia (NH_3) gas as a nitriding gas, and a third process gas containing $BC1_3$ gas as a boron-containing gas are selectively supplied into the process field **5** accommodating wafers W. At this time, the first process gas and third process gas are mixed in the gas mixture tank **42**, and the mixture gas thus formed is supplied into the process field. It should be noted that this film formation method is an example where a fourth process gas containing C_2H_4 gas (ethylene gas) as a carbon hydride gas is not supplied.

[0105] At first, the wafer boat **12** at room temperature, which supports a number of, e.g., 50 to 100, wafers having a diameter of 300 mm, is loaded into the process container **4** heated at a predetermined temperature, and the process container **4** is airtightly closed. Then, the interior of the process container **4** is vacuum-exhausted and kept at a predetermined process pressure, and the wafer temperature is increased to a process temperature for film formation. At this time, the apparatus is in a waiting state until the temperature becomes stable. Then, while the wafer boat **12** is rotated, the first to third process gases are intermittently supplied from the respective gas distribution nozzles **38** and **40** at controlled flow rates.

[0106] Specifically, the first process gas containing DCS gas and the third process gas containing BCl_3 gas are supplied into the gas mixture tank **42** to form a mixture gas. The mixture gas is supplied from the gas spouting holes **40**A of the gas distribution nozzle **40** to form gas flows parallel with the wafers W on the wafer boat **12**. While being supplied, molecules of DCS gas and $BC1_3$ gas and molecules and atoms of decomposition products generated by their decomposition are adsorbed on the wafers W.

[0107] On the other hand, the second process gas containing NH_3 gas is supplied from the gas spouting holes **38**A of the gas distribution nozzle **38** to form gas flows parallel with the wafers W on the wafer boat **12**. The second process gas is selectively excited and partly turned into plasma when it passes through the plasma generation area PS between the pair of electrodes **74**. At this time, for example, radicals (activated species), such as N*, NH*, NH_2*, and NH_3*, are produced (the symbol [*] denotes that it is a radical). The radicals flow out from the opening **70** of the gas exciting section **66** toward the center of the process container **4**, and are supplied into gaps between the wafers W in a laminar flow state.

[0108] The radicals react with molecules of DCS gas adsorbed on the surface of the wafers W, so that a thin film is formed on the wafers W. Further, at this time, B atoms generated by decomposition of $BC1_3$ gas are taken into the thin film, so a film of SiBN doped with boron as an impurity is formed. Alternatively, when DCS gas and $BC1_3$ gas flow onto radicals adsorbed on the surface of the wafers W, the same reaction is caused, so an SIBN film doped with boron is formed on the wafers W.

[0109] **FIG. 3** is a timing chart of the gas supply and RF (radio frequency) application of a film formation method according to the first embodiment. As shown in **FIG. 3**, the film formation method according to this embodiment is arranged to alternately repeat first to fourth steps T**1** to T**4**. A cycle comprising the first to fourth steps T**1** to T**4** is repeated a number of times, and thin films of SiBN formed by respective cycles are laminated, thereby arriving at an SiBN film having a target thickness.

[0110] Specifically, the first step T**1** is arranged to perform supply of the mixture gas of the first process gas (denoted as DCS in **FIG. 3**) and the third process gas (denoted as BCl_3 in **FIG. 3**) to the process field **5**, while stopping supply of the second process gas (denoted as NH_3 in **FIG. 3**) to the process field **5**. The second step T**2** is arranged to stop supply of the mixture gas of the first and third process gases and the second process gas to the process field **5**. The third step T**3** is arranged to perform supply of the second process gas to the process field **5**, while stopping supply of the mixture gas of the first and third process gases to the process field **5**. Further, halfway through the third step T**3**, the RF power supply **76** is set in the ON state to turn the second process gas into plasma by the gas exciting section **66**, so as to supply the second process gas in an activated state to the process field **5** during a sub-step T**3***b*. The fourth step T**4** is arranged to stop supply of the mixture gas of the first and third process gases and the second process gas to the process field **5**.

[0111] In the third step T**3**, the RF power supply **76** is turned on after a predetermined time Δt passes, to turn the second process gas into plasma by the gas exciting section **66**, so as to supply the second process gas in an activated state to the process field **5** during the sub-step T**3***b*. The predetermined time Δt is defined as the time necessary for stabilizing the flow rate of NH_3 gas, which is set at, e.g., about 5 seconds. However, the second process gas may be turned into plasma by the gas exciting section **66** over the entire period of supplying the second process gas. Since the RF power supply is turned on to generate plasma after the flow rate of the second process gas is stabilized, the uniformity of radical concentration among the wafers W (uniformity in the vertical direction) is improved.

[0112] Each of the second and fourth steps T**2** and T**4** is used as a purge step to remove the residual gas within the process container **4**. The term "purge" means removal of the residual gas within the process container **4** by vacuum-exhausting the interior of the process container **4** while supplying an inactive gas, such as N_2 gas, into the process container **4**, or by vacuum-exhausting the interior of the process container **4** while stopping supply of all the gases.

In this respect, the second and fourth steps T**2** and T**4** may be arranged such that the first half utilizes only vacuum-exhaust and the second half utilizes both vacuum-exhaust and inactive gas supply. Further, the first and third steps T**1** and T**3** may be arranged to stop vacuum-exhausting the process container **4** while supplying each of the first to third process gases. However, where supplying each of the first to third process gases is performed along with vacuum-exhausting the process container **4**, the interior of the process container **4** can be continuously vacuum-exhausted over the entirety of the first to fourth steps T**1** to T**4**.

[0113] In **FIG. 3**, the first step T**1** is set to be within a range of about 1 to 20 seconds, and, for example, at about 10 seconds, the second step T**2** is set to be within a range of about 5 to 15 seconds, and, for example, at about 10 seconds, the third step T**3** is set to be within a range of about 1 to 30 seconds, and, for example, at about 20 seconds, the sub-step T3*b* is set to be within a range of about 1 to 25 seconds, and, for example, at about 10 seconds, and the fourth step T**4** is set to be within a range of about 5 to 15 seconds, and, for example, at about 10 seconds. In general, the film thickness obtained by one cycle of the first to fourth steps T**1** to T**4** is about 0.11 to 0.13 nm. Accordingly, for example, where the target film thickness is 70 nm, the cycle is repeated about 600 times. However, these values of time and thickness are merely examples and thus are not limiting.

[0114] The process conditions of the film formation process are as follows. The flow rate of DCS gas is set to be within a range of 50 to 2,000 sccm, e.g., at 1,000 sccm (1 slm). The flow rate of NH_3 gas is set to be within a range of 500 to 5,000 sccm, e.g., at 1,000 sccm. The flow rate of $BC1_3$ gas is set to be within a range of 1 to 15 sccm, e.g., at 2 sccm. Accordingly, the flow rate of $BC1_3$ gas is far smaller than the flow rate of DCS gas.

[0115] The process temperature is lower than ordinary CVD processes, and is set to be within a range of 300 to 700° C., and preferably a range of 550 to 630° C. If the process temperature is lower than 300° C., essentially no film is deposited because hardly any reaction is caused. If the process temperature is higher than 700° C., a low quality CVD film is deposited, and existing films, such as a metal film, suffer thermal damage.

[0116] The process pressure is set to be within a range of 13 Pa (0.1 Torr) to 1,330 Pa (10 Torr), and preferably a range of 40 Pa (0.3 Torr) to 266 Pa (2 Torr). For example, the process pressure is set at 1 Torr during the first step (adsorption step) T**1**, and at 0.3 Torr during the third step (nitridation step using plasma) T**3**. If the process pressure is lower than 13 Pa, the film formation rate becomes lower than the practical level. If the process pressure is higher than 1,330 Pa, it becomes difficult to generate plasma.

[0117] As described above, the first process gas containing DCS gas for providing the main material of a thin film, and the third process gas containing BCl_3 gas for providing a sub-material of the thin film are uniformly mixed at first in the gas mixture tank **42** to form a mixture gas. The mixture gas is then intermittently supplied into the process field **5** through a plurality of gas spouting holes **40**A arrayed at intervals in the vertical direction. In this case, although the amount of BCl_3 gas is small, it can be essentially uniformly distributed within the process container **4** in the vertical direction without using a carrier gas. Consequently, the ratio of the composition elements in SiBN thin films to be formed becomes more uniform, regardless of wafer position.

[0118] In other words, the supply amount of the third process gas is far smaller than the supply amount of the first process gas. In this case, the third process gas in a smaller supply amount is made to accompany the first process gas in a larger supply amount, so that it can be uniformly distributed within the process container **4** in the vertical direction. Particularly, where the supply amount of one source gas is 1/100 or less of the supply amount of the other source gas, the above-described effect of uniformizing the ratio of the composition elements in films is more influential.

[0119] When $BC1_3$ gas is adsorbed on the wafer surface, the adsorption amount depends on the partial pressure of $BC1_3$ gas. According to this embodiment, BCl_3 gas is supplied into the process container **4** uniformly in the vertical direction without using a carrier gas. In this case, the partial pressure of $BC1_3$ gas can be higher than that in the case of a carrier gas being used, so adsorption of BCl_3 gas on the wafer surface is promoted. Consequently, while the film formation rate per unit cycle is maintained, the time necessary for one cycle is shortened, so the throughput is improved.

[0120] For example, in an experiment, a conventional film formation method took about 15 seconds until BCl_3 gas was sufficiently adsorbed on a wafer surface. On the other hand, the present embodiment took only two or three seconds for the same. Accordingly, the conventional method took about 30 seconds for one cycle, while the present embodiment shortened this period to only 8 seconds.

[0121] Typically, the mixture gas may be formed and supplied by either of the following two methods. The first method comprises continuously supplying the first and third process gases from the first and third process gas supply circuits **30** and **32** into the gas mixture tank **42**, while supplying the mixture gas pulse-wise from the gas mixture tank **42** into the process field **5**. The second method comprises simultaneously supplying the first and third process gases pulse-wise in a first phase from the first and third process gas supply circuits **30** and **32** into the gas mixture tank **42**, while supplying the mixture gas pulse-wise in a second phase reverse to the first phase from the gas mixture tank **42** into the process field **5**.

[0122] In order to realize these methods, the switching valves **50**A and **52**A of the first and third process gas supply circuits **30** and **32** and the switching valve **44**A of the mixture gas supply circuit **35** are opened and closed in accordance with instructions from the main control section **60**, as follows. In the first method, over a plurality of cycles from the start to the end of the film formation process, the switching valves **50**A and **52**A are kept opened and the switching valve **44**A is opened and closed pulse-wise. In the second method, over a plurality of cycles from the start to the end of the film formation process, the switching valves **50**A and **52**A are opened and closed pulse-wise while the switching valve **44**A is closed and opened pulse-wise in the reverse phase.

[0123] In the film formation method described above, the fourth process gas containing C_2H_4 gas (ethylene gas) as a carbon hydride gas is not supplied, but the fourth process gas may be supplied, as needed. In this case, the fourth process gas is supplied into the gas mixture tank **42** at a controlled flow rate, simultaneously with the first and third process gases. Where a mixture gas of the first, third, and fourth process gases is used, a thin film to be formed is an insulating film of SiBCN (boron doped silicon carbon nitride) containing carbon.

[**0124**] <Second Embodiment>

[**0125**] **FIG. 4** is a sectional view showing a film formation apparatus (vertical CVD apparatus) according to a second embodiment of the present invention. This film formation apparatus **2**X has the same structure as the film formation apparatus **2** shown in **FIG. 1** except for the first, third, and fourth process gas supply circuits **30**, **32**, and **34** and the mixture gas supply circuit **35**. Accordingly, an explanation will be give of the film formation apparatus **2**X, focusing on the difference from the film formation apparatus **2**.

[**0126**] In the film formation apparatus **2**X, the first, third, and fourth process gas supply circuits **30**, **32**, and **34** are connected to a common mixture gas supply circuit **35**X. The mixture gas supply circuit **35**X includes a mixture gas supply pipe **40**X configured to mix the first and third process gases, and further the fourth process gas in addition thereto, as needed. The mixture gas supply pipe **40**X is formed of a quartz pipe, which is a proximal end portion of a gas distribution nozzle **40**.

[**0127**] The first, third, and fourth process gas supply circuits **30**, **32**, and **34** have tanks **102**, **104**, and **106**, respectively, disposed immediately before the mixture gas supply pipe **40**X to temporarily store the corresponding process gases. Since the tanks **102** and **106** need to handle a large gas flow rate, they are larger than the tank **104**. For example, each of the tanks **102** and **106** has a volume of about four liters, while the tank **104** has a volume of about 0.05 liters (both to be changed depending on the gas flow rate). The tanks **102**, **104**, and **106** are connected to the mixture gas supply pipe **40**X through gas supply lines **103**, **105**, and **107** provided with switching valves **103**A, **105**A, and **107**A, respectively.

[**0128**] The tanks **102**, **104**, and **106** of the first, third, and fourth process gas supply circuits **30**, **32**, and **34** are connected to gas sources **30**S, **32**S, and **34**S of DCS gas, $BC1_3$ gas, and C_2H_4 gas, respectively, through gas supply lines (gas passages) **50**, **52**, and **54**. The gas supply lines **50**, **52**, and **54** are provided with switching valves **50**A, **52**A, and **54**A and flow rate controllers **50**B, **52**B, and **54**B, such as mass flow controllers, respectively. With this arrangement, DCS gas, $BC1_3$ gas, and C_2H_4 gas can be supplied at controlled flow rates.

[**0129**] Next, an explanation will be given of a film formation method (so called ALD (Atomic Layer Deposition) film formation) performed in the apparatus shown in **FIG. 4**. It should be noted that this film formation method is also an example where a fourth process gas containing C_2H_4 gas (ethylene gas) as a carbon hydride gas is not supplied. The gas supply and RF (radio frequency) application of this film formation method are performed in accordance with the timing chart shown in **FIG. 3**. At this time, in order to form and supply a mixture gas (denoted as DCS+$BC1_3$ in **FIG. 3**), the switching valves **103**A and **105**A are simultaneously opened and closed to supply first and third process gases temporarily stored in the tanks **102** and **104** into the mixture gas supply pipe **40**X and mix them in the pipe **40**X. The mixture gas is supplied from the gas spouting holes **40**A of the gas distribution nozzle **40** to form gas flows parallel with the wafers W on the wafer boat **12**. As a consequence, this apparatus can provide the same operation and effect as those obtained in the apparatus shown in **FIG. 1**.

[**0130**] Typically, the mixture gas may be formed and supplied by either of the following two methods (also in the following explanation, the fourth process gas is not supplied). The first method comprises continuously supplying the first and third process gases into the respective tanks **102** and **104** of the first and third process gas supply circuits **30** and **32**, while supplying the gases pulse-wise from the respective tanks **102** and **104** into the mixture gas supply pipe **40**X. The second method comprises simultaneously supplying the first and third process gases pulse-wise in a first phase into the respective tanks **102** and **104** of the first and third process gas supply circuits **30** and **32**, while supplying the gases pulse-wise in a second phase reverse to the first phase from the respective tanks **102** and **104** into the mixture gas supply pipe **40**X.

[**0131**] In order to realize these methods, the switching valves **50**A and **52**A of the first and third process gas supply circuits **30** and **32** and the switching valves **103**A and **105**A downstream from the tanks are opened and closed in accordance with instructions from the main control section **60**, as follows. In the first method, over a plurality of cycles from the start to the end of the film formation process, the switching valves **50**A and **52**A are kept opened and the switching valves **103**A and **105**A are opened and closed pulse-wise. In the second method, over a plurality of cycles from the start to the end of the film formation process, the switching valves **50**A and **52**A are opened and closed pulse-wise while the switching valves **103**A and **105**A are closed and opened pulse-wise in the reverse phase.

[**0132**] **FIG. 5** is a view showing part of a gas supply system used in a film formation apparatus according to a modification of the second embodiment (the fourth process gas supply circuit is not shown). In this modification, the tank **104** of the third process gas supply circuit **32** is omitted because the flow rate of the third process gas containing BCl_3 gas is far smaller than the flow rate of the first process gas containing DCS gas. Even with this arrangement, the third process gas in a smaller amount is made to be uniformly mixed with the first process gas in a larger amount within the mixture gas supply pipe **40**X, so that the third process gas is uniformly supplied.

[**0133**] <Common Matters to First and Second Embodiments>

[**0134**] Each of the methods according to the first and second embodiments is performed under the control of the main control section **60** in accordance with a process program, as described above. **FIG. 6** is a block diagram schematically showing the structure of the main control section **60**. The main control section **60** includes a CPU **210**, which is connected to a storage section **212**, an input section **214**, and an output section **216**. The storage section **212** stores process programs and process recipes. The input section **214** includes input devices, such as a keyboard, a pointing device, and a storage media drive, to interact with an operator. The output section **216** outputs control signals for controlling components of the processing apparatus.

FIG. 6 also shows a storage medium 218 attached to the computer in a removable state.

[0135] Each of the methods according to the first and second embodiments may be written as program instructions for execution on a processor, into a computer readable storage medium or media to be applied to a semiconductor processing apparatus. Alternately, program instructions of this kind may be transmitted by a communication medium or media and thereby applied to a semiconductor processing apparatus. Examples of the storage medium or media are a magnetic disk (flexible disk, hard disk (a representative of which is a hard disk included in the storage section 212), etc.), an optical disk (CD, DVD, etc.), a magneto-optical disk (MO, etc.), and a semiconductor memory. A computer for controlling the operation of the semiconductor processing apparatus reads program instructions stored in the storage medium or media, and executes them on a processor, thereby performing a corresponding method, as described above.

[0136] In the embodiments described above, for example, the exciting section 66 for generating plasma of the film formation apparatus 2 is integrally combined with the process container 4. Alternatively, the exciting section 66 may be separately disposed from the process container 4, so as to excite NH_3 gas outside the process container 4 (so called remote plasma), and then supply the excited NH_3 gas into the process container 4. Further, NH_3 gas may be supplied without being activated, and, in this case, the members associating with the gas exciting section 66 are not necessary. However, in this case, the process temperature needs to be increased to some extent to compensate for energy decrease due to no plasma being used.

[0137] In the embodiments described above, for example, the distribution nozzle 40 having a number of gas spouting holes 40A is used as a nozzle for supplying the mixture gas. Alternatively, a linear or straight pipe similar to the gas nozzle 46, or a bent or L-shaped pipe may be used for the same purpose. Where the straight pipe or L-shaped pipe is used, the mixture gas is supplied from below or above the process field 5. In this case, an exhaust port 68 is formed at the top or bottom of the process container 4 to cause the mixture gas to sufficiently flow within the process field 5 in the vertical direction.

[0138] In the embodiments described above, for example, the first process gas contains DCS gas as a silane family gas. In this respect, the silane family gas may be one or more gases selected from the group consisting of dichlorosilane (DCS), hexachlorodisilane (HCD), monosilane (SiH_4), disilane (Si_2Cl_6), hexamethyl-disilazane (HMDS), tetrachlorosilane (TCS), disilylamine (DSA), trisilylamine (TSA), bistertial-butylaminosilane (BTBAS).

[0139] In the embodiments described above, the second process gas contains a nitriding gas, which may be NH_3 gas or N_2 gas. Where the present invention is applied to formation of a film based on silicon oxynitride, an oxynitriding gas, such as dinitrogen oxide (N_2O) or nitrogen oxide (NO), may be used in place of the nitriding gas. In this case, a film to be formed is a film based on silicon oxynitride that contains oxygen (O).

[0140] In the embodiments described above, for example, the third process gas contains $BC1_3$ gas as a boron-containing gas. In this respect, the boron-containing gas may be one or more gases selected from the group consisting of $BC1_3$, B_2H_6, BF_3, and $B(CH_3)_3$.

[0141] In the embodiments described above, for example, the fourth process gas contains ethylene gas as a carbon hydride gas. In this respect, the carbon hydride gas may be one or more gases selected from the group consisting of acetylene, ethylene, methane, ethane, propane, and butane.

[0142] In the embodiments described above, for example, an SiBN film or SiBCN film is formed. Alternatively, for example, the present invention may be applied to a process for forming a BCN film (carbon-containing boron nitride film). In this case, a boron-containing gas and a carbon hydride gas are used as source gases and mixed. The present invention can be applied to various film formation processes which use a plurality of source gases that does not cause any problem if they are mixed before being supplied into a process container. For example, the present invention may be applied to a film formation process using an oxidizing gas, such as O_2 gas, as a reaction gas.

[0143] A target substrate is not limited to a semiconductor wafer, and it may be another substrate, such as an LCD substrate or glass substrate.

[0144] Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

What is claimed is:

1. A film formation apparatus for a semiconductor process, comprising:

a process container having a process field configured to accommodate a plurality of target substrates stacked at intervals;

a support member configured to support the target substrates inside the process field;

a heater configured to heat the target substrates inside the process field;

an exhaust system configured to exhaust gas inside the process field;

a process gas supply system configured to supply process gases to the process field so as to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film;

a control section configured to control an operation of the apparatus including the process gas supply system,

wherein the process gas supply system comprises

a gas mixture tank disposed outside the process container and configured to mix the first and third process gases to form a mixture gas, a mixture gas supply line configured to supply the mixture gas from the gas mixture tank to the process field,

first and third process gas supply circuits configured to supply the first and third process gases to the gas mixture tank, respectively,

a second process gas supply circuit having a second process gas supply line configured to supply the second process gas to the process field without passing through the gas mixture tank,

first and second switching valves disposed on the mixture gas supply line and the second process gas supply line, respectively, and

wherein the control section controls the first and second switching valves to be opened and closed so as to alternately and pulse-wise supply the mixture gas from the gas mixture tank and the second process gas from the second process gas supply circuit to the process field.

2. The apparatus according to claim 1, wherein the control section performs control to continuously supply the first and third process gases from the first and third process gas supply circuits to the gas mixture tank, while supplying the mixture gas pulse-wise from the gas mixture tank to the process field.

3. The apparatus according to claim 1, wherein the control section performs control to simultaneously supply the first and third process gases pulse-wise in a first phase from the first and third process gas supply circuits to the gas mixture tank, while supplying the mixture gas pulse-wise in a second phase reverse to the first phase from the gas mixture tank to the process field.

4. The apparatus according to claim 1, wherein the mixture gas supply line and the second process gas supply line comprise first and second supply ports, respectively, each of which comprises a plurality of gas spouting holes arrayed over the target substrates in a vertical direction to form gas flows parallel with the target substrates.

5. The apparatus according to claim 1, wherein the third process gas is supplied to the process field in an amount $1/100$ or less of the first process gas.

6. The apparatus according to claim 1, wherein the first process gas contains a silane family gas, the second process gas contains a nitriding gas or oxynitriding gas, and the third process gas contains a doping gas.

7. The apparatus according to claim 6, wherein the process gas supply system further comprises a fourth process gas supply circuit configured to supply a fourth process gas containing a carbon hydride gas to the gas mixture tank.

8. The apparatus according to claim 6, wherein the first process gas contains at least one gas selected from the group consisting of dichlorosilane, hexachlorodisilane, monosilane, disilane, hexamethyldisilazane, tetrachlorosilane, disilylamine, trisilylamine, and bistertialbutylaminosilane, the second process gas contains at least one gas selected from the group consisting of ammonia, nitrogen, dinitrogen oxide, and nitrogen oxide, and the third process gas contains at least one gas selected from the group consisting of BCl_3, B_2H_6, BF_3, and $B(CH_3)_3$.

9. The apparatus according to claim 1, further comprises an exciting mechanism configured to activate the second process gas by generating plasma.

10. The apparatus according to claim 9, wherein the exciting mechanism comprises a plasma generation area disposed in a space communicating with the process field and between a supply port of the second process gas and the target substrates.

11. A film formation apparatus for a semiconductor process, comprising:

a process container having a process field configured to accommodate a plurality of target substrates stacked at intervals;

a support member configured to support the target substrates inside the process field;

a heater configured to heat the target substrates inside the process field;

an exhaust system configured to exhaust gas inside the process field;

a process gas supply system configured to supply process gases to the process field so as to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film, and the third process gas is supplied to the process field in an amount smaller than that of the first process gas;

a control section configured to control an operation of the apparatus including the process gas supply system,

wherein the process gas supply system comprises

a mixture gas supply line configured to mix the first and third process gases to form a mixture gas and supply the mixture gas to the process field,

first and third process gas supply circuits having first and third process gas supply lines configured to supply the first and third process gases to the mixture gas supply line, respectively,

a second process gas supply circuit having a second process gas supply line configured to supply the second process gas to the process field without passing through the mixture gas supply line,

first, second, and third switching valves disposed on the first, second, and third process gas supply lines, respectively,

a first tank disposed on the first process gas supply line immediately before the first switching valve to temporarily store the first process gas, and

wherein the control section controls the first, second, and third switching valves to be opened and closed so as to alternately and pulse-wise supply the mixture gas from the mixture gas supply line and the second process gas from the second process gas supply circuit to the process field.

12. The apparatus according to claim 11, wherein the control section controls the first and third switching valve to be simultaneously opened and closed.

13. The apparatus according to claim 11, wherein the process gas supply system further comprises a second tank disposed on the third process gas supply line immediately before the third switching valve to temporarily store the third process gas

14. The apparatus according to claim 11, wherein the mixture gas supply line and the second process gas supply line comprise first and second supply ports, respectively, each of which comprises a plurality of gas spouting holes arrayed over the target substrates in a vertical direction to form gas flows parallel with the target substrates.

15. The apparatus according to claim 11, wherein the third process gas is supplied to the process field in an amount 1/100 or less of the first process gas.

16. The apparatus according to claim 11, wherein the first process gas contains a silane family gas, the second process gas contains a nitriding gas or oxynitriding gas, and the third process gas contains a doping gas.

17. The apparatus according to claim 16, wherein the process gas supply system further comprises a fourth process gas supply circuit configured to supply a fourth process gas containing a carbon hydride gas to the mixture gas supply line.

18. The apparatus according to claim 16, wherein the first process gas contains at least one gas selected from the group consisting of dichlorosilane, hexachlorodisilane, monosilane, disilane, hexamethyldisilazane, tetrachlorosilane, disilylamine, trisilylamine, and bistertialbutylaminosilane, the second process gas contains at least one gas selected from the group consisting of ammonia, nitrogen, dinitrogen oxide, and nitrogen oxide, and the third process gas contains at least one gas selected from the group consisting of BCl_3, B_2H_6, BF_3, and $B(CH_3)_3$.

19. The apparatus according to claim 11, further comprises an exciting mechanism configured to activate the second process gas by generating plasma.

20. The apparatus according to claim 19, wherein the exciting mechanism comprises a plasma generation area disposed in a space communicating with the process field and between a supply port of the second process gas and the target substrates.

21. A film formation method for a semiconductor process, comprising:

heating a plurality of target substrates stacked at intervals within a process field in a process container; and

supplying process gases to the process field to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film,

wherein said supplying the process gases comprises

supplying the first and third process gases to a gas mixture tank disposed outside the process container to form a mixture gas,

supplying the mixture gas from the gas mixture tank to the process field, and

supplying the second process gas to the process field without passing through the gas mixture tank,

so as to alternately and pulse-wise supply the mixture gas and the second process gas to the process field.

22. A film formation method for a semiconductor process, comprising:

heating a plurality of target substrates stacked at intervals within a process field in a process container; and

supplying process gases to the process field to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film, and the third process gas is supplied to the process field in an amount smaller than that of the first process gas,

wherein said supplying the process gases comprises

supplying the first and third process gases to a mixture gas supply line to form a mixture gas and supply the mixture gas to the process field, while temporarily storing the first process gas in a first tank disposed immediately before the mixture gas supply line, and

supplying the second process gas to the process field without passing through the mixture gas supply line,

so as to alternately and pulse-wise supply the mixture gas and the second process gas to the process field.

23. A computer readable medium containing program instructions for execution on a processor, which, when executed by the processor, cause a film formation apparatus for a semiconductor process to execute

heating a plurality of target substrates stacked at intervals within a process field in a process container; and

supplying process gases to the process field to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film,

wherein said supplying the process gases comprises

supplying the first and third process gases to a gas mixture tank disposed outside the process container to form a mixture gas,

supplying the mixture gas from the gas mixture tank to the process field, and

supplying the second process gas to the process field without passing through the gas mixture tank,

so as to alternately and pulse-wise supply the mixture gas and the second process gas to the process field.

24. A computer readable medium containing program instructions for execution on a processor, which, when executed by the processor, cause a film formation apparatus for a semiconductor process to execute

heating a plurality of target substrates stacked at intervals within a process field in a process container; and

supplying process gases to the process field to deposit a thin film on the target substrates, wherein the process gases include a first process gas for providing a main material of the thin film, a second process gas for reacting with the first process gas, and a third process gas for providing a sub-material of the thin film, and the third process gas is supplied to the process field in an amount smaller than that of the first process gas, wherein said supplying the process gases comprises

supplying the first and third process gases to a mixture gas supply line to form a mixture gas and supply the mixture gas to the process field, while temporarily storing the first process gas in a first tank disposed immediately before the mixture gas supply line, and

supplying the second process gas to the process field without passing through the mixture gas supply line,

so as to alternately and pulse-wise supply the mixture gas and the second process gas to the process field.

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