(19) **United States**
(12) **Patent Application Publication**
**FUKIAGE et al.**

(10) **Pub. No.: US 2016/0322218 A1**
(43) **Pub. Date: Nov. 3, 2016**


(54) **FILM FORMING METHOD AND FILM FORMING APPARATUS**


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(21) Appl. No.: **15/140,551**

(22) Filed: **Apr. 28, 2016**

(30) **Foreign Application Priority Data**

May 1, 2015 (JP) ................................ 2015-094143

**Publication Classification**

(51) **Int. Cl.**

| | |
|---|---|
| ***H01L 21/02*** | (2006.01) |
| ***C23C 16/46*** | (2006.01) |
| ***C23C 16/36*** | (2006.01) |
| ***H01J 37/32*** | (2006.01) |
| ***C23C 16/455*** | (2006.01) |

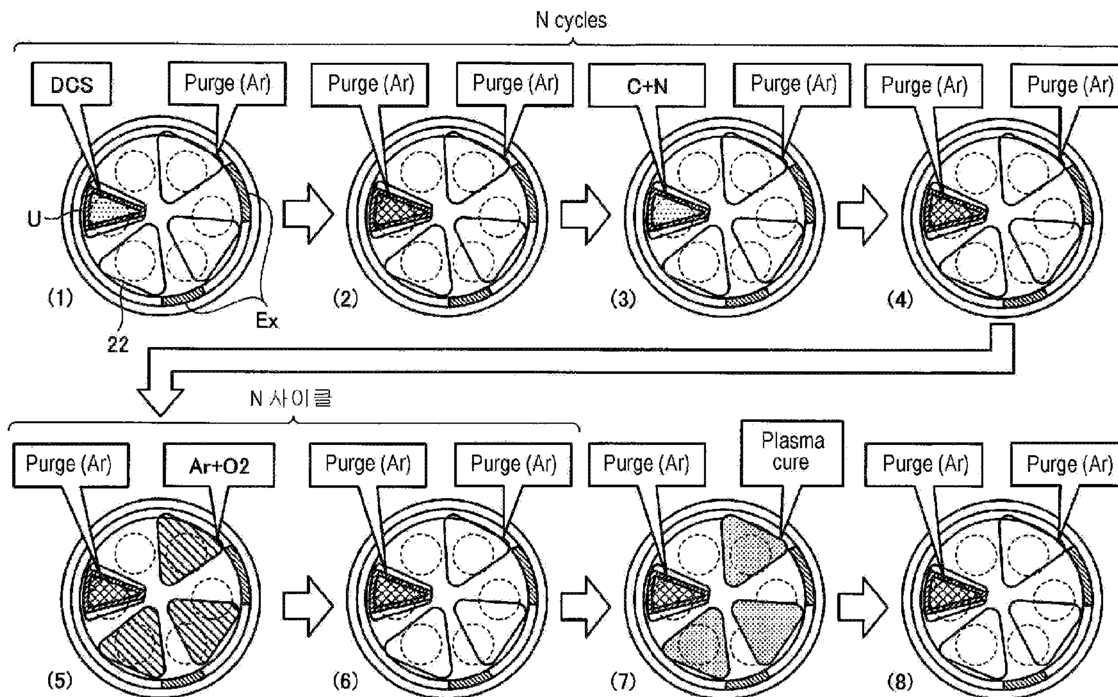
(52) **U.S. Cl.**

CPC ... ***H01L 21/02274*** (2013.01); ***H01L 21/02211*** (2013.01); ***H01L 21/0217*** (2013.01); ***H01L 21/02167*** (2013.01); ***H01L 21/0214*** (2013.01); ***H01J 37/3222*** (2013.01); ***H01J 37/32899*** (2013.01); ***C23C 16/4554*** (2013.01); ***C23C 16/45565*** (2013.01); ***C23C 16/45551*** (2013.01); ***C23C 16/36*** (2013.01); ***H01J 37/32752*** (2013.01); ***H01J 37/3244*** (2013.01); ***C23C 16/45519*** (2013.01); ***C23C 16/46*** (2013.01); *H01J 2237/327* (2013.01); *H01J 2237/338* (2013.01)



(57) **ABSTRACT**

A film forming method for forming a nitride film on a workpiece substrate accommodated within a process vessel, including: performing a first reaction of supplying a first precursor gas to the workpiece substrate accommodated within the process vessel; performing a second reaction of supplying a second precursor gas to the workpiece substrate accommodated within the process vessel; performing a modification of generating plasma of a modifying gas just above the workpiece substrate by supplying the modifying gas into the process vessel and supplying microwaves from an antenna into the process vessel, and plasma-processing, by the plasma thus generated, a surface of the workpiece substrate subjected to the first and second reactions using the first and second precursor gases.

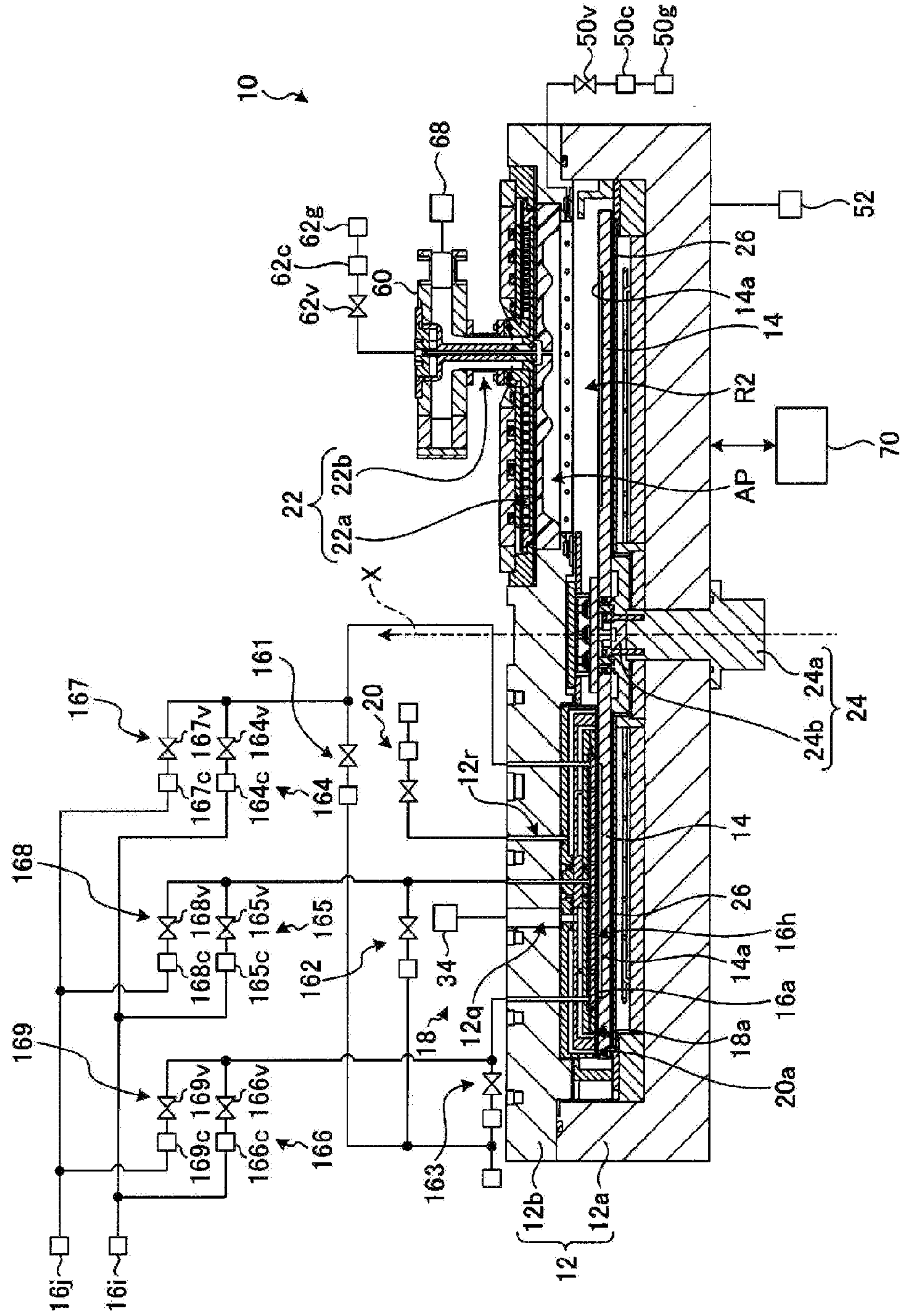



FIG. 1

FIG. 2

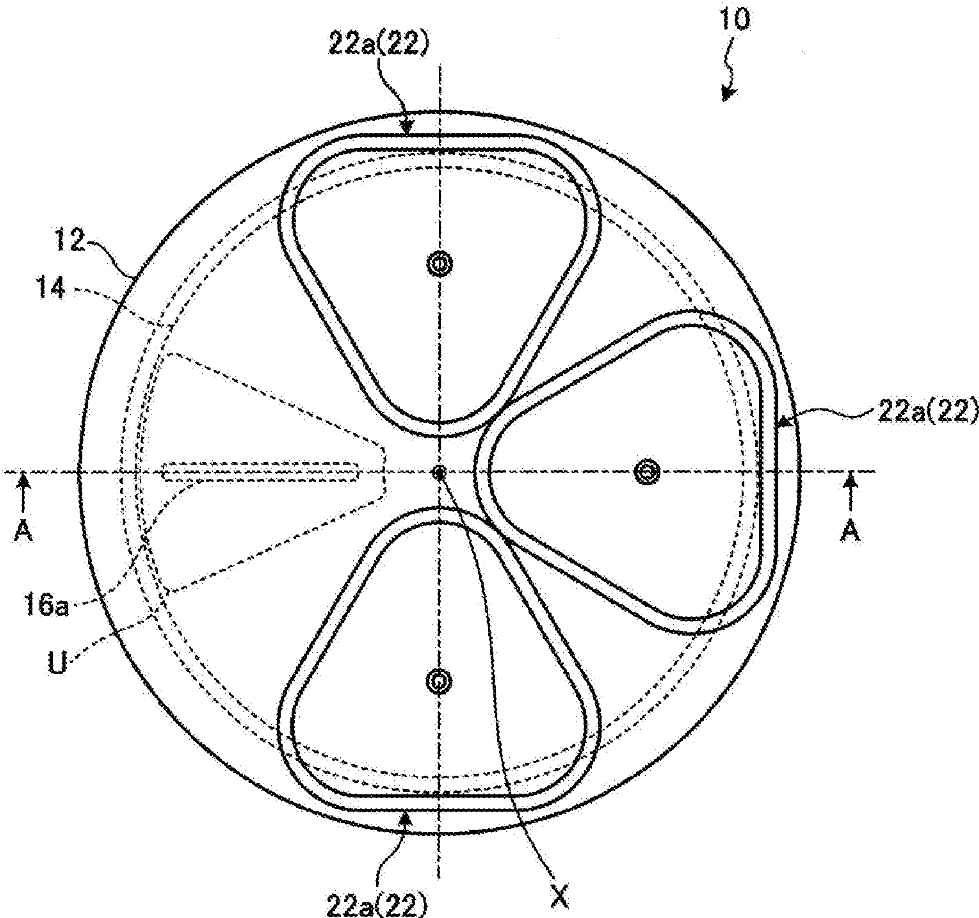


FIG. 3

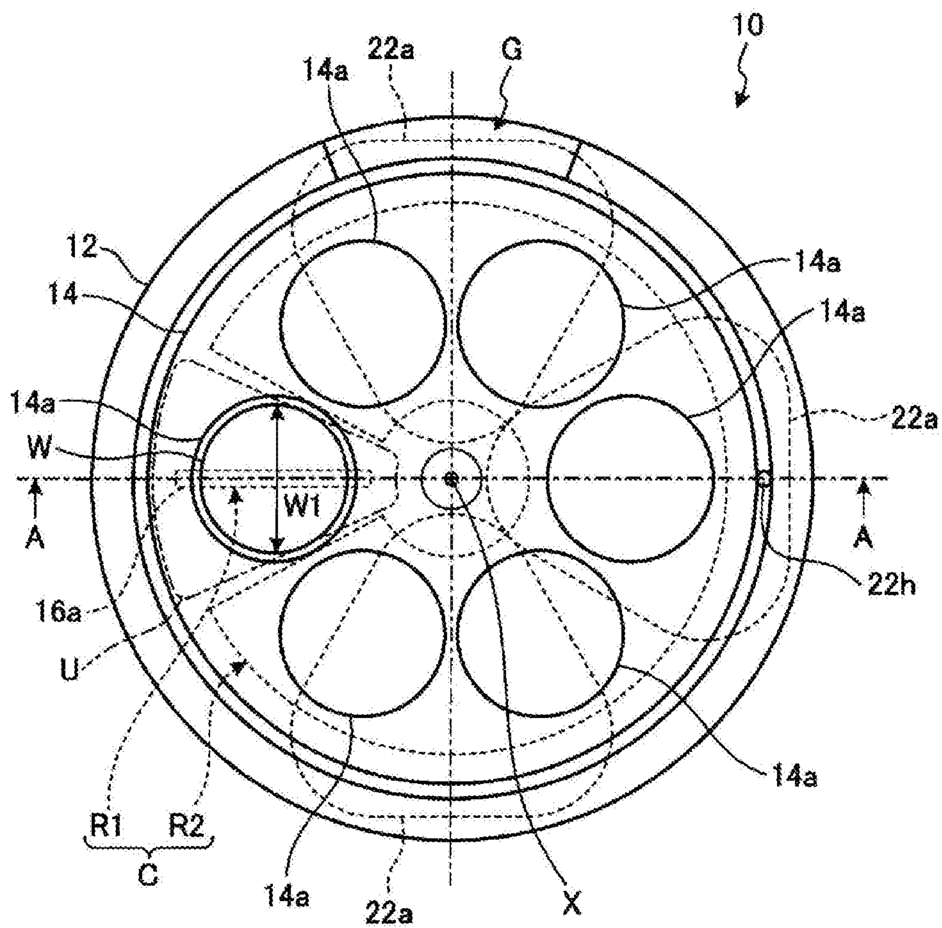


FIG. 4

10
16
X
161b
161p
121p
161a
161
161d
161v
161c
167
167c
167v
164c
164v
164
162b
162a
162d
162
122p
162p
162v
162c
168
168c
168v
165c
165v
165
163b
163a
163d
163
123p
163p
163v
163c
169
169c
169v
166c
166v
166
16g
16j
16i
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24a
24b
M1
M2
M3
M4
U
26
14a
14
16h
R1

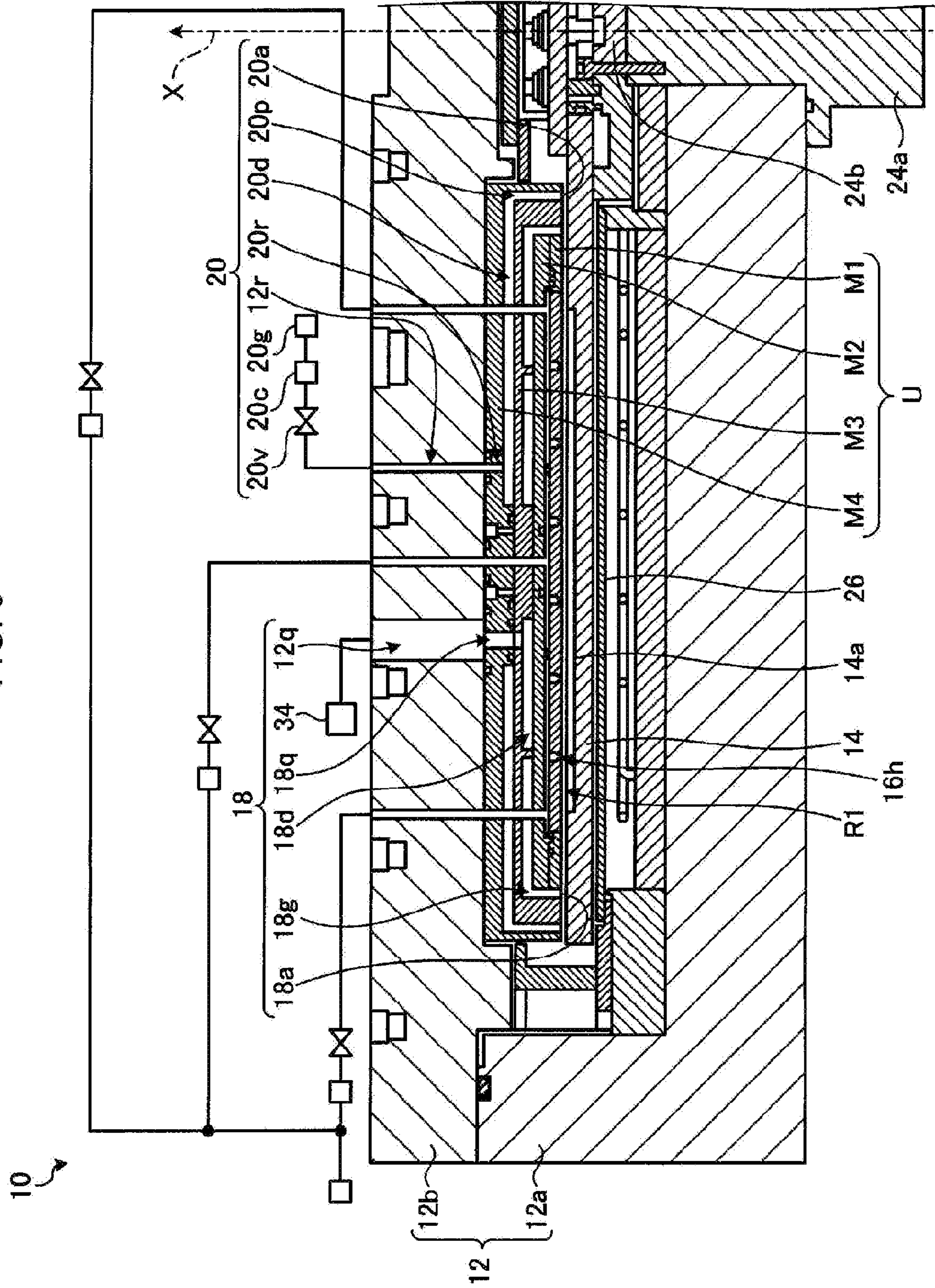
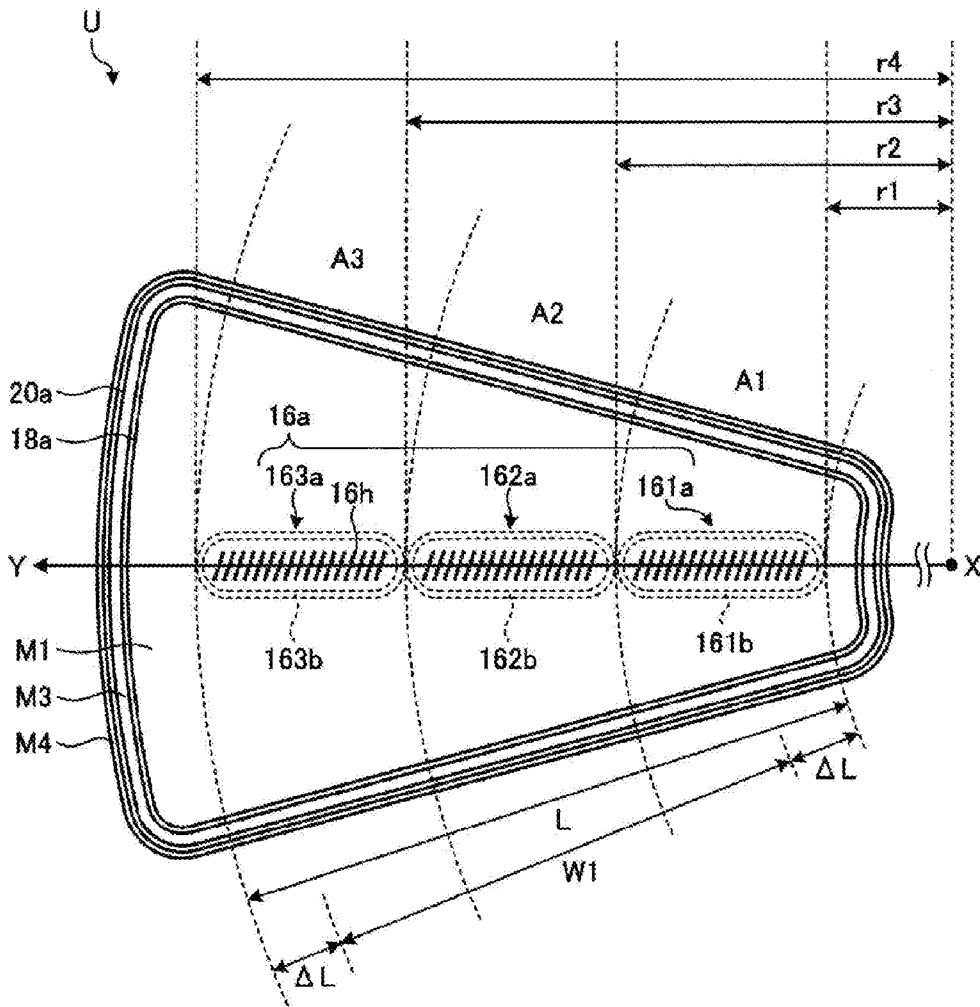



FIG. 5

FIG. 6



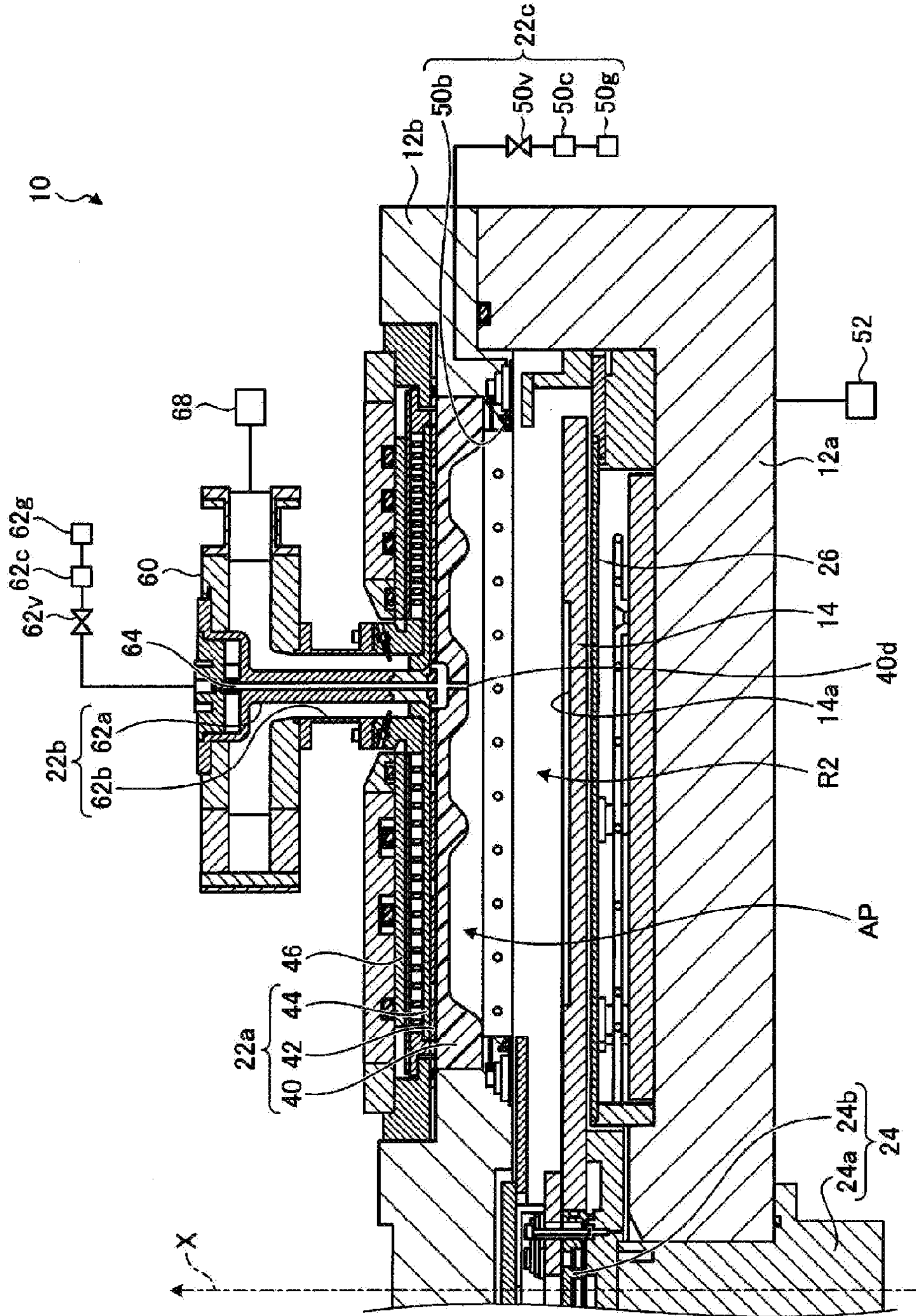
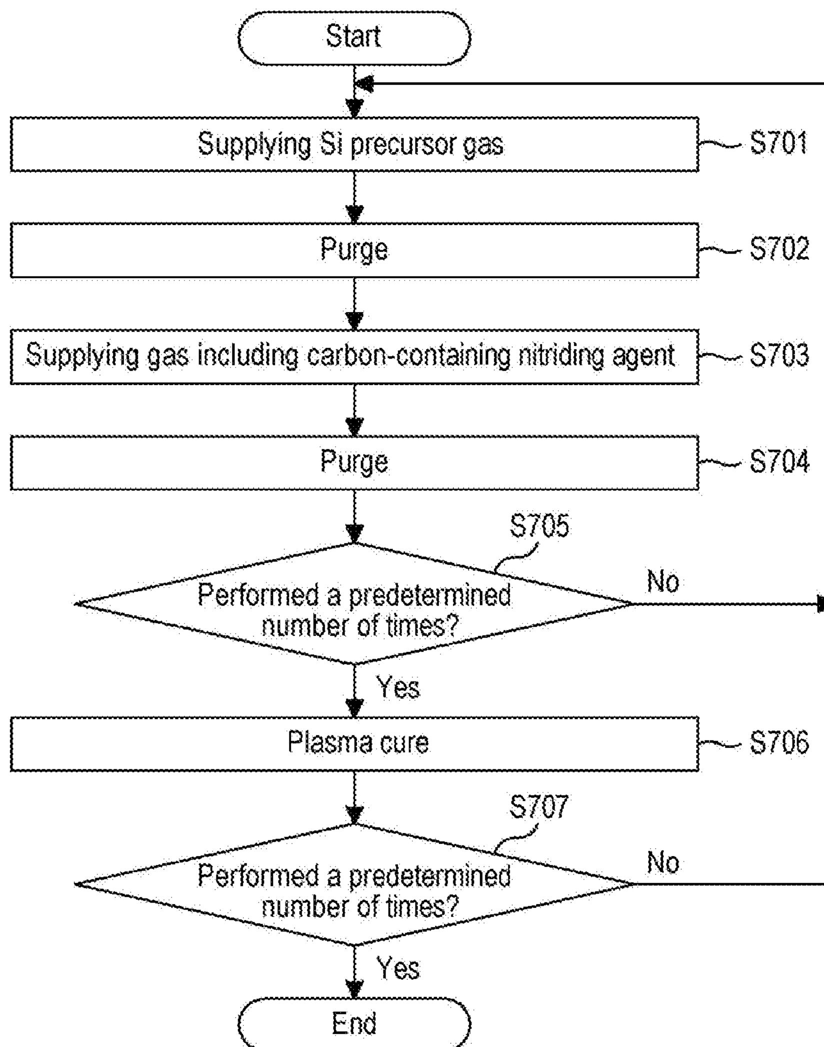


FIG. 7
10
12b
50b
22c
50v
50c
50g
68
60
62v
62c
62g
64
22b
62b
62a
52
12a
26
14
40d
14a
R2
AP
46
22a
40
42
44
24a
24b
24
X

FIG. 8



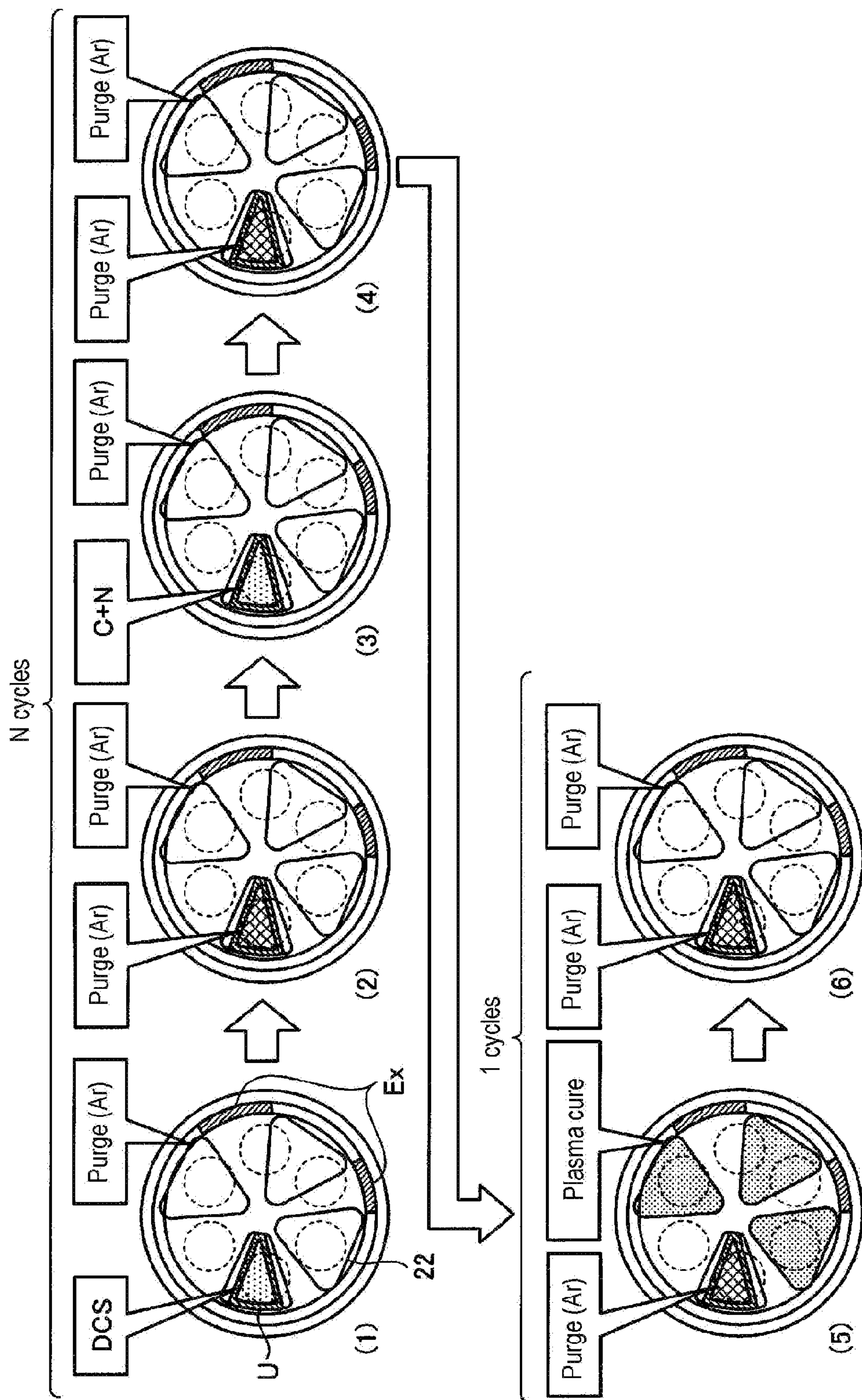
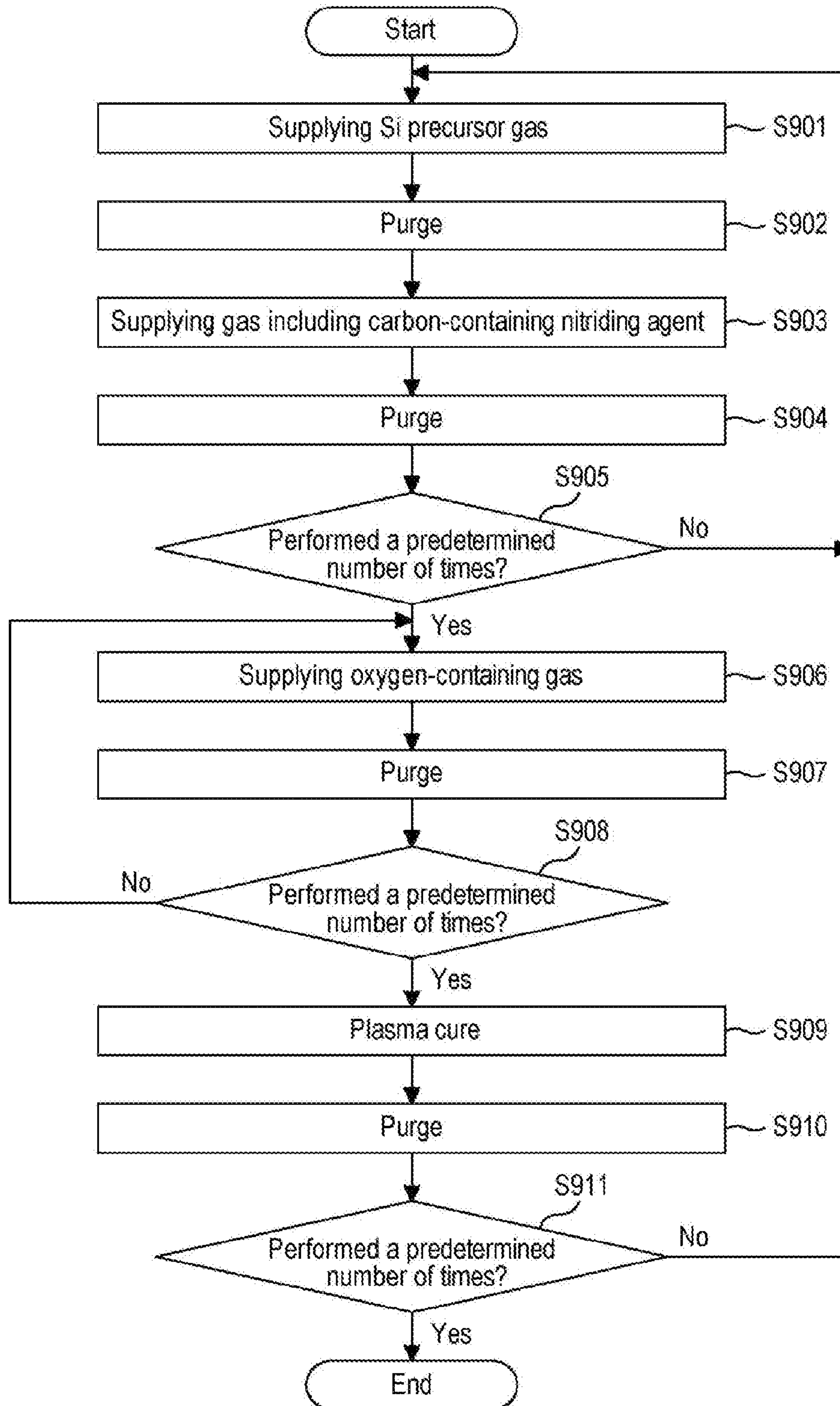


FIG. 9
N cycles
DCS
Purge (Ar)
Purge (Ar)
Purge (Ar)
C+N
Purge (Ar)
Purge (Ar)
Purge (Ar)
Ex
22
U
(1)
(2)
(3)
(4)
1 cycles
Purge (Ar)
Plasma cure
Purge (Ar)
Purge (Ar)
(5)
(6)

FIG. 10



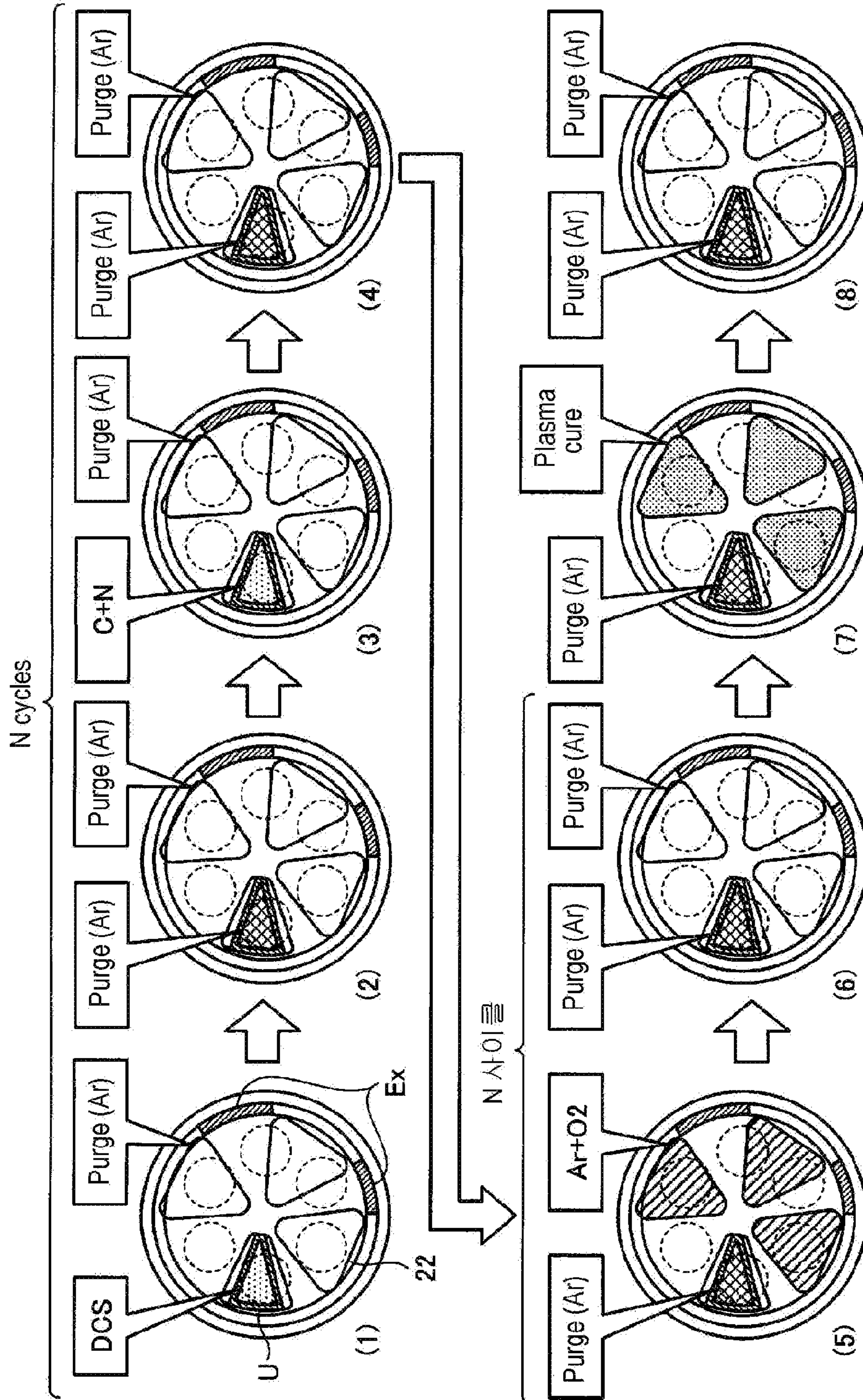
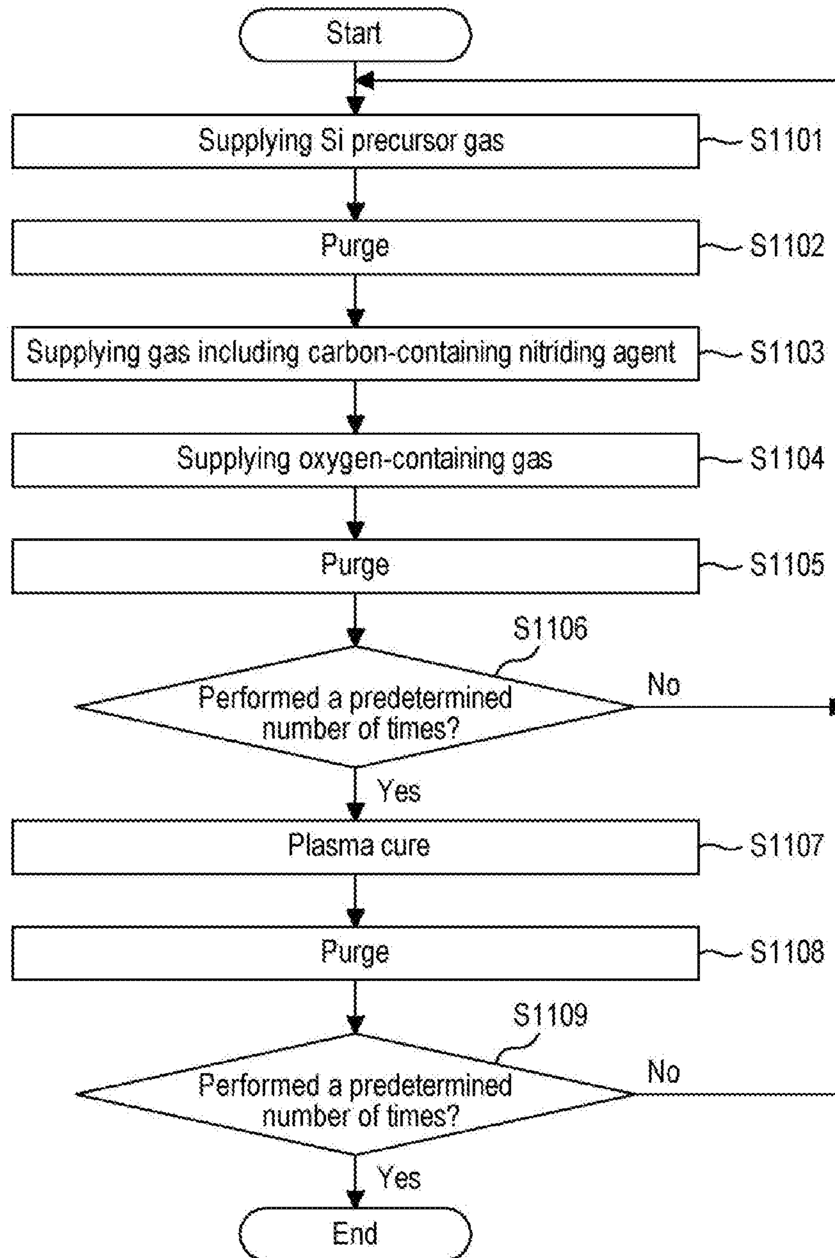


FIG. 11
N cycles
DCS
Purge (Ar)
Purge (Ar)
Purge (Ar)
C+N
Purge (Ar)
Purge (Ar)
Purge (Ar)
U
22
Ex
(1)
(2)
(3)
(4)
N 사이클
Purge (Ar)
Ar+O2
Purge (Ar)
Purge (Ar)
Purge (Ar)
Plasma cure
Purge (Ar)
Purge (Ar)
(5)
(6)
(7)
(8)

FIG. 12



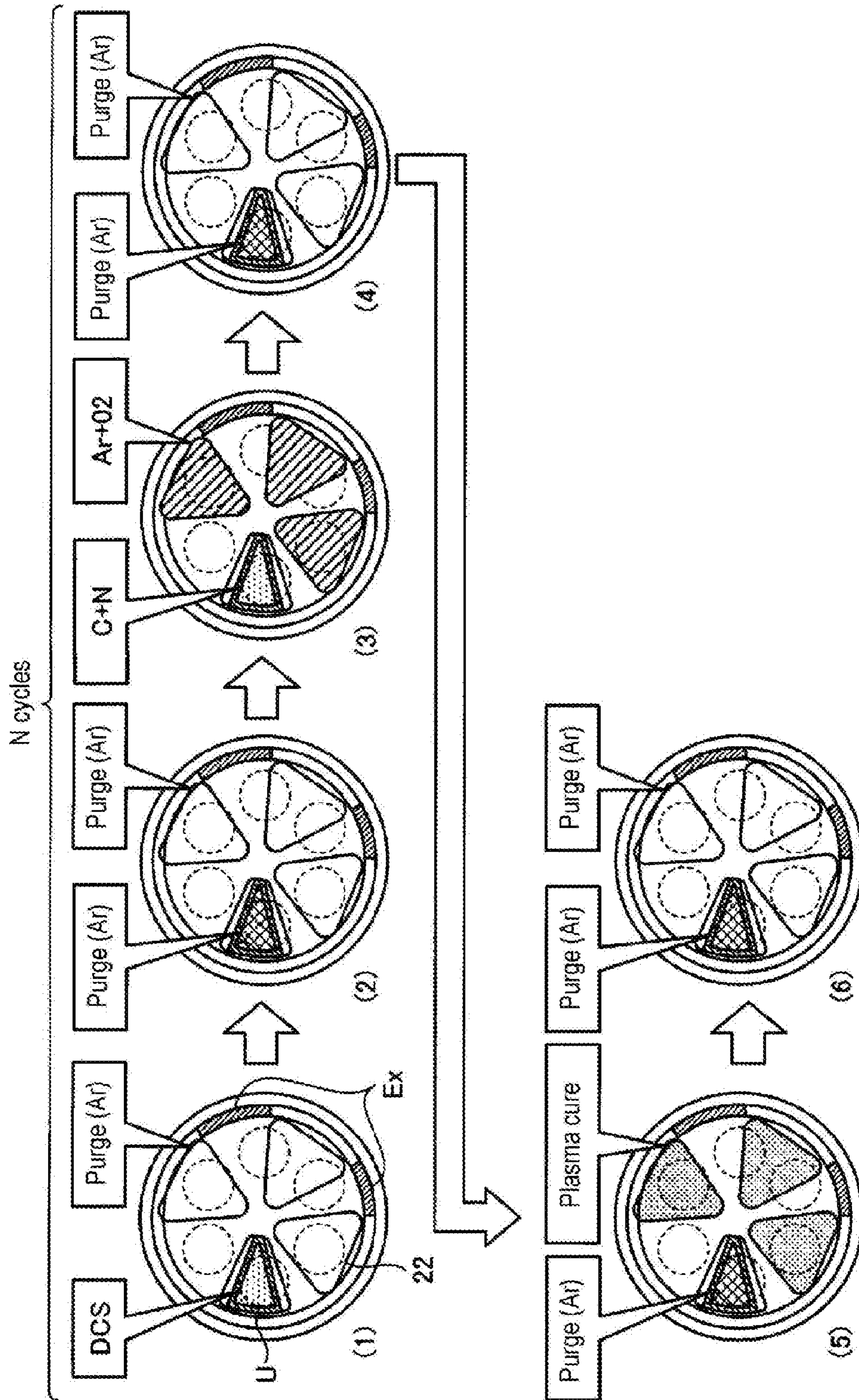



FIG. 13

FIG. 14

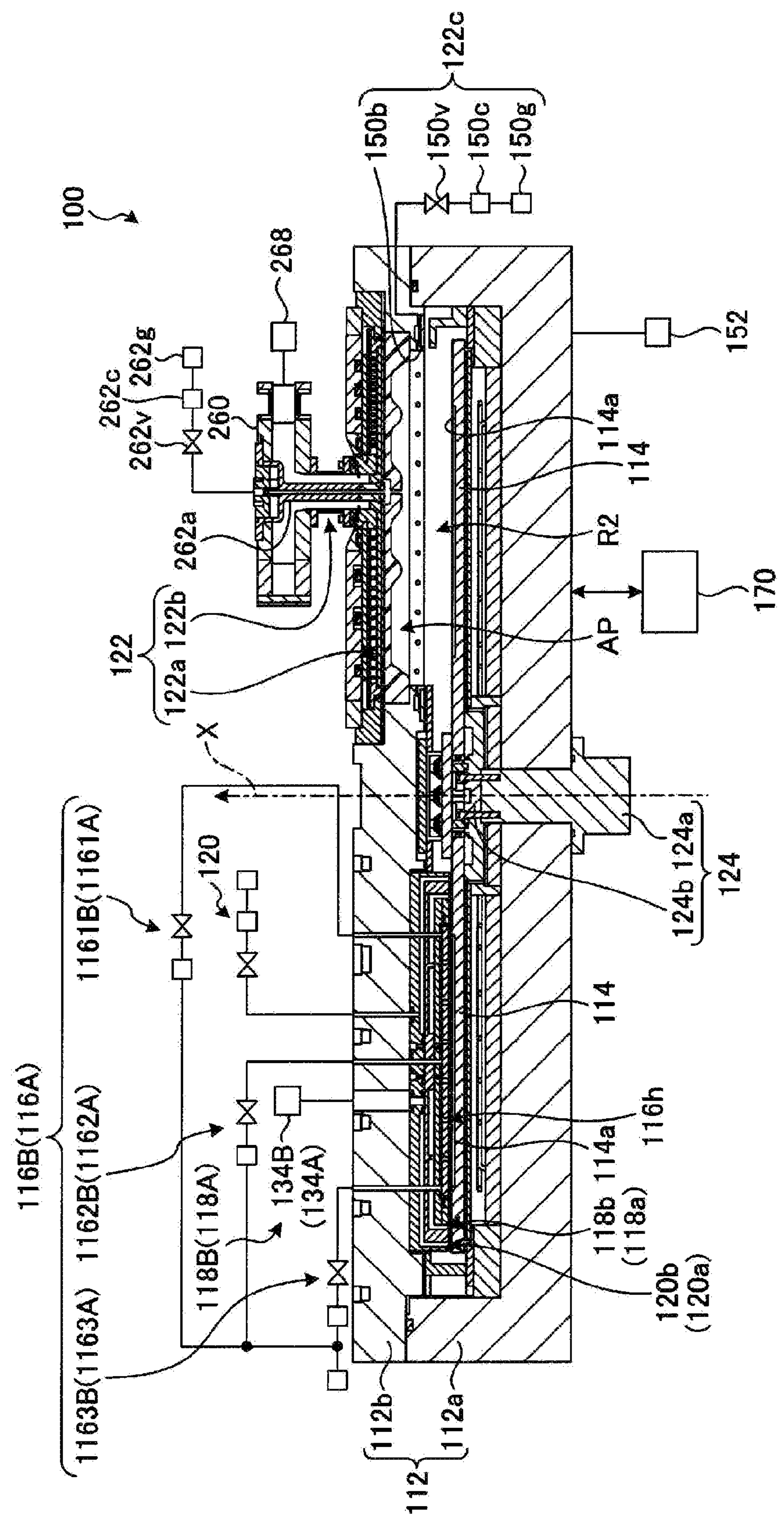


FIG. 15

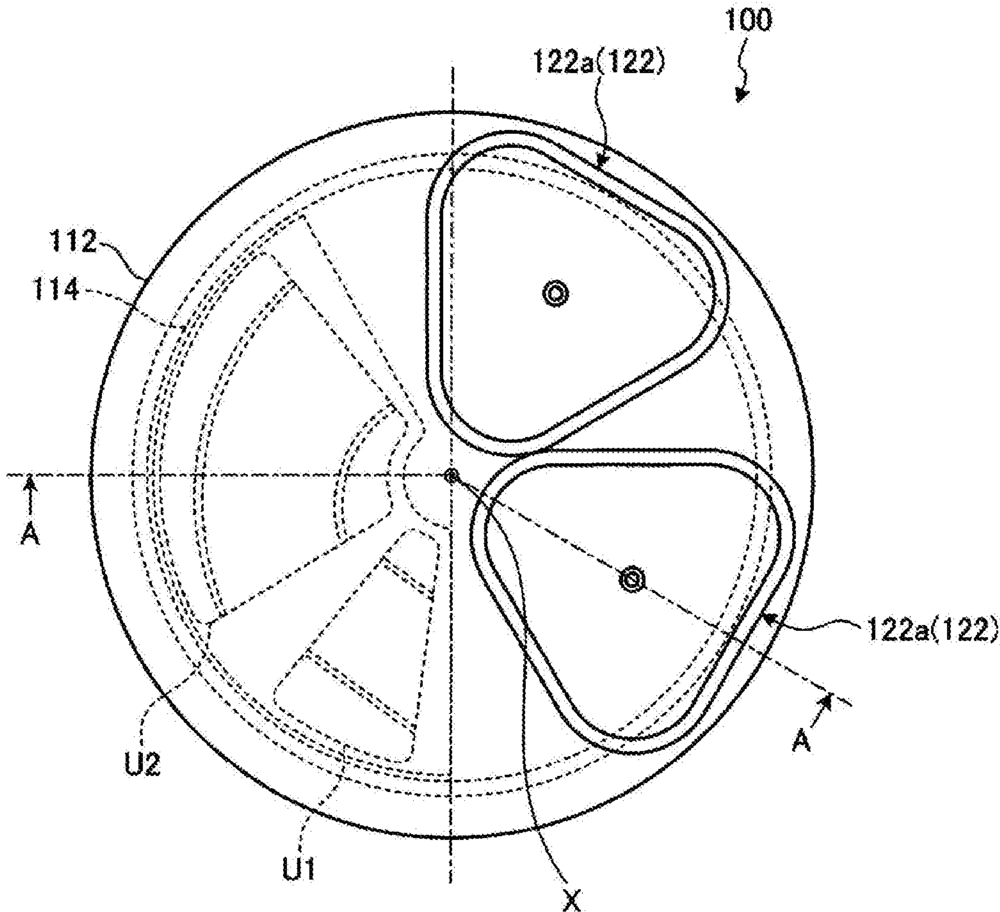


FIG. 16

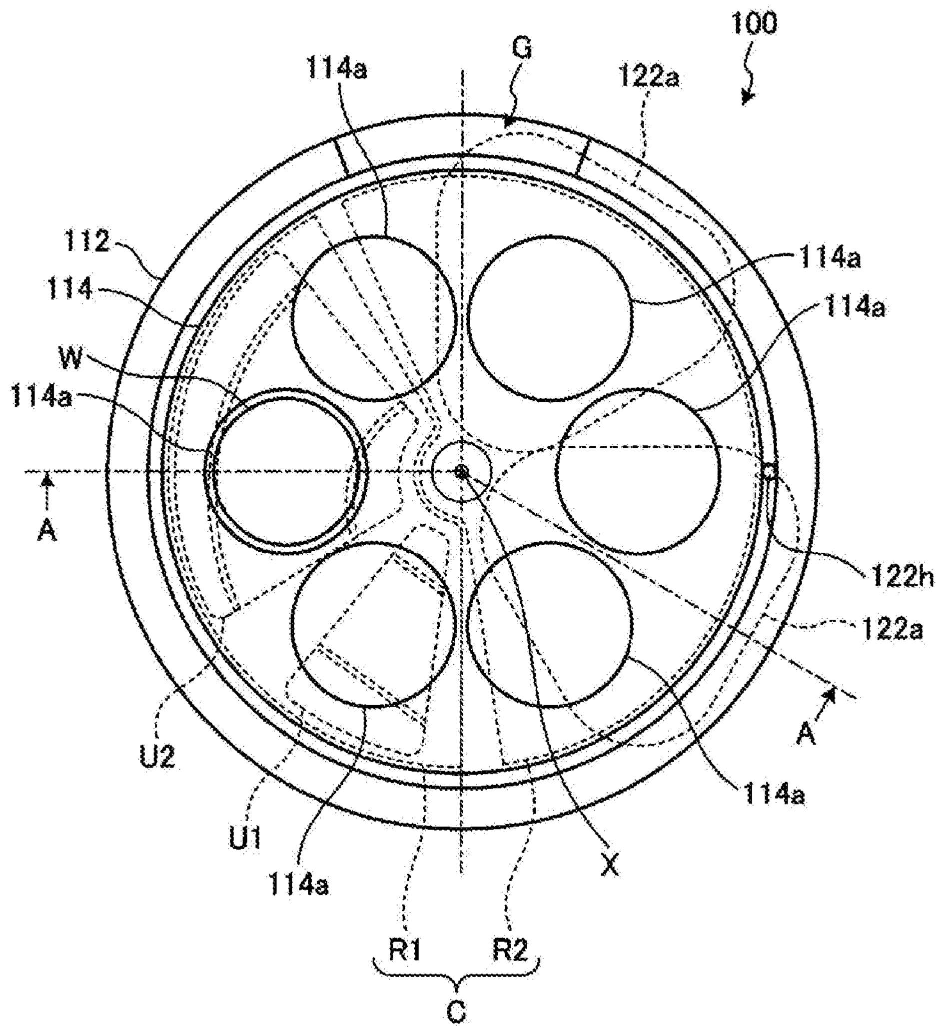
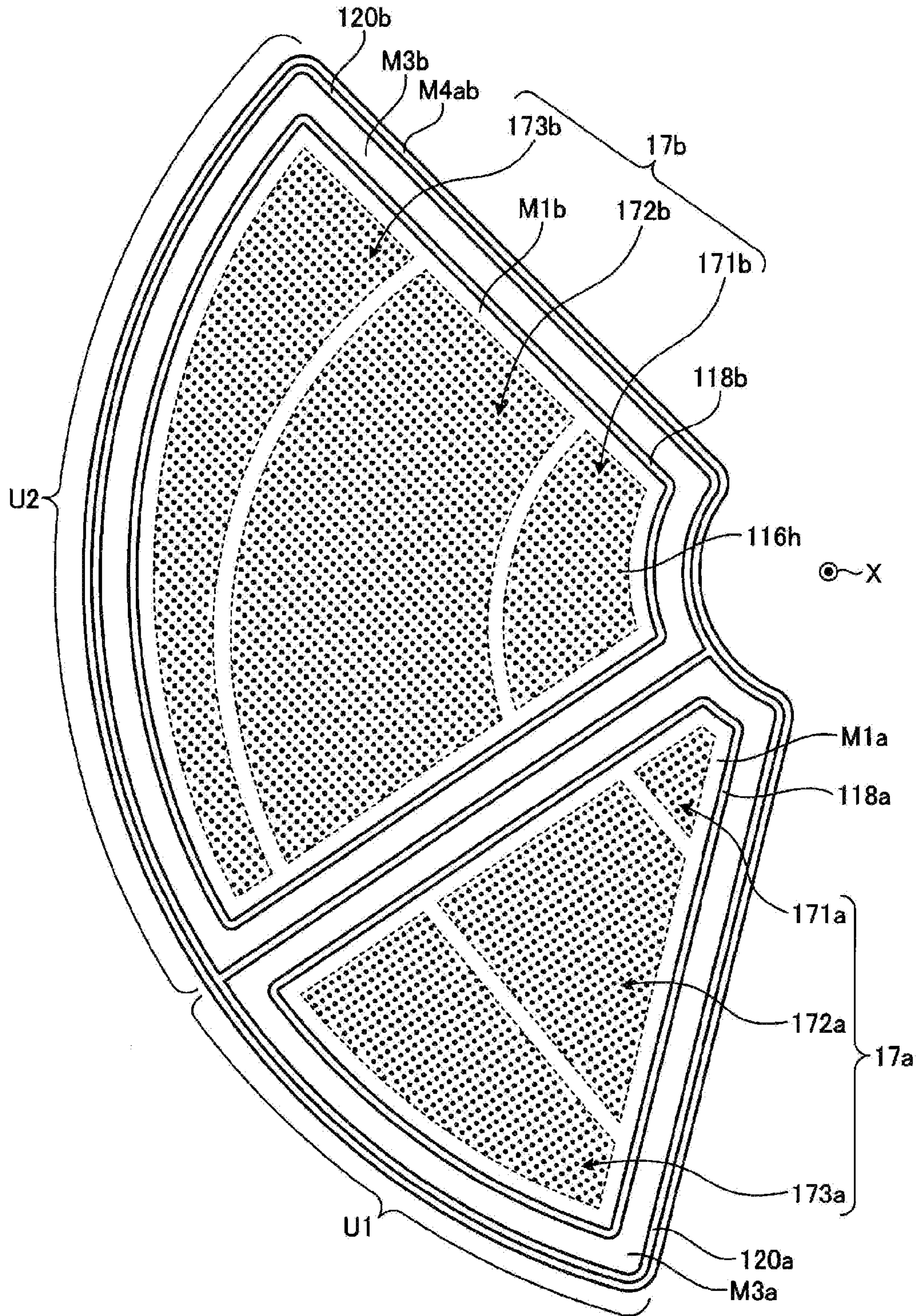
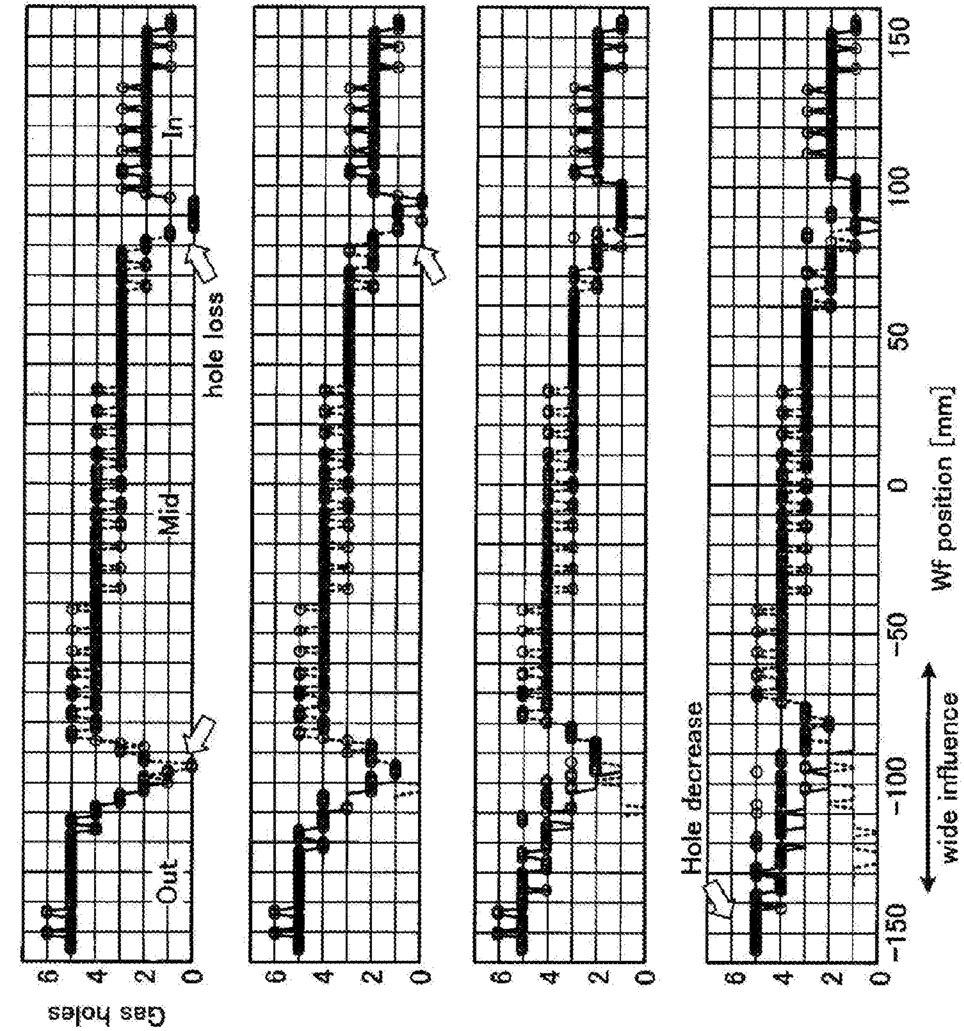


FIG. 17





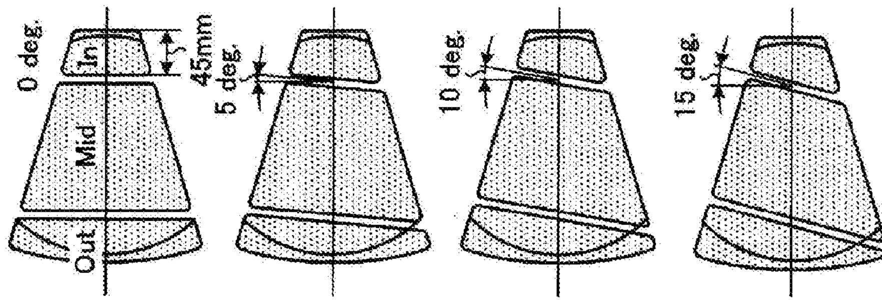




FIG. 18A

FIG. 18B

FIG. 18C

FIG. 18D

FIG. 19

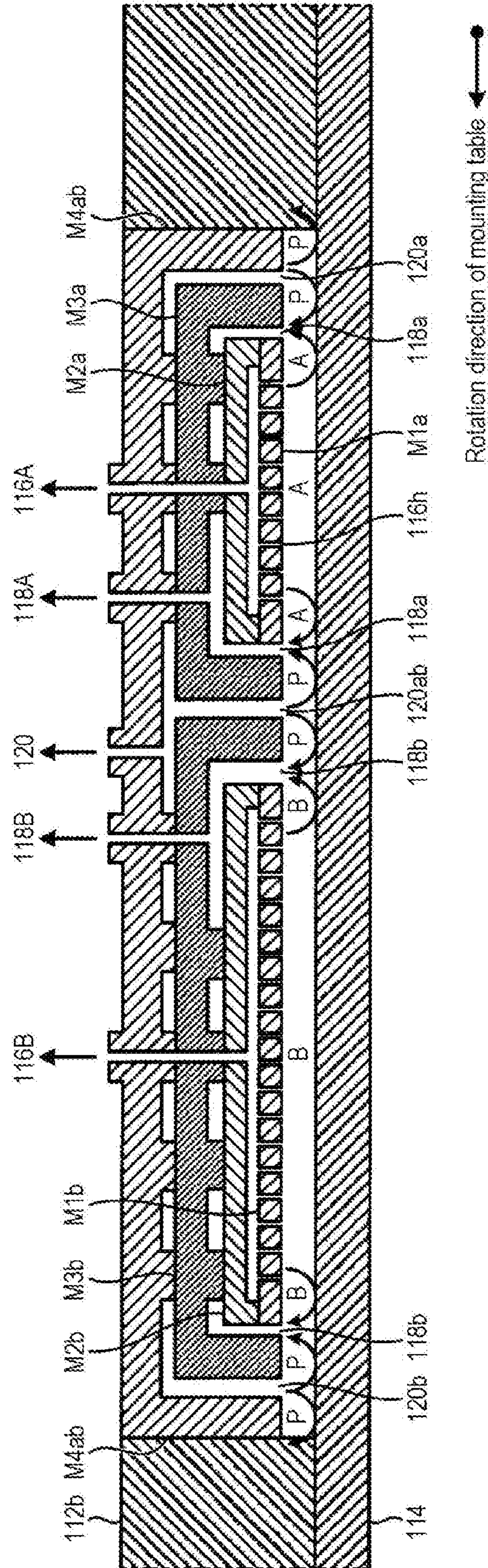


FIG. 20

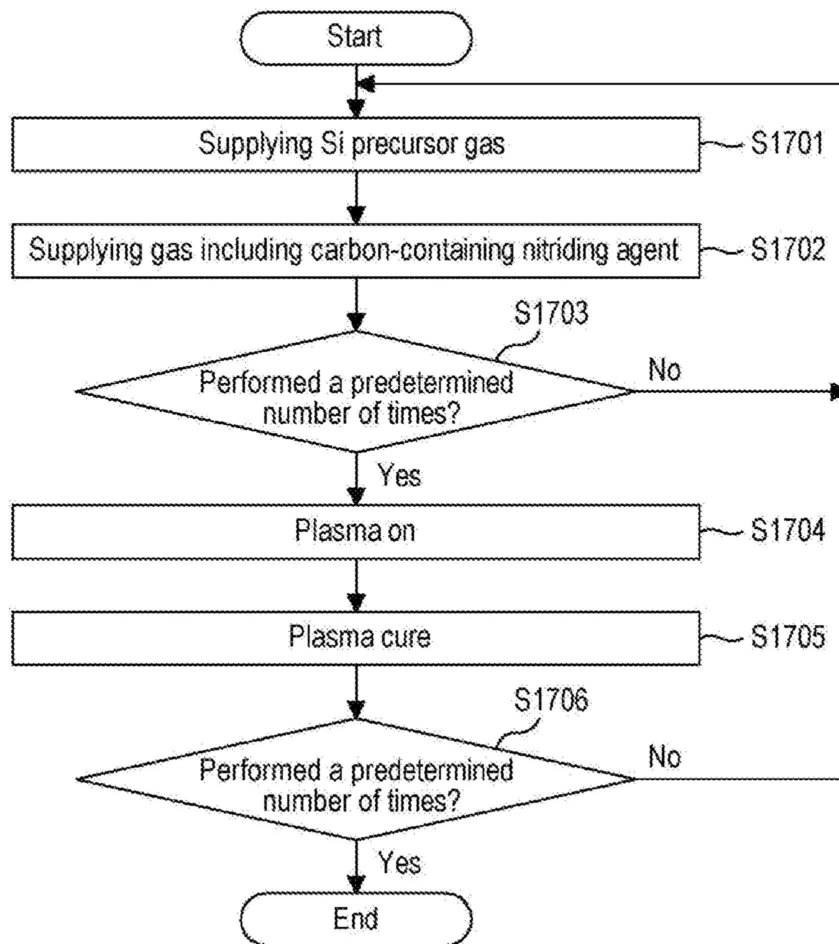


FIG. 21

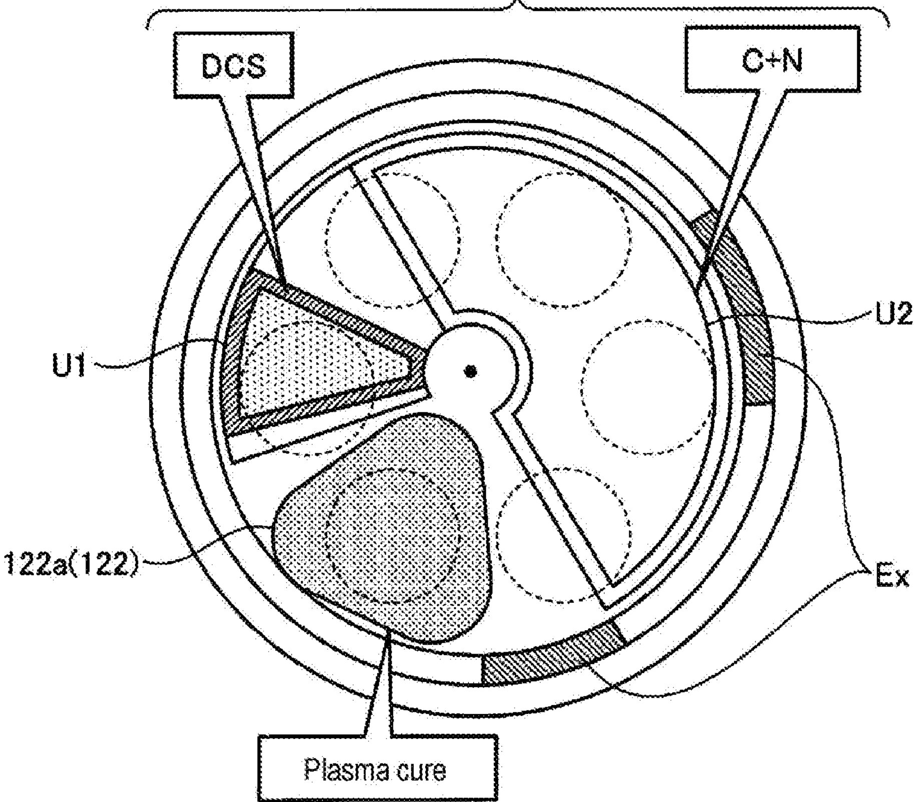


FIG. 22

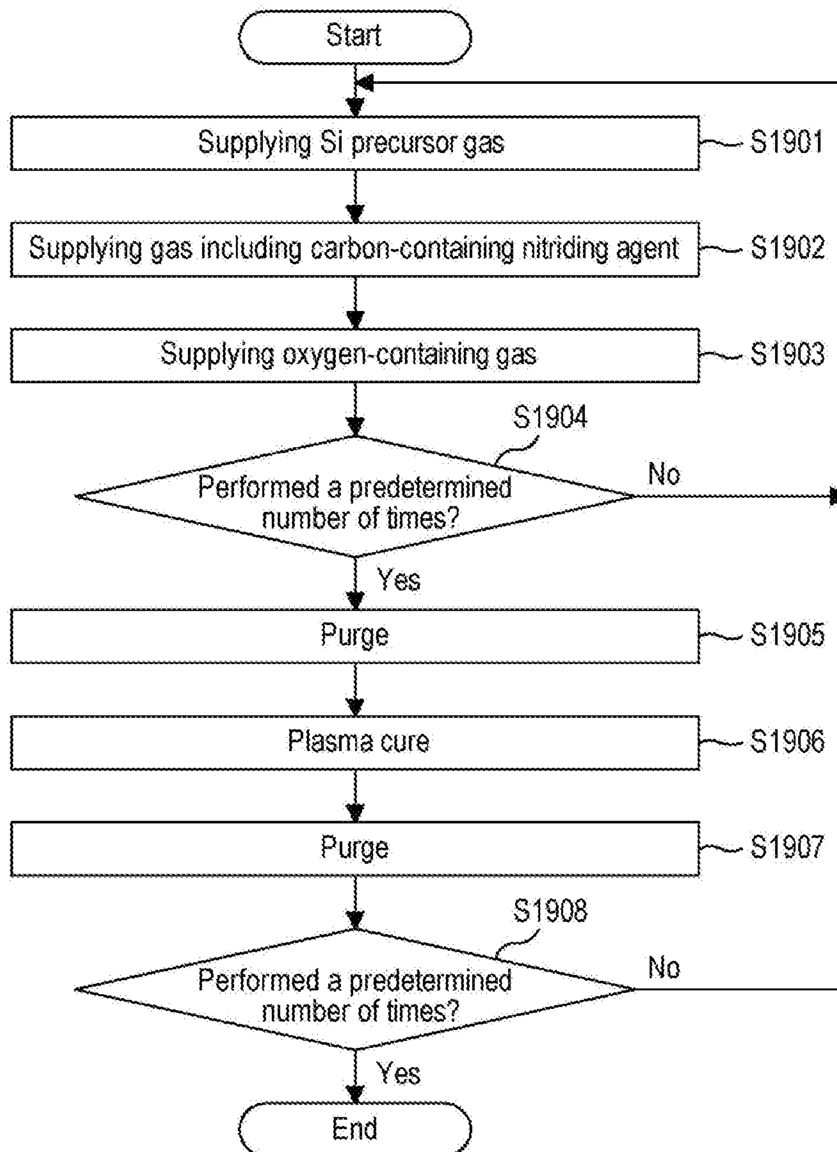


FIG. 23

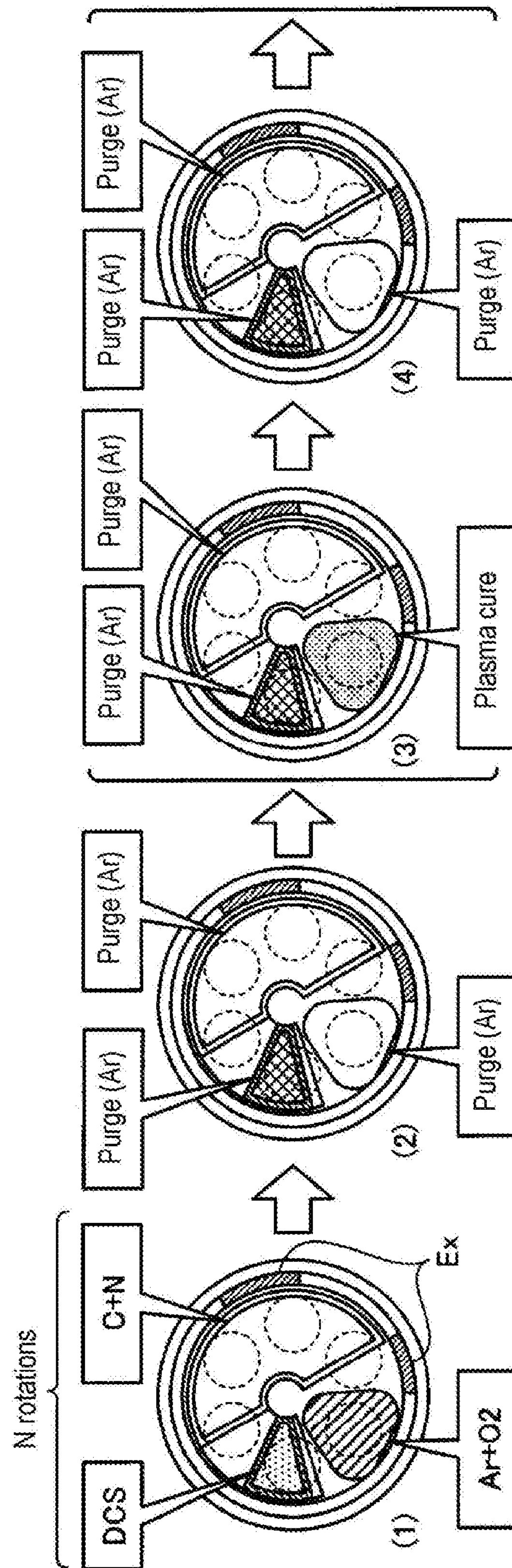


FIG. 24

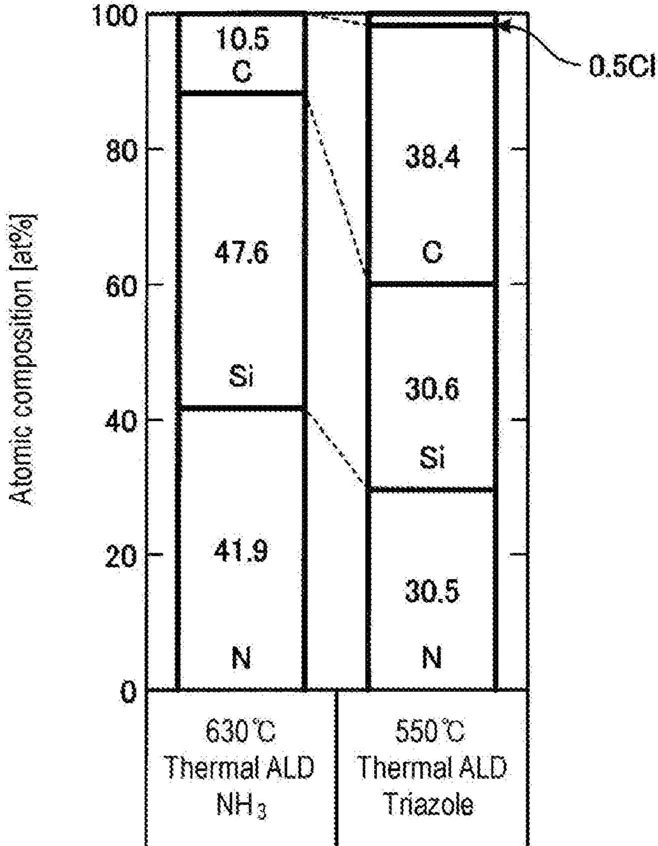


FIG. 25

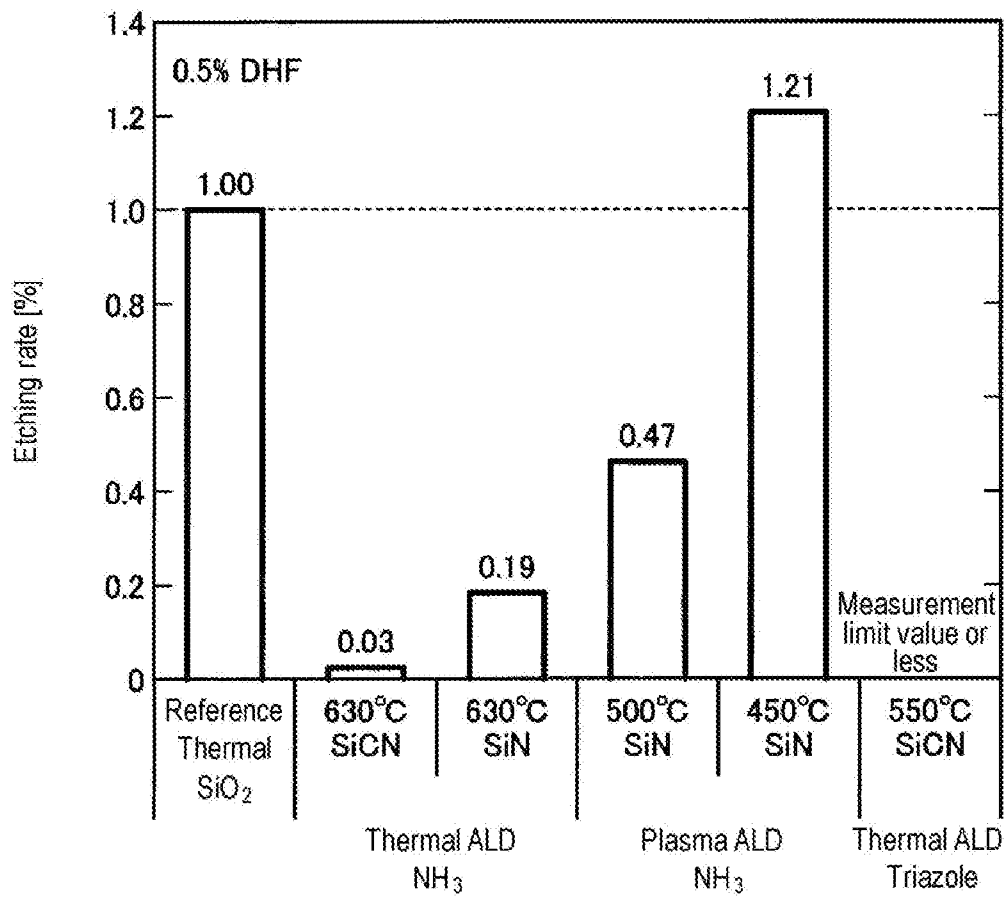


FIG. 26

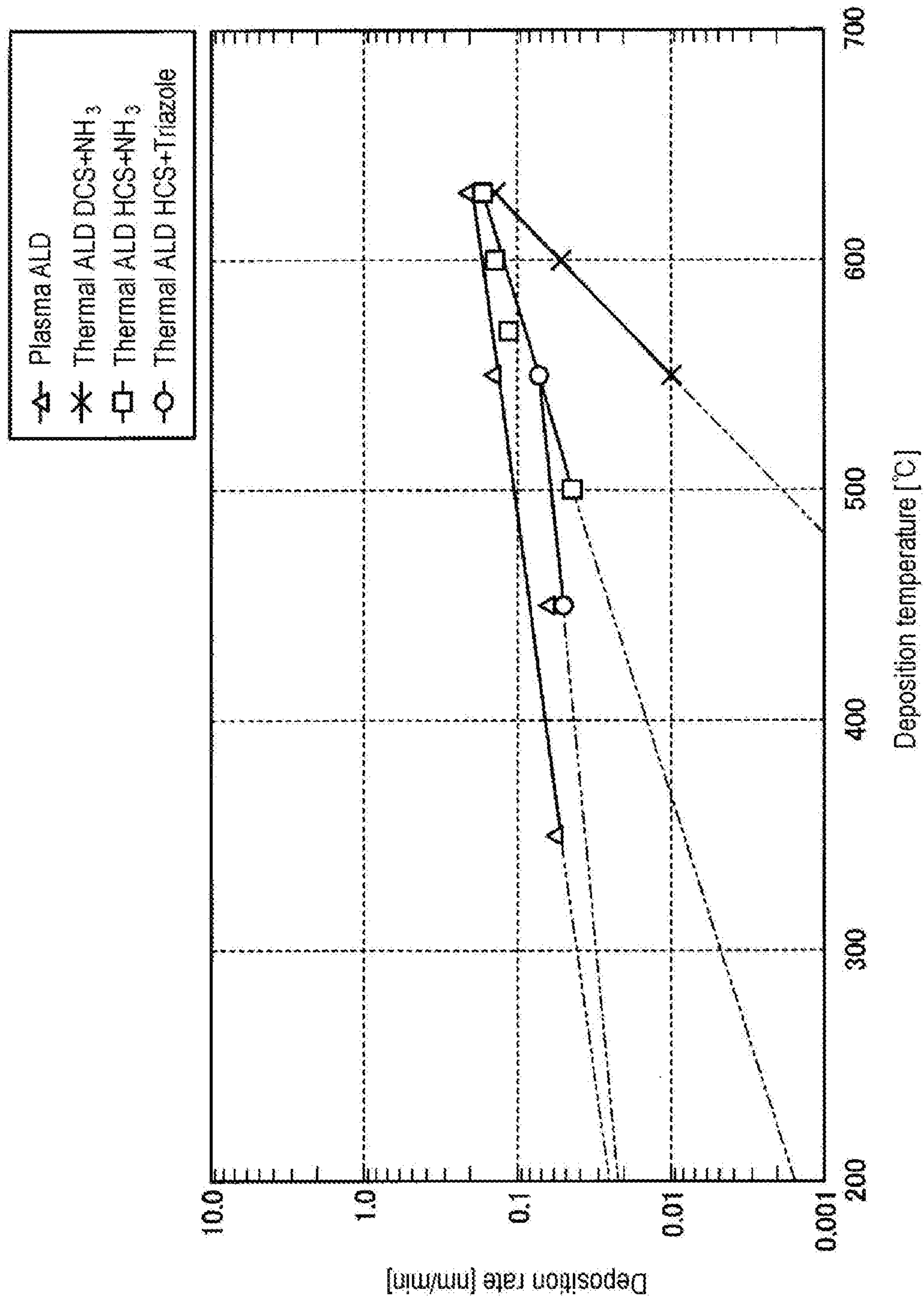
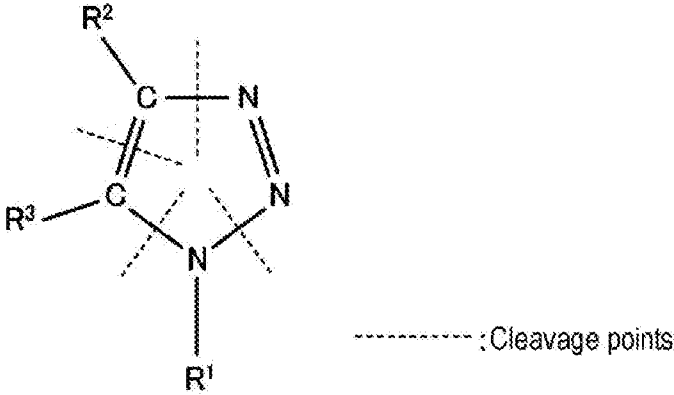


FIG. 27




1,2,3-triazole-based compound

# FILM FORMING METHOD AND FILM FORMING APPARATUS

## CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of Japanese Patent Application No. 2015-094143, filed on May 1, 2015, in the Japan Patent Office, the disclosure of which is incorporated herein in its entirety by reference.

## TECHNICAL FIELD

[0002] Various aspects and embodiments of the present disclosure relate to a film forming method and a film forming apparatus.

## BACKGROUND

[0003] As film forming apparatuses for forming a film on a substrate, a single-substrate-type film forming apparatus which processes a wafer one by one and a batch-type film forming apparatus which processes a plurality of wafers at a time are used. In the batch-type film forming apparatus, for example, a plurality of wafers is arranged and disposed in a vertical direction of the apparatus so that a larger amount of wafers can be processed. In addition, a semi-batch-type film forming apparatus, which realizes deposition by disposing several wafers on a circular mounting table and rotating the mounting table, is used. In the semi-batch-type film forming apparatus, a region for supplying a precursor gas and a region for generating plasma of a reaction gas are provided in different regions within a process chamber. Substrates sequentially pass through these regions, whereby films having a desired thickness are formed on the substrates.

[0004] The semi-batch-type film forming apparatus includes a mounting table, a shower head and a plasma generation part. The mounting table supports the substrates and rotates about a rotary shaft. The shower head and the plasma generation part are disposed to face the mounting table and are arranged along a circumferential direction. The shower head has a substantially fan-shaped plane shape and supplies a precursor gas to the workpiece substrates passing under the shower head. The plasma generation part supplies a reaction gas and radiates microwaves, which are supplied from a waveguide, through a substantially fan-shaped antenna, thereby generating plasma of the reaction gas. An exhaust port is formed around the shower head and the plasma generation part. Injection holes for supplying a purge gas are formed in a peripheral edge of the shower head.

[0005] In a process which makes use of the aforementioned film forming apparatus, a heat treatment is performed at a temperature of about 600 to 650 degrees C., thereby forming a film of SiN, SiCN, SiBN, SiOCN or the like. However, in a film forming technique, even higher miniaturization is required. Specifically, a highly-reproducible film forming process, which is capable of meeting the miniaturization requirements while realizing low-temperature deposition and low thermal budget and capable of producing a high-performance film, is required.

## SUMMARY

[0006] According to one embodiment of the present disclosure, a film forming method for forming a nitride film on a workpiece substrate accommodated within a process vessel includes: performing a first reaction of supplying a first precursor gas to the workpiece substrate accommodated within the process vessel; performing a second reaction of supplying a second precursor gas to the workpiece substrate accommodated within the process vessel; performing a modification of generating plasma of a modifying gas just above the workpiece substrate by supplying the modifying gas into the process vessel and supplying microwaves from an antenna into the process vessel, and plasma-processing, by the plasma thus generated, a surface of the workpiece substrate subjected to the first and second reaction steps using the first and second precursor gases.

[0007] According to another embodiment of the present disclosure, a film forming apparatus includes: a process vessel divided into a plurality of regions along a circumferential direction in which workpiece substrates are moved about an axis by a rotation of a mounting table, the mounting table being configured to hold the workpiece substrates and installed to rotate about the axis so that the workpiece substrates move around the axis; a first shower head disposed to face the mounting table and configured to supply a first precursor gas to a first region among the plurality of regions of the process vessel; a second shower head disposed to face the mounting table and configured to supply a second precursor gas to a second region adjoining the first region among the plurality of regions of the process vessel; and a plasma generation part disposed to face the mounting table and configured to generate plasma of a modifying gas just above the workpiece substrates by supplying the modifying gas to a third region among the plurality of regions of the process vessel and supplying microwaves from an antenna to the third region

## BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate embodiments of the present disclosure, and together with the general description given above and the detailed description of the embodiments given below, serve to explain the principles of the present disclosure.

[0009] FIG. **1** is a sectional view illustrating one example of a film forming apparatus according to a first embodiment.

[0010] FIG. **2** is a top view illustrating one example of the film forming apparatus according to the first embodiment.

[0011] FIG. **3** is a plane view illustrating one example of a state in which a top portion of a process vessel is removed from the film forming apparatus illustrated in FIG. **2**.

[0012] FIG. **4** is an enlarged sectional view illustrating one example of a left portion of an axis X in FIG. **1**.

[0013] FIG. **5** is an enlarged sectional view illustrating one example of the left portion of the axis X in FIG. **1**.

[0014] FIG. **6** is a view illustrating one example of a lower surface of a unit U.

[0015] FIG. **7** is an enlarged sectional view illustrating one example of a right portion of an axis X in FIG. **1**.

[0016] FIG. **8** is a flowchart illustrating a flow of one example of a film forming process of a SiCN film implemented in the film forming apparatus according to the first embodiment.

[0017] FIG. **9** is a schematic view for explaining the flow of one example of the film forming process of the SiCN film implemented in the film forming apparatus according to the first embodiment.

[0018] FIG. **10** is a flowchart illustrating a flow of one example of a film forming process of a SiOCN film implemented in the film forming apparatus according to the first embodiment.

[0019] FIG. **11** is a schematic view for explaining the flow of one example of the film forming process of the SiOCN film implemented in the film forming apparatus according to the first embodiment.

[0020] FIG. **12** is a flowchart illustrating a flow of another example of the film forming process of the SiOCN film implemented in the film forming apparatus according to the first embodiment.

[0021] FIG. **13** is a schematic view for explaining the flow of another example of the film forming process of the SiOCN film implemented in the film forming apparatus according to the first embodiment.

[0022] FIG. **14** is a sectional view illustrating one example of a film forming apparatus according to a second embodiment.

[0023] FIG. **15** is a top view illustrating one example of the film forming apparatus according to the second embodiment.

[0024] FIG. **16** is a plane view illustrating one example of a state in which a top portion of a process vessel is removed from the film forming apparatus illustrated in FIG. **15**.

[0025] FIG. **17** is a view illustrating one example of an arrangement of injection holes of a shower head provided in the film forming apparatus according to the second embodiment.

[0026] FIGS. **18**A to **18**D are views for explaining the relationship between the arrangement of the injection holes of the shower head and the quality of a film as formed.

[0027] FIG. **19** is a schematic sectional view illustrating a configuration of two shower heads in the film forming apparatus according to the second embodiment.

[0028] FIG. **20** is a flowchart illustrating one example of a film forming process of a SiCN film implemented in the film forming apparatus according to the second embodiment.

[0029] FIG. **21** is a schematic view for explaining the flow of one example of the film forming process of the SiCN film implemented in the film forming apparatus according to the second embodiment.

[0030] FIG. **22** is a flowchart illustrating one example of a film forming process of a SiOCN film implemented in the film forming apparatus according to the second embodiment.

[0031] FIG. **23** is a schematic view for explaining the flow of one example of the film forming process of the SiOCN film implemented in the film forming apparatus according to the second embodiment.

[0032] FIG. **24** is a view illustrating an atomic composition of a SiCN film of Example 1.

[0033] FIG. **25** is a view for explaining an etching rate of the SiCN film of Example 1.

[0034] FIG. **26** is a view for explaining the relationship between a deposition temperature of the SiCN film of Example 1 and a deposition rate thereof.

[0035] FIG. **27** is a view illustrating cleavage points of a 1,2,3-triazole-based compound.

## DETAILED DESCRIPTION

[0036] Reference will now be made in detail to various embodiments, examples of which are illustrated in the accompanying drawings. In the following detailed description, numerous specific details are set forth in order to provide a thorough understanding of the present disclosure. However, it will be apparent to one of ordinary skill in the art that the present disclosure may be practiced without these specific details. In other instances, well-known methods, procedures, systems, and components have not been described in detail so as not to unnecessarily obscure aspects of the various embodiments.

[0037] One embodiment of a film forming method disclosed herein is directed to a film forming method for forming a nitride film on a workpiece substrate accommodated within a process vessel. The film forming method includes performing a first reaction of supplying a first precursor gas to the workpiece substrate accommodated within the process vessel. The film forming method further includes performing a second reaction of supplying a second precursor gas to the workpiece substrate accommodated within the process vessel. The film forming method further includes performing a modification of generating plasma of a modifying gas just above the workpiece substrate by supplying the modifying gas into the process vessel and supplying microwaves from an antenna into the process vessel, and plasma-processing, by the plasma thus generated, a surface of the workpiece substrate subjected to the first and second reactions using the first and second precursor gases.

[0038] In one embodiment of the film forming method disclosed herein, the first precursor gas contains silicon and the second precursor gas contains carbon atoms and nitrogen atoms.

[0039] In one embodiment of the film forming method disclosed herein, the modification is performed once each time when the first and second reactions are repeatedly performed a predetermined number of times.

[0040] In one embodiment of the film forming method disclosed herein, the film forming method further includes performing a third reaction of supplying a third gas to the workpiece substrate accommodated within the process vessel. The film forming method further includes performing a removal of purging a mechanism for supplying the first precursor gas, the second precursor gas and the third gas, the removal being performed after the first reaction, the second reaction and the third reaction but before the modification.

[0041] In one embodiment of the film forming method disclosed herein, the third gas contains oxygen atoms.

[0042] In one embodiment of the film forming method disclosed herein, the first precursor gas contains one of monochlorosilane, dichlorosilane, trichlorosilane, tetrachlorosilane and hexachlorodisilane.

[0043] In one embodiment of the film forming method disclosed herein, the second precursor gas is supplied into the process vessel together with ammonia.

[0044] In one embodiment of the film forming method disclosed herein, the second precursor gas is pyrolyzed at a temperature of 200 degrees C. or more and 550 degrees C. or less.

[0045] In one embodiment of the film forming method disclosed herein, the modifying gas is a mixed gas of $NH_3$ and $H_2$.

[0046] A film forming apparatus according to one embodiment disclosed herein includes a process vessel divided into a plurality of regions along a circumferential direction in which workpiece substrates are moved about an axis by the

rotation of a mounting table configured to hold the workpiece substrates and installed to rotate about the axis so that the workpiece substrates can move around the axis. The film forming apparatus further includes a first shower head disposed to face the mounting table and configured to supply a first precursor gas to a first region among the plurality of regions of the process vessel. The film forming apparatus further includes a second shower head disposed to face the mounting table and configured to supply a second precursor gas to a second region adjoining the first region among the plurality of regions of the process vessel. The film forming apparatus further includes a plasma generation part disposed to face the mounting table and configured to generate plasma of a modifying gas just above the workpiece substrates by supplying the modifying gas to a third region among the plurality of regions of the process vessel and supplying microwaves from an antenna to the third region.

**[0047]** In one embodiment of the film forming apparatus disclosed herein, the first shower head is smaller in size than the second shower head.

**[0048]** In one embodiment of the film forming apparatus disclosed herein, the film forming apparatus further includes a gas supply/exhaust mechanism configured to prevent entry of plasma into a space between the first and second shower heads by supplying a purge gas between the first and second shower heads and around the first and second shower heads.

**[0049]** In one embodiment of the film forming apparatus disclosed herein, the first shower head is configured to supply the first precursor gas containing silicon and the second shower head is configured to supply the second precursor gas containing carbon atoms and nitrogen atoms.

**[0050]** In one embodiment of the film forming apparatus disclosed herein, the plasma generation part includes a first gas supply part configured to supply an oxygen gas to the third region and a second gas supply part configured to, after supplying the oxygen gas, supply a purge gas in order to remove the oxygen gas.

**[0051]** In one embodiment of the film forming apparatus disclosed herein, each of the first and second shower heads is divided into a plurality of regions, in which flow rates of an injected gas are independently controlled, radially outward from the axis of the process vessel by straight lines or curved lines extending along the circumferential direction of the process vessel. Furthermore, an inclination angle of the straight lines or the curved lines of the first shower head with respect to a radial direction of the process vessel is larger than an inclination angle of the straight lines or the curved lines of the second shower head with respect to the radial direction of the process vessel.

## First Embodiment

### One Example of a Configuration of Film Forming Apparatus 10

**[0052]** FIG. **1** is a sectional view illustrating one example of a film forming apparatus **10** according to a first embodiment. FIG. **2** is a top view illustrating one example of the film forming apparatus **10** according to the first embodiment. FIG. **3** is a plane view illustrating one example of a state in which a top portion of a process vessel **12** is removed from the film forming apparatus **10** illustrated in FIG. **2**. FIG. **1** illustrates a cross section taken along line A-A in FIGS. **2** and **3**. FIGS. **4** and **5** are enlarged sectional views illustrating one example of a left portion of an axis X in FIG. **1**. FIG. **6** is a view illustrating one example of a lower surface of a unit U. FIG. **7** is an enlarged sectional view illustrating one example of a right portion of an axis X in FIG. **1**. The film forming apparatus **10** illustrated in FIGS. **1** to **7** mainly includes a process vessel **12**, a mounting table **14**, a first gas supply part **16**, an exhaust part **18**, a second gas supply part **20** and a plasma generation part **22**.

**[0053]** As illustrated in FIG. **1**, the process vessel **12** includes a lower member **12*a*** and an upper member **12*b***. The lower member **12*a*** has a substantially cylindrical shape with the upper side thereof opened. The lower member **12*a*** includes a sidewall and a bottom wall which define a recess for forming a process chamber C. The upper member **12*b*** is a lid having a substantially cylindrical shape. The upper member **12*b*** covers and closes an upper opening of the recess of the lower member **12*a***, thereby forming the process chamber C. An elastic sealing member for hermetically sealing the process chamber C, for example, an O-ring, is installed in a peripheral portion between the lower member **12*a*** and the upper member **12*b***.

**[0054]** The film forming apparatus **10** includes the mounting table **14** disposed within the process chamber C defined by the process vessel **12**. The mounting table **14** is rotationally driven about the axis X by a drive mechanism **24**. The drive mechanism **24** includes a drive device **24*a*** such as a motor or the like and a rotary shaft **24*b***. The drive mechanism **24** is installed on the lower member **12*a*** of the process vessel **12**.

**[0055]** The rotary shaft **24*b*** has a center axis coaxial with the axis X and extends into the process chamber C. The rotary shaft **24*b*** is rotated about the axis X by the drive power transmitted from the drive device **24*a***. The central portion of the mounting table **14** is supported by the rotary shaft **24*b***. Thus, the mounting table **14** rotates about the axis X together with the rotary shaft **24*b***. Furthermore, an elastic sealing member such as an O-ring or the like for hermetically sealing the process chamber C is installed between the lower member **12*a*** of the process vessel **12** and the drive mechanism **24**.

**[0056]** The film forming apparatus **10** includes a heater **26** disposed under the mounting table **14** within the process chamber C and configured to heat substrates W as workpiece substrates mounted in substrate mounting regions **14*a***. Specifically, the heater **26** heats the mounting table **14**, thereby heating the substrates W.

**[0057]** For example, as illustrated in FIGS. **2** and **3**, the process vessel **12** is a substantially cylindrical vessel having a center axis coaxial with the axis X. The process vessel **12** includes the process chamber C defined therein. A unit U provided with an injection part **16*a*** is installed in the process chamber C. The unit U is one example of a shower head. The process vessel **12** is made of metal such as Al (aluminum) or the like with the inner surface thereof subjected to an anti-plasma process, for example, an alumite process or a thermal spray process of $Y_2O_3$ (yttrium oxide). The film forming apparatus **10** includes a plurality of plasma generation parts **22** disposed within the process vessel **12**. Each of the plasma generation parts **22** includes an antenna **22*a*** disposed above the process vessel **12** and configured to output microwaves. In FIGS. **2** and **3**, three antennas **22*a*** are installed above the process vessel **12**. However, the number of the antennas **22*a*** is not limited thereto but may be two or less or four or more.

**[0058]** For example, as illustrated in FIG. **3**, the film forming apparatus **10** includes the mounting table **14** having a plurality of substrate mounting regions **14***a* defined on the upper surface thereof. The mounting table **14** is a substantially disc-shaped member having a center axis coaxial with the axis X. A plurality of (six, in the example illustrated in FIG. **3**) substrate mounting regions **14***a* for holding the substrates W is formed on the upper surface of the mounting table **14** in a concentric relationship about the axis X. The substrates W are disposed within the substrate mounting regions **14***a*. The substrate mounting regions **14***a* support the substrates W so that the substrates W are not misaligned during rotation of the mounting table **14**. The substrate mounting regions **14***a* are substantially circular recesses which are substantially identical in shape with the substantially circular substrates W. The diameter of the recesses of the substrate mounting regions **14***a* is substantially equal to the diameter W**1** of the substrates W mounted in the substrate mounting regions **14***a*. That is to say, the diameter of the recesses of the substrate mounting regions **14***a* may be set such that the mounted substrates W are fitted to the recesses and are not displaced from the fitted positions by a centrifugal force even when the mounting table **14** is rotated.

**[0059]** The film forming apparatus **10** includes a gate valve G installed in the outer edge of the process vessel **12** so that the substrates W can be loaded into or unloaded from the process chamber C through the gate valve G by a transfer device such as a robot arm or the like. Furthermore, the film forming apparatus **10** includes an exhaust port **22***h* formed under the outer edge of the mounting table **14**. An exhaust device **52** is connected to the exhaust port **22***h*. The film forming apparatus **10** controls the operation of the exhaust device **52**, thereby maintaining the internal pressure of the process chamber C at a target pressure.

**[0060]** For example, as illustrated in FIG. **3**, the process chamber C includes a first region R**1** and a second region R**2** arranged along the circumferential direction about the axis X. The substrates W mounted in the substrate mounting regions **14***a* sequentially pass through the first region R**1** and the second region R**2** upon rotation of the mounting table **14**.

[One Example of a Configuration of Unit U (Shower Head) and Gas Supply/Exhaust Mechanism]

**[0061]** For example, as illustrated in FIGS. **4** and **5**, the unit U which supplies and exhausts a gas is disposed above the first region R**1** so as to face the upper surface of the mounting table **14**. The unit U has a structure in which a first member M**1**, a second member M**2**, a third member M**3** and a fourth member M**4** are stacked one above another. The unit U is installed in the process vessel **12** so as to make contact with the lower surface of the upper member **12***b* of the process vessel **12**.

**[0062]** In the unit U, a gas supply/exhaust mechanism is installed for supplying and exhausting a desired gas to and from the first region R**1**. The gas supply/exhaust mechanism includes, for example, the first gas supply part **16**, the exhaust part **18** and the second gas supply part **20**.

[One Example of a Configuration of First Gas Supply Part **16**]

**[0063]** For example, as illustrated in FIG. **4**, the first gas supply part **16** includes a first inner gas supply part **161**, a first middle gas supply part **162** and a first outer gas supply part **163**. For example, as illustrated in FIGS. **1** and **4**, the first gas supply part **16** further includes a second inner gas supply part **164**, a second middle gas supply part **165** and a second outer gas supply part **166**. For example, as illustrated in FIGS. **1** and **4**, the first gas supply part **16** further includes a third inner gas supply part **167**, a third middle gas supply part **168** and a third outer gas supply part **169**.

**[0064]** For example, as illustrated in FIGS. **4** and **5**, a gas supply path **161***p*, a gas supply path **162***p* and a gas supply path **163***p* extending through the second member M**2** to the fourth member M**4** are formed in the unit U. The gas supply path **161***p* is connected at its upper end to a gas supply path **121***p* formed in the upper member **12***b* of the process vessel **12**. A gas supply source **16***g* of a first precursor gas is connected to the gas supply path **121***p* via a valve **161***v* and a flow rate controller **161***c* such as a mass flow controller or the like. The first precursor gas is one example of a process gas. Furthermore, the gas supply path **161***p* is connected at its lower end to a buffer space **161***d* formed between the first member M**1** and the second member M**2** and surrounded by an elastic member **161***b*, for example, an O-ring. Injection holes **16***h* of an inner injection part **161***a* installed in the first member M**1** are connected to the buffer space **161***d*.

**[0065]** Furthermore, the gas supply path **162***p* is connected at its upper end to a gas supply path **122***p* formed in the upper member **12***b* of the process vessel **12**. The gas supply source **16***g* of the first precursor gas is connected to the gas supply path **122***p* via a valve **162***v* and a flow rate controller **162***c* such as a mass flow controller or the like. Furthermore, the gas supply path **162***p* is connected at its lower end to a buffer space **162***d* formed between the first member M**1** and the second member M**2** and surrounded by an elastic member **162***b*, for example, an O-ring. Injection holes **16***h* of a middle injection part **162***a* installed in the first member M**1** are connected to the buffer space **162***d*.

**[0066]** Furthermore, the gas supply path **163***p* is connected at its upper end to a gas supply path **123***p* formed in the upper member **12***b* of the process vessel **12**. The gas supply source **16***g* of the first precursor gas is connected to the gas supply path **123***p* via a valve **163***v* and a flow rate controller **163***c* such as a mass flow controller or the like. Furthermore, the gas supply path **163***p* is connected at its lower end to a buffer space **163***d* formed between the first member M**1** and the second member M**2** and surrounded by an elastic member **163***b*, for example, an O-ring. Injection holes **16***h* of an outer injection part **163***a* installed in the first member M**1** are connected to the buffer space **163***d*.

**[0067]** For example, as illustrated in FIGS. **4** and **5**, the buffer space **161***d* of the first inner gas supply part **161**, the buffer space **162***d* of the first middle gas supply part **162** and the buffer space **163***d* of the first outer gas supply part **163** form independent spaces. The flow rates of the first precursor gas flowing through the respective buffer spaces are independently controlled by the flow rate controller **161***c*, the flow rate controller **162***c* and the flow rate controller **163***c*.

**[0068]** The first gas supply part **16** supplies a first precursor gas to the first region R**1** using the first inner gas supply part **161**, the first middle gas supply part **162** and the first outer gas supply part **163** configured as above.

**[0069]** Furthermore, the first gas supply part **16** supplies a purge gas to the first region R**1** using the second inner gas supply part **164**, the second middle gas supply part **165** and the second outer gas supply part **166**. The second inner gas

supply part **164** includes a valve **164**v and a flow rate controller **164**c such as a mass flow controller or the like. A gas supply source **16**i of a purge gas is connected to the gas supply path **121**p via the valve **164**v and the flow rate controller **164**c. Furthermore, the second middle gas supply part **165** includes a valve **165**v and a flow rate controller **165**c such as a mass flow controller or the like. The gas supply source **16**i of the purge gas is connected to the gas supply path **122**p via the valve **165**v and the flow rate controller **165**c. Moreover, the second outer gas supply part **166** includes a valve **166**v and a flow rate controller **166**c such as a mass flow controller or the like. The gas supply source **16**i of the purge gas is connected to the gas supply path **123**p via the valve **166**v and the flow rate controller **166**c.

**[0070]** Furthermore, the first gas supply part **16** supplies a second precursor gas to the first region R**1** using the third inner gas supply part **167**, the third middle gas supply part **168** and the third outer gas supply part **169**. The third inner gas supply part **167** includes a valve **167**v and a flow rate controller **167**c such as a mass flow controller or the like. A gas supply source **16**j of a second precursor gas is connected to the gas supply path **121**p via the valve **167**v and the flow rate controller **167**c. Furthermore, the third middle gas supply part **168** includes a valve **168**v and a flow rate controller **168**c such as a mass flow controller or the like. The gas supply source **16**j of the second precursor gas is connected to the gas supply path **122**p via the valve **168**v and the flow rate controller **168**c. Moreover, the third outer gas supply part **169** includes a valve **169**v and a flow rate controller **169**c such as a mass flow controller or the like. The gas supply source **16**j of the second precursor gas is connected to the gas supply path **123**p via the valve **169**v and the flow rate controller **169**c.

**[0071]** The second inner gas supply part **164**, the second middle gas supply part **165** and the second outer gas supply part **166** of the first gas supply part **16** serve just like the first inner gas supply part **161**, the first middle gas supply part **162** and the first outer gas supply part **163**, respectively. Furthermore, the third inner gas supply part **167**, the third middle gas supply part **168** and the third outer gas supply part **169** of the first gas supply part **16** serve just like the first inner gas supply part **161**, the first middle gas supply part **162** and the first outer gas supply part **163**, respectively.

**[0072]** The first precursor gas forms a Si film on the surface of the substrate W passing through the first region R**1**. The first precursor gas may be, for example, monochlorosilane, dichlorosilane (DCS), trichlorosilane, tetrachlorosilane or hexachlorodisilane (HCD). The first precursor gas is supplied to the first region R**1**. Atoms or molecules of the first precursor gas are chemisorbed onto the surface of the substrate W passing through the first region R**1**.

**[0073]** Furthermore, the second precursor gas nitrides the Si film formed on the surface of the substrate W passing through the first region R**1** and adds carbon to the Si film. Thus, the Si film is changed to a SiCN film. The second precursor gas may be, for example, a gas containing nitrogen and carbon. The second precursor gas may be, for example, a gas including a carbon-containing nitriding agent. The second precursor gas is pyrolyzed in a temperature zone of, for example, 200 degrees C. or more and 550 degrees C. or less, thereby generating an active decomposition product. Examples of the second precursor gas will be described later in detail.

**[0074]** The purge gas is used to remove a process gas from the gas supply parts. The purge gas may be, for example, a gas that does not incur a chemical reaction. The purge gas may be, for example, an inert gas such as argon (Ar) or the like. Furthermore, the purge gas may be, for example, a mixed gas of an Ar gas and an $N_2$ gas.

**[0075]** As described above, in the unit U, the first inner gas supply part **161**, the first middle gas supply part **162** and the first outer gas supply part **163** of the first gas supply part **16** supply the first precursor gas into the first region R**1**. The second inner gas supply part **164**, the second middle gas supply part **165** and the second outer gas supply part **166** of the first gas supply part **16** supply the purge gas into the first region R**1**. The third inner gas supply part **167**, the third middle gas supply part **168** and the third outer gas supply part **169** of the first gas supply part **16** supply the second precursor gas into the first region R**1**.

**[0076]** In this way, by supplying the purge gas after supplying the first precursor gas, it is possible to remove the gas remaining within the gas supply/exhaust mechanism. This makes it possible to supply plural kinds of desired gases to the first region R**1** while preventing mixture of the first precursor gas and the second precursor gas. In the case where a process is not affected by the mixture of the first precursor gas and the second precursor gas, it is not necessary to install a plurality of gas supply/exhaust mechanisms. For example, it may be possible to employ a configuration in which plural kinds of gases are supplied by the first inner gas supply part **161**, the first middle gas supply part **162** and the first outer gas supply part **163**.

[One Example of a Configuration of Second Gas Supply Part **20**]

**[0077]** Next, descriptions will be made on the second gas supply part **20** which supplies a purge gas to a peripheral edge portion of the first region R**1**.

**[0078]** As illustrated in FIGS. **4** and **5**, a gas supply path **20**r extending through the fourth member M**4** is formed in the unit U. The gas supply path **20**r is connected at its upper end to a gas supply path **12**r formed in the upper member **12**b of the process vessel **12**. A gas supply source **20**g of a purge gas is connected to the gas supply path **12**r via a valve **20**v and a flow rate controller **20**c.

**[0079]** The gas supply path **20**r is connected at its lower end to a space **20**d formed between the lower surface of the fourth member M**4** and the upper surface of the third member M**3**. Furthermore, the fourth member M**4** defines a recess that accommodates the first member M**1** to the third member M**3**. A gap **20**p is formed between the inner surface of the fourth member M**4** defining the recess and the outer surface of the third member M**3**. The gap **20**p is connected to the space **20**d. The lower end of the gap **20**p serves as an injection hole **20**a.

**[0080]** Since the injection hole **20**a is formed near the outer edge of the unit U as described above, the first precursor gas and the second precursor gas injected from the injection holes **16**h formed nearer to the center of the unit U are prevented from flowing out of the first region R**1**.

[One Example of a Configuration of Exhaust Part **18**]

**[0081]** Next, descriptions will be made on one example of the exhaust part **18** which exhausts the purge gas injected from the peripheral edge portion of the first region R**1** and

exhausts the first precursor gas, the second precursor gas and the purge gas injected from the central portion of the first region R**1**.

**[0082]** For example, as illustrated in FIGS. **4** and **5**, an exhaust path **18***q* extending through the third member M**3** and the fourth member M**4** is formed in the unit U. The exhaust path **18***q* is connected at its upper end to an exhaust path **12***q* formed in the upper member **12***b* of the process vessel **12**. The exhaust path **12***q* is connected to the exhaust device **34** such as a vacuum pump or the like. Furthermore, the exhaust path **18***q* is connected at its lower end to a space **18***d* formed between the lower surface of the third member M**3** and the upper surface of the second member M**2**.

**[0083]** The third member M**3** includes a recess that accommodates the first member M**1** and the second member M**2**. A gap **18***g* is formed between the inner surface of the third member M**3**, which defines the recess of the third member M**3**, and the outer surfaces of the first member M**1** and the second member M**2**. The space **18***d* is connected to the gap **18***g*. The lower end of the gap **18***g* serves as an exhaust port **18***a*.

**[0084]** As described above, the exhaust port **18***a* is formed between the injection hole **20***a* from which the purge gas is injected and the injection holes **16***h* from which the first and second precursor gases are injected. This makes it possible to efficiently exhaust the purge gas, the first precursor gas and the second precursor gas.

[One Example of Arrangement of Injection Part **16***a*]

**[0085]** For example, as illustrated in FIG. **6**, the injection part **16***a* is installed on the lower surface of the unit U, which faces the mounting table **14**, along a Y-axis direction extending away from the axis X. The region facing the injection part **16***a* among the regions included in the process chamber C is the first region R**1**. The first region R**1** is one example of an adsorption/reaction process region. The injection part **16***a* injects precursor gases toward the substrates W mounted on the mounting table **14**. For example, as illustrated in FIG. **6**, the injection part **16***a* includes the inner injection part **161***a*, the middle injection part **162***a* and the outer injection part **163***a*.

**[0086]** For example, as illustrated in FIG. **6**, the inner injection part **161***a* is formed within an inner annular region A**1** included in the lower surface of the unit U among an annular region existing within a range of distance r**1** to r**2** from the axis X. Furthermore, the middle injection part **162***a* is formed within a middle annular region A**2** included in the lower surface of the unit U among an annular region existing within a range of distance r**2** to r**3** from the axis X. Moreover, the outer injection part **163***a* is formed within an outer annular region A**3** included in the lower surface of the unit U among an annular region existing within a range of distance r**3** to r**4** from the axis X.

**[0087]** The radius r**4** of the outer circumference of the outer annular region A**3** is larger than the radius r**3** of the outer circumference of the middle annular region A**2**. Furthermore, the radius r**3** of the outer circumference of the middle annular region A**2** is larger than the radius r**2** of the outer circumference of the inner annular region A**1**. The inner annular region A**1**, the middle annular region A**2** and the outer annular region A**3** are one example of a first annular region.

**[0088]** For example, as illustrated in FIG. **6**, the length L from r**1** to r**4**, which is the Y-direction extension range of the injection part **16***a* formed on the lower surface of the unit U, is larger than the Y-axis passing length of the substrate W having a diameter W**1**, by a predetermined distance ΔL or more in the direction extending toward the axis X and by a predetermined distance ΔL or more in the direction extending away from the axis X. The predetermined distance ΔL is determined by the distance between the substrate W and the unit U in the direction of the axis X. In the present embodiment, the predetermined distance ΔL may be, for example, several millimeters. The predetermined distance ΔL is one example of a second distance.

**[0089]** For example, as illustrated in FIG. **6**, each of the inner injection part **161***a*, the middle injection part **162***a* and the outer injection part **163***a* includes a plurality of injection holes **16***h*. The first precursor gas and the second precursor gas are injected from the respective injection holes **16***h* to the first region R**1**. As the first precursor gas and the second precursor gas are supplied to the first region R**1**, a film is formed on the surface of the substrate W passing through the first region R**1**, by the atoms or molecules of the first precursor gas and the second precursor gas.

**[0090]** In the present embodiment, in order to enable injection of the precursor gases at different flow rates from the inner injection part **161***a* and the middle injection part **162***a*, for example, as illustrated in FIGS. **4** and **5**, the elastic member **161***b* and the elastic member **162***b* are disposed between the buffer space **161***d* of the first inner gas supply part **161** and the buffer space **162***d* of the first middle gas supply part **162**. Similarly, the elastic member **162***b* and the elastic member **163***b* are disposed between the buffer space **162***d* of the first middle gas supply part **162** and the buffer space **163***d* of the first outer gas supply part **163**. Thus, in the unit U according to the present embodiment, for example, as illustrated in FIG. **6**, a gap (of, for example, about several millimeters) corresponding to the region where the elastic member **161***b* and the elastic member **162***b* are disposed exists in the Y-axis direction between the injection holes **16***h* included in the inner injection part **161***a* and the injection holes **16***h* included in the middle injection part **162***a*. Similarly, a gap (of, for example, about several millimeters) corresponding to the region where the elastic member **162***b* and the elastic member **163***b* are disposed exists in the Y-axis direction between the injection holes **16***h* included in the middle injection part **162***a* and the injection holes **16***h* included in the outer injection part **163***a*.

**[0091]** For example, as illustrated in FIGS. **4** and **5**, the exhaust port **18***a* of the exhaust part **18** is formed above the first region R**1** so as to face the upper surface of the mounting table **14**. For example, as illustrated in FIG. **6**, the exhaust port **18***a* is formed on the lower surface of the unit U so as to surround the periphery of the injection part **16***a*. The gases existing within the process chamber C are exhausted through the exhaust port **18***a* by the operation of the exhaust device **34** such as a vacuum pump or the like.

**[0092]** For example, as illustrated in FIGS. **4** and **5**, the injection hole **20***a* of the second gas supply part **20** is formed above the first region R**1** so as to face the upper surface of the mounting table **14**. For example, as illustrated in FIG. **6**, the injection hole **20***a* is formed on the lower surface of the unit U so as to surround the periphery of the exhaust port **18***a*. The second gas supply part **20** injects the purge gas to the first region R**1** through the injection hole **20***a*. The purge gas injected by the second gas supply part **20** may be, for example, an inert gas such as Ar (argon) or the like. As the purge gas is injected toward the surface of the substrate W,

the atoms or molecules of the first precursor gas and the second precursor gas (the remaining gas components) excessively adhering to the substrate W are removed from the substrate W. Thus, an atomic layer or a molecular layer of the atoms or molecules of the first precursor gas and the second precursor gas are formed on the surface of the substrate W.

**[0093]** The unit U injects the purge gas from the injection hole **20***a* and exhausts the purge gas from the exhaust port **18***a* along the surface of the mounting table **14**. Thus, the unit U restrains the first precursor gas and the second precursor gas supplied to the first region R**1** from being leaked out of the first region R**1**. Since the unit U injects the purge gas from the injection hole **20***a* and exhausts the purge gas from the exhaust port **18***a* along the surface of the mounting table **14**, it is possible for the unit U to restrain the modifying gas or radicals of the modifying gas supplied to the second region R**2** from entering the first region R**1**. That is to say, the unit U separates the first region R**1** and the second region R**2** by injecting the purge gas from the second gas supply part **20** and exhausting the purge gas from the exhaust part **18**.

[One Example of Configuration of Plasma Generation Part **22**]

**[0094]** For example, as illustrated in FIG. **7**, the film forming apparatus **10** includes the plasma generation part **22** installed in an aperture AP of the upper member **12***b* existing above the second region R**2** so as to face the upper surface of the mounting table **14**. The plasma generation part **22** includes the antenna **22***a* and a coaxial waveguide **22***b* configured to supply microwaves and a modifying gas to the antenna **22***a*. For example, three apertures AP are formed in the upper member **12***b*. The film forming apparatus **10** includes, for example, three plasma generation parts **22**.

**[0095]** The plasma generation part **22** supplies a modifying gas and microwaves to the second region R**2** to generate plasma of the modifying gas in the second region R**2**. The nitride film formed on the surface of the substrate W can be modified by an active species generated by the plasma of the modifying gas. As the modifying gas, it may be possible to use, for example, one of an $N_2$ gas, an $NH_3$ gas, an Ar gas, an $H_2$ gas and a He gas, or a mixed gas obtained by appropriately mixing these gases. In the present embodiment, an Ar gas is used as the modifying gas. At a modifying step, the flow rate of the Ar gas may be, for example, 150 sccm.

**[0096]** For example, as illustrated in FIG. **7**, in the plasma generation part **22**, the antenna **22***a* is air-tightly disposed so as to close the aperture AP. The antenna **22***a* includes a top plate **40**, a slot plate **42** and a slow-wave plate **44**. The top plate **40** is a member having a substantially equilateral triangle shape formed of a dielectric body. The top plate **40** may be made of, for example, alumina or ceramic. The top plate **40** is supported by the upper member **12***b* so that the lower surface thereof is exposed to the second region R**2** from the aperture AP formed in the upper member **12***b* of the process vessel **12**. An injection hole **40***d* extending through the top plate **40** in the thickness direction is formed on the lower surface of the top plate **40**.

**[0097]** The slot plate **42** is disposed on the upper surface of the top plate **40**. The slot plate **42** is a plate-shaped metal-made member having a substantially equilateral triangle shape. The slot plate **42** has an opening formed in a position overlapping with the injection hole **40***d* in the direction of the axis X. Furthermore, the slot plate **42** has plural pairs of slots. Each of the slot pairs includes two slot holes orthogonal to each other or intersecting each other.

**[0098]** The slow-wave plate **44** is installed on the upper surface of the slot plate **42**. The slow-wave plate **44** is a member having a substantially equilateral triangle shape formed of a dielectric body. The slow-wave plate **44** may be made of, for example, alumina or ceramic. The slow-wave plate **44** has a substantially cylindrical opening in which an outer conductor **62***b* of the coaxial waveguide **22***b* is disposed.

**[0099]** A metal-made cooling plate **46** is installed on the upper surface of the slow-wave plate **44**. The cooling plate **46** cools the antenna **22***a* through the slow-wave plate **44** using a coolant which flows through a flow path formed within the cooling plate **46**. The cooling plate **46** is pressed against the upper surface of the slow-wave plate **44** by a spring or the like not shown in the drawings. Thus, the lower surface of the cooling plate **46** makes close contact with the upper surface of the slow-wave plate **44**.

**[0100]** The coaxial waveguide **22***b* includes an inner conductor **62***a* and the outer conductor **62***b* which have a substantially cylindrical hollow shape. The inner conductor **62***a* extends from the upper side of the antenna **22***a* and passes through the opening of the slow-wave plate **44** and the opening of the slot plate **42**. A space **64** formed within the inner conductor **62***a* communicates with the injection hole **40***d* of the top plate **40**. Furthermore, a gas supply source **62***g* of a modifying gas is connected to the upper end of the inner conductor **62***a* via a valve **62***v* and a flow rate control part **62***c* such as a mass flow controller or the like. The modifying gas supplied from the valve **62***v* to the coaxial waveguide **22***b* passes through the space **64** formed within the inner conductor **62***a*. Then, the modifying gas is injected from the injection hole **40***d* of the top plate **40** to the second region R**2**.

**[0101]** The outer conductor **62***b* is installed so as to surround the inner conductor **62***a* with a gap left between the outer circumferential surface of the inner conductor **62***a* and the inner circumferential surface of the outer conductor **62***b*. The lower end of the outer conductor **62***b* is connected to an opening portion of the cooling plate **46**.

**[0102]** The film forming apparatus **10** includes a waveguide **60** and a microwave generator **68**. Microwaves of, for example, 2.45 GHz, generated by the microwave generator **68** are propagated to the coaxial waveguide **22***b* through the waveguide **60** and are propagated through a gap between the inner conductor **62***a* and the outer conductor **62***b*. The microwaves propagated through the slow-wave plate **44** are propagated from the slot holes of the slot plate **42** to the top plate **40** and are radiated from the top plate **40** to the second region R**2**.

**[0103]** Furthermore, a modifying gas is also supplied from a modifying gas supply part **22***c* to the second region R**2**. The modifying gas supply part **22***c* includes injection parts **50***b*. For example, the injection parts **50***b* are installed inside the upper member **12***b* of the process vessel **12** so as to extend around the aperture AP. The injection parts **50***b* inject the modifying gas supplied from the gas supply source **50***g* toward the second region R**2** existing under the top plate **40**. The gas supply source **50***g* of the modifying gas is connected to the injection parts **50***b* via a valve **50***v* and a flow rate control part **50***c* such as a mass flow controller or the like.

**[0104]** In the embodiment of the film forming apparatus **10** illustrated in FIG. **7**, the modifying gas supply part **22***c* is installed so as to supply a gas differing from the gas supplied from the gas supply source **62***g*. By employing this configuration, it is possible to use plural kinds of gases as the modifying gas. However, the present disclosure is not limited thereto. The film forming apparatus **10** may be configured so as to supply only one kind of gas. Furthermore, as will be described later, a gas used in a process other than the modifying process may be supplied from the gas supply source **62***g* or the gas supply source **50***g*.

**[0105]** In the plasma generation part **22**, the modifying gas is supplied to the second region R**2** by the injection hole **40***d* of the top plate **40** and the injection parts **50***b* of the modifying gas supply part **22***c*. The microwaves are radiated to the second region R**2** by the antenna **22***a*. Thus, the plasma generation part **22** generates plasma of the modifying gas in the second region R**2**.

**[0106]** As will be described later, in the first embodiment, when forming a SiCN film, an Ar gas is supplied to the second region R**2** during a purge process and a modifying process. Furthermore, when forming an SiOCN film, an $O_2$ gas is supplied to the second region R**2** in order to supply oxygen molecules to the substrate. The Ar gas is supplied to the second region R**2** during the purge process and the modifying process. Thus, the film forming apparatus **10** is configured such that the Ar gas is supplied from the modifying gas supply part **22***c* of the plasma generation part **22** and such that the $O_2$ gas is supplied from the gas supply source **62***g*. The gas to be supplied may be switched in response to a control signal transmitted from a control part **70** which will be described later.

**[0107]** For example, as illustrated in FIG. **1**, the film forming apparatus **10** includes the control part **70** for controlling the respective components of the film forming apparatus **10**. The control part **70** may be a computer which includes a control device such as a central processing unit (CPU) or the like, a memory device such as a memory or the like, and an input/output device. The control part **70** controls the respective components of the film forming apparatus **10** by allowing the CPU to operate according to a control program stored in the memory.

**[0108]** The control part **70** transmits a control signal, which controls the rotation speed of the mounting table **14**, to the drive device **24***a*. Furthermore, the control part **70** transmits a control signal, which controls the temperature of the substrate W, to a power source connected to the heater **26**. Furthermore, the control part **70** transmits a control signal, which controls the flow rates of the first precursor gas, the second precursor gas and the purge gas supplied by the first gas supply part **16**, to the valves **161***v* to **169***v* and the flow rate controllers **161***c* to **169***c*. Furthermore, the control part **70** transmits a control signal, which controls the exhaust amount of the exhaust device **34** connected to the exhaust port **18***a*, to the exhaust device **34**.

**[0109]** Furthermore, the control part **70** transmits a control signal, which controls the flow rate of the purge gas, to the valve **20***v* and the flow rate controller **20***c*. Furthermore, the control part **70** transmits a control signal, which controls the generation power of microwaves, to the microwave generator **68**. Furthermore, the control part **70** transmits a control signal, which controls the flow rate of the modifying gas, to the valve **50***v*, the valve **62***v*, the flow rate control part **50***c* and the flow rate control part **62**. Furthermore, the control part **70** transmits a control signal, which controls the exhaust amount from the exhaust port **22***h*, to the exhaust device **52**.

**[0110]** In the film forming apparatus **10** configured as above, as the mounting table **14** makes rotation, the first precursor gas is injected from the first gas supply part **16** onto the substrate W passing through the first region R**1**. The excessively-chemisorbed first precursor gas is removed from the substrate W by the second gas supply part **20**. Then, when the substrate W passes through the first region R**1** again along with the rotation of the mounting table **14**, the second precursor gas is injected from the first gas supply part **16**. Then, when the substrate W passes through the second region R**2** along with the rotation of the mounting table **14**, the substrate W is exposed to the plasma of the modifying gas generated by the plasma generation part **22**. The film forming apparatus **10** forms a film having a predetermined thickness on the substrate W by repeating the aforementioned operation with respect to the substrate W.

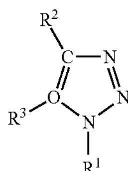
**[0111]** Furthermore, in the film forming apparatus **10** configured as above, as the mounting table **14** makes rotation, the first precursor gas is injected from the first gas supply part **16** onto the substrate W passing through the first region R**1**. Then, when the substrate W passes through the first region R**1** again along with the rotation of the mounting table **14**, the second precursor gas is injected from the first gas supply part **16** to the substrate W passing through the first region R**1**. Then, when the substrate W passes through the second region R**2** along with the rotation of the mounting table **14**, a third gas (e.g., an $O_2$ gas) supplied from the plasma generation part **22** is injected onto the substrate W. Then, when the substrate W passes through the second region R**2** again along with the rotation of the mounting table **14**, the substrate W is exposed to the plasma of the modifying gas generated by the plasma generation part **22**. The film forming apparatus **10** forms a film having a predetermined thickness on the substrate W by repeating the aforementioned operation with respect to the substrate W.

[One Example of a Second Precursor Gas]

**[0112]** In the first embodiment, the first precursor gas and the second precursor gas are supplied to the first region R**1**, thereby forming a SiCN film or a SiOCN film. At this time, when forming the SiCN film or the SiOCN film, nitriding can be realized using heat treatment without using plasma.

**[0113]** In the case where a SiC film is nitrided without using plasma, the deposition temperature is set low. However, if the deposition temperature falls within a temperature zone of, for example, less than 630 degrees C., the deposition rate is sharply reduced as compared with a case where plasma is used. Thus, in order to maintain a high deposition rate while reducing the deposition temperature, a gas to be described below may be used as the second precursor gas.

**[0114]** Hereinafter, as one example of the second precursor gas, a gas including a carbon-containing nitriding agent will be described. The gas includes a nitriding agent. The nitriding agent is a compound of nitrogen and carbon, which is represented by the following chemical formula (1).




**[0115]** In chemical formula (1), R', $R^2$ and $R^3$ are linear or branched alkyl groups having 1 to 8 carbon atoms, which may have hydrogen atoms or substituents. The compound represented by chemical formula (1) is a 1,2,3-triazole-based compound.

**[0116]** Examples of the linear or branched alkyl groups having 1 to 8 carbon atoms may include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a t-butyl group, an n-pentyl group, an isopentyl group, a t-pentyl group, an n-hexyl group, an isohexyl group, a t-hexyl group, an n-heptyl group, an isoheptyl group, a t-heptyl group, an n-octyl group, an isooctyl group and a t-octyl group. Specifically, the linear or branched alkyl groups may be the methyl group, the ethyl group or the n-propyl group. More specifically, the linear or branched alkyl groups may be the methyl group.

**[0117]** Furthermore, the substituent may be a linear or branched monoalkylamino group or dialkylamino group substituted with an alkyl group having 1 to 4 carbon atoms. For example, the substituent may be a monomethylamino group, a dimethylamino group, a monoethylamino group, a diethylamino group, a monopropylamino group, a monoisopropylamino group or an ethylmethylamino group. Specifically, the substituent may be the monomethylamino group or the dimethylamino group. More specifically, the substituent may be the dimethylamino group.

**[0118]** Furthermore, the substituent may be a linear or branched alkoxy group having 1 to 8 carbon atoms. For example, the substituent may be a methoxy group, an ethoxy group, a propoxy group, a butoxy group, a pentoxy group, a hexyloxy group, a heptyloxy group or an octyloxy group. Specifically, the substituent may be the methoxy group, the ethoxy group or the propoxy group. More specifically, the substituent may be the methoxy group.

**[0119]** Examples of the specific compound represented by chemical formula (1) may include 1H-1,2,3-triazole, 1-methyl-1,2,3-triazole, 1,4-dimethyl-1,2,3-triazole, 1,4,5-trimethyl-1,2,3 triazole, 1-ethyl-1,2,3-triazole, 1,4-diethyl-1,2,3-triazole and 1,4,5-triethyl-1,2,3-triazole. These compounds may be used either independently or in combination.

**[0120]** In the case where the gas including a carbon-containing nitriding agent is used as the second precursor gas, the nitriding and the C adding can be simultaneously performed during the same step using one kind of compound. This is because the 1,2,3-triazole-based compound contains N atoms and C atoms. Thus, a step of carbonizing a Si film or a step of carbonizing a SiN film becomes unnecessary. It is therefore possible to enhance the throughput.

**[0121]** Furthermore, in the case where the gas including a carbon-containing nitriding agent is used as the second precursor gas, it is possible to maintain a high deposition rate even when the deposition temperature is reduced.

**[0122]** The 1,2,3-triazole-based compound contains an "N═N—N" bond within a five-membered ring. In the "N═N—N" bond, the "N═N" portion tends to be decomposed to become nitrogen ($N_2$, N═N). Thus, the 1,2,3-triazole-based compound, unlike the usual ring-opening cleavage, has a tendency to undergo cleavage and decomposition at a plurality of points. That is to say, the 1,2,3-triazole-based compound generates "N≡N". Thus, an electronically unsaturated state occurs within the compound. A decomposition product obtained as a result of cleavage and decomposition of the 1,2,3-triazole-based compound is active. For that reason, even when the deposition temperature is low and falls within a temperature range of, for example, 200 degrees C. or more and 550 degrees C. or less, it is possible to nitride a Si film and, ultimately, to add C.

**[0123]** Furthermore, in the case where a film is formed using the gas including a carbon-containing nitriding agent, it is possible to produce a C-rich SiCN film. Furthermore, the additional amount of C can be adjusted by controlling the flow rate of the 1,2,3-triazole-based compound. Thus, after producing the C-rich film, a modifying process is performed using plasma, thereby removing easily-desorbed C. In this state, a film forming process is further performed. This makes it possible to improve film quality.

[One Example of a Flow of the Film Forming Process According to the First Embodiment (in the Case of SiCN Film)]

**[0124]** Next, one example of a flow of a film forming process of a SiCN film using the film forming apparatus **10** according to the first embodiment will be described with reference to FIG. **8**. FIG. **8** is a flowchart illustrating a flow of one example of a film forming process of a SiCN film implemented in the film forming apparatus **10** according to the first embodiment.

**[0125]** In the film forming process illustrated in FIG. **8**, a silicon wafer having a $SiO_2$ film formed on the surface thereof may be used as the substrate W. However, the film formed on the substrate W is not limited to the $SiO_2$ film but may be any film that enables formation of a SiCN film. Hexachlorodisilane (HCD) may be used as a Si precursor gas which is the first precursor gas. As the second precursor gas, it may be possible to use a gas including the aforementioned 1H-1,2,3-triazole as the carbon-containing nitriding agent.

**[0126]** As illustrated in FIG. **8**, in the case of forming a SiCN film on the substrate W, the substrate W is first mounted in each of the substrate mounting regions **14*a*** and then the operation of the film forming apparatus **10** is started. That is to say, the control of the film forming apparatus **10** using the control part **70** is started. As the mounting table **14** rotates, the substrate W is first moved into the first region R**1**. At this time, in the first gas supply part **16**, the respective valves and the respective flow rate controllers are controlled so that the first precursor gas is supplied to the first region R**1**. Then, the first precursor gas is supplied by the first gas supply part **16** (the first inner gas supply part **161**, the first middle gas supply part **162** and the first outer gas supply part **163**) and is injected toward the substrate W (step S**701**). The first precursor gas is a Si precursor gas. By virtue of step S**701**, a Si film is formed on the substrate W.

**[0127]** After the substrate W has passed through the first region R**1**, the respective valves and the respective flow rate

controllers of the first gas supply part **16** are controlled so that the purge gas is supplied. Then, the first precursor gas remaining in the supply system of the first gas supply part **16** is purged (step S**702**).

**[0128]** If the substrate W is moved into the first region R**1** again, the respective valves and the respective flow rate controllers of the first gas supply part **16** are controlled so as to supply the second precursor gas. Then, the first gas supply part **16** (the third inner gas supply part **167**, the third middle gas supply part **168** and the third outer gas supply part **169**) supplies the second precursor gas and injects the second precursor gas toward the substrate W (step S**703**). The second precursor gas may be, for example, a gas including a carbon-containing nitriding agent. By virtue of step S**703**, a SiCN film is formed on the substrate W.

**[0129]** After the substrate W has passed through the first region R**1**, the respective valves and the respective flow rate controllers of the first gas supply part **16** are controlled so that the purge gas is supplied. Then, the second precursor gas remaining in the supply system of the first gas supply part **16** is purged (step S**704**).

**[0130]** Subsequently, the film forming apparatus **10**, namely the control part **70**, determines whether the processes of steps S**701** to S**704** have been performed a predetermined number of times (step S**705**). If the control part **70** determines that the processes of steps S**701** to S**704** have not been performed a predetermined number of times (if "No" at step S**705**), the flow comes back to step S**701** where the supply of the first precursor gas is performed by the first gas supply part **16**. On the other hand, if it is determined that the processes of steps S**701** to S**704** have been performed a predetermined number of times (if "Yes" at step S**705**), the control part **70** causes the plasma generation part **22** to supply the modifying gas, thereby performing a plasma cure (modifying process) (step S**706**). Then, the control part **70** determines whether the plasma cure has been performed a predetermined number of times (step S**707**). If it is determined that the plasma cure has not been performed a predetermined number of times (if "No" at step S**707**), the control part **70** controls the film forming apparatus **10** so as to perform the process of step S**701** again. On the other hand, if it is determined that the plasma cure has been performed a predetermined number of times (if "Yes" at step S**707**), the control part **70** terminates the processes.

**[0131]** In this way, the first precursor gas and the second precursor gas are supplied to the first region R**1** and the modifying gas for the modifying process is supplied to the second region R**2**. That is to say, the thermal process and the modifying process using plasma are combined and realized in the semi-batch apparatus. Furthermore, the plasma generation part **22** may be configured such that when not performing the plasma cure, an Ar gas is supplied and exhausted to perform a purge operation. In the unit U, the exhaust part **18** and the second gas supply part **20** are always operated during the process to prevent the first precursor gas and the second precursor gas from flowing out of the first region R**1** and to prevent the plasma from entering the first region R**1**.

**[0132]** FIG. **9** is a schematic view for explaining the flow of one example of the film forming process of the SiCN film implemented in the film forming apparatus **10** according to the first embodiment. One example of the film forming process of the SiCN film performed in the film forming apparatus **10** will be described again with reference to FIG. **9**.

**[0133]** As illustrated in FIG. **9**, if the film forming process is started, when the mounting table **14** makes a first rotation, a Si precursor gas as the first precursor gas, namely DCS, is injected onto the substrate W by the first gas supply part **16** ((**1**) in FIG. **9**). When injecting the DCS, the supply of the purge gas using the second gas supply part **20** and the exhaust using the exhaust part **18** are also performed. The substrate W passed through the first region R**1** passes through the plasma region, namely the second region R**2**. At this time, the plasma generation part **22** is controlled so as to supply an Ar gas as the purge gas without performing the generation and supply of the modifying plasma ((1) in FIG. **9**). By the process performed during the first rotation, a Si film is formed on the substrate W.

**[0134]** If the mounting table **14** comes into a second rotation, the first gas supply part **16** is controlled so as to supply the purge gas to the first region R1 ((2) in FIG. **9**). The reason for supplying the purge gas from the first gas supply part **16** at this step is to purge the first precursor gas remaining within the first gas supply part **16** and to prevent the first precursor gas from being mixed with the second precursor gas supplied at the third rotation of the mounting table **14**. Even at the second rotation, similar to the first rotation, the Ar gas is supplied to the plasma region to perform a purge operation.

**[0135]** If the mounting table **14** comes into a third rotation, the first gas supply part **16** supplies a gas (C+N) including a carbon-containing nitriding agent, which is the second precursor gas, to the first region R1 ((3) in FIG. **9**). Thus, the Si film formed on the substrate W is nitrided and carbon is implanted into the substrate w, whereby a SiCN film is formed. At this time, ammonia ($NH_3$) may be supplied together with the gas including a carbon-containing nitriding agent. By supplying $NH_3$ together with the gas including a carbon-containing nitriding agent, it is possible to increase the deposition rate. Particularly, in the case where it is difficult to increase a gas flow rate by increasing a vapor pressure in the second region R**2**, the use of $NH_3$ makes it possible to increase the production efficiency. Even at the third rotation, similar to the first and second rotations, the Ar gas is supplied to the plasma region to perform a purge operation.

**[0136]** At a fourth rotation, similar to the second rotation, the first gas supply part **16** supplies the Ar gas as the purge gas to the first region R1 to perform a purge operation. Similarly, the Ar gas is also supplied to the plasma region to perform a purge operation ((4) in FIG. **9**).

**[0137]** The processes (1) to (4) in FIG. **9** are repeatedly performed until a SiCN film having a predetermined film thickness is formed. In the example illustrated in FIG. **9**, the processes (1) to (4) are performed N cycles (where N is an arbitrary natural number).

**[0138]** If a SiCN film having a predetermined thickness is formed by performing the processes (1) to (4) in FIG. **9** N cycles, at the next rotation, the purge gas is supplied to the first region R**1** by the first gas supply part **16**. Furthermore, the modifying gas is supplied to the plasma region, namely the second region R**2**, by the plasma generation part **22** to generate plasma of the modifying gas ((5) in FIG. **9**). Then, the SiCN film formed on the substrate W is exposed to the plasma of the modifying gas, whereby the carbon atoms not

sufficiently adsorbed to the substrate W are removed from the substrate W. In the example of the process (5) illustrated in FIG. **9**, the modifying process is performed in all three plasma generation parts **22** provided in the film forming apparatus **10**. However, the present disclosure is not limited thereto. The modifying process may be performed only in one or two plasma generation parts **22** and the purge gas may be supplied in the remaining plasma generation part **22**.

**[0139]** At the next rotation after the modifying process is completed, similar to the second rotation and the fourth rotation, the first gas supply part **16** supplies the purge gas. The supply of the purge gas is performed even in the plasma region ((6) in FIG. **9**). Then, the flow comes back to the process (1) to repeat the processes. After repeatedly performing the SiCN film forming processes (1) to (4), the insufficiently-adsorbed carbon atoms are removed by the plasma cure ((5) in FIG. **9**). Then, the SiCN film forming processes are repeated again. Thus, the film quality can be increased by leaving the carbon atoms sufficiently adsorbed to the film. By performing the plasma cure, it is possible to strengthen the bonding state of the already-adsorbed carbon atoms within the SiCN film and to improve the film quality. In FIG. **9**, the portions indicated by Ex are exhaust portions.

[One Example of the Flow of a Film Forming Process According to the First Embodiment (in the Case of SiOCN Film (1))]

**[0140]** FIG. **10** is a flowchart illustrating a flow of one example of a film forming process of a SiOCN film implemented in the film forming apparatus **10** according to the first embodiment. As illustrated in FIG. **10**, in the case of forming a SiOCN film on the substrate W, the substrate W is first mounted in each of the substrate mounting regions **14***a* and then the operation of the film forming apparatus **10** is started. That is to say, the control of the film forming apparatus **10** using the control part **70** is started. As the mounting table **14** rotates, the substrate W is first moved into the first region R**1**. At this time, in the first gas supply part **16**, the respective valves and the respective flow rate controllers are controlled so that the first precursor gas is supplied to the first region R**1**. Then, the first precursor gas is supplied by the first gas supply part **16** and is injected toward the substrate W (step S**901**). The first precursor gas may be, for example, a Si precursor gas such as DCS or the like. By virtue of step S**901**, a Si film is formed on the substrate W.

**[0141]** After the substrate W has passed through the first region R**1**, the respective valves and the respective flow rate controllers of the first gas supply part **16** are controlled so that the purge gas is supplied. Then, the first precursor gas remaining in the supply system of the first gas supply part **16** is purged (step S**902**). If the substrate W is moved into the first region R**1** again, the respective valves and the respective flow rate controllers of the first gas supply part **16** are controlled so as to supply the second precursor gas. Then, the first gas supply part **16** supplies the second precursor gas and injects the second precursor gas toward the substrate W (step S**903**). The second precursor gas may be, for example, a gas including a carbon-containing nitriding agent. By virtue of step S**903**, a SiCN film is formed on the substrate W.

**[0142]** After the substrate W has passed through the first region R**1**, the respective valves and the respective flow rate controllers of the first gas supply part **16** are controlled so that the purge gas is supplied. Then, the second precursor gas remaining in the supply system of the first gas supply part **16** is purged (step S**904**).

**[0143]** Subsequently, the film forming apparatus **10**, namely the control part **70**, determines whether the processes of steps S**901** to S**904** have been performed a predetermined number of times (step S**905**). If the control part **70** determines that the processes of steps S**901** to S**904** have not been performed a predetermined number of times (if "No" at step S**905**), the flow comes back to step S**901** where the supply of the first precursor gas is performed by the first gas supply part **16**. On the other hand, if it is determined that the processes of steps S**901** to S**904** have been performed a predetermined number of times (if "Yes" at step S**905**), the control part **70** causes the plasma generation part **22** to supply a third gas to the plasma region, namely the second region R**2** (step S**906**). In the present embodiment, an $O_2$ gas is supplied as the third gas. By virtue of step S**906**, a SiOCN film is formed on the substrate W.

**[0144]** With regard to the switching of the gases supplied to the plasma region, for example, the plasma generation part **22** is configured such that the Ar gas is supplied from the gas supply source **62***g* and the $O_2$ gas is supplied from the gas supply source **50***g*. The supply timings of different kinds of gases may be controlled in conformity with the rotation of the mounting table **14**. At the next rotation of the mounting table **14**, the purge gas is supplied from the plasma generation part **22** to the plasma region to perform a purge operation (step S**907**).

**[0145]** Subsequently, the control part **70** determines whether the processes of steps S**906** and S**907** have been performed a predetermined number of times (step S**908**). If the control part **70** determines that the processes of steps S**906** and S**907** have not been performed a predetermined number of times (if "No" at step S**908**), the flow comes back to step S**906** to repeat the processes. On the other hand, if it is determined that the processes of steps S**906** and S**907** have been performed a predetermined number of times (if "Yes" at step S**908**), the control part **70** causes the plasma generation part **22** to supply the modifying gas, thereby performing a plasma cure (step S**909**). For example, an Ar gas is supplied as the modifying gas. At the next rotation, the purge gas is supplied to both the first region R**1** and the second region R**2** (step S**910**). Then, the control part **70** determines whether the plasma cure has been performed a predetermined number of times (step S**911**). If it is determined that the plasma cure has not been performed a predetermined number of times (if "No" at step S**911**), the control part **70** controls the film forming apparatus **10** so as to perform the process of step S**901** again. On the other hand, if it is determined that the plasma cure has been performed a predetermined number of times (if "Yes" at step S**911**), the control part **70** terminates the processes. In this way, a modified SiOCN film is formed on the substrate W.

**[0146]** FIG. **11** is a schematic view for explaining the flow of one example of the film forming process of the SiOCN film implemented in the film forming apparatus **10** according to the first embodiment. The processes (1) to (4) illustrated in FIG. **11** are the same as the processes (1) to (4) illustrated in FIG. **9**. Furthermore, the process (1) illustrated in FIG. **11** corresponds to the process of step S**901** illustrated in FIG. **10**. The process (2) illustrated in FIG. **11** corresponds to the process of step S**902** illustrated in FIG. **10**. The process (3) illustrated in FIG. **11** corresponds to the process

of step **S903** illustrated in FIG. **10**. The process (4) illustrated in FIG. **11** corresponds to the process of step **S904** illustrated in FIG. **10**. By virtue of the processes (1) to (4) illustrated in FIG. **11**, a SiCN film is formed on the substrate W.

**[0147]** In the example illustrated in FIG. **11**, the processes (1) to (4) are repeatedly performed N cycles. After the processes (1) to (4) are performed N cycles, as in the process (5) illustrated in FIG. **11**, an Ar gas is supplied to the first region **R1** to perform a purge operation. Furthermore, an Ar gas and an $O_2$ gas are supplied to the second region **R2** by the plasma generation part **22** so that oxygen atoms are adsorbed to the substrate W. At the next rotation of the mounting table **14**, an Ar gas is supplied to the first region **R1** and the second region **R2** to perform a purge operation ((6) in FIG. **11**). Similar to the processes (1) to (4), the processes (5) and (6) illustrated in FIG. **11** are performed N cycles. Furthermore, the processes (5) and (6) illustrated in FIG. **11** correspond to steps **S906** and **S907** illustrated in FIG. **10**.

**[0148]** After the processes (5) and (6) illustrated in FIG. **11** are performed N cycles, a plasma cure is performed in the second region **R2** while supplying the Ar gas to the first region **R1** to perform a purge operation. That is to say, the Ar gas as the modifying gas is supplied by the plasma generation part **22**, thereby generating plasma of the modifying gas and curing the SiOCN film formed on the substrate W ((7) in FIG. **11**). At the next rotation of the mounting table **14**, the Ar gas is supplied again to both the first region **R1** and second region **R2** to perform a purge operation ((8) in FIG. **11**).

**[0149]** In the example illustrated in FIGS. **10** and **11**, the supply of the Si precursor gas and the supply of the gas including the carbon-containing nitriding agent are first performed a predetermined number of times (steps **S901** to **S904** in FIG. **10** and processes (1) to (4) in FIG. **11**). Thus, a SiCN film is formed on the substrate W. Thereafter, the supply of a gas including oxygen is repeated a predetermined number of times (steps **S906** and **S907** in FIG. **10** and processes (5) and (6) in FIG. **11**). Thus, a SiOCN film is formed on the substrate W. Then, a plasma cure is performed to remove the carbon atoms not sufficiently fixed to the interior of the film at this step (steps **S909** and **S910** in FIG. **10** and processes (7) and (8) in FIG. **11**). Then, the flow comes back to the process of supplying the first precursor gas and the second precursor gas (the Si precursor gas and the gas including a carbon-containing nitriding agent), thereby performing the formation process of the SiCN film and the supply process of the oxygen atoms. By repeating the processes while removing the weakly-bonded carbon atoms in this way, it is possible to strengthen the bonds between the atoms included in the film and to improve the film quality.

**[0150]** In the example of the process (5) illustrated in FIG. **11**, the Ar gas and the $O_2$ gas are supplied from all three plasma generation parts **22**. However, the present disclosure is not limited thereto. The number of the plasma generation parts **22** that supplies the $O_2$ gas may be adjusted depending on the amount of $O_2$ to be adsorbed.

[One Example of the Flow of a Film Forming Process According to the First Embodiment (in the Case of SiOCN Film (2))]

**[0151]** FIG. **12** is a flowchart illustrating a flow of another example of the film forming process of the SiOCN film implemented in the film forming apparatus **10** according to the first embodiment. The processes of steps **S1101** to **S1104**, **S1105**, **S1107** and **S1108** illustrated in FIG. **12** are the same as the processes of steps **S901** to **S903**, **S906**, **S907** and **S909** to **S911** illustrated in FIG. **10**. The processes illustrated in FIG. **12** differ from the processes illustrated in FIG. **10** in that the number of times of the formation process of the SiCN film and the number of times of the supply process of the of the oxygen atoms are collectively determined in the processes illustrated in FIG. **12** whereas the number of times of the formation process of the SiCN film and the number of times of the supply process of the of the oxygen atoms are independently determined in the processes illustrated in FIG. **10**. In other respects, the processes illustrated in FIG. **12** are the same as the processes illustrated in FIG. **10**.

**[0152]** As illustrated in FIG. **12**, in the case of forming a SiOCN film on the substrate W, the substrate W is first mounted in each of the substrate mounting regions **14*a*** and then the operation of the film forming apparatus **10** is started. That is to say, the control of the film forming apparatus **10** using the control part **70** is started. As the mounting table **14** rotates, the substrate W is first moved into the first region **R1**. At this time, in the first gas supply part **16**, the respective valves and the respective flow rate controllers are controlled so that the first precursor gas is supplied to the first region **R1**. Then, the first precursor gas is supplied by the first gas supply part **16** and is injected toward the substrate W (step **S1101**). The first precursor gas may be, for example, a Si precursor gas such as DCS or the like.

**[0153]** After the substrate W has passed through the first region **R1**, the respective valves and the respective flow rate controllers of the first gas supply part **16** are controlled so that the purge gas is supplied. Then, the first precursor gas remaining in the supply system of the first gas supply part **16** is purged (step **S1102**). If the substrate W is moved into the first region **R1** again, the respective valves and the respective flow rate controllers of the first gas supply part **16** are controlled so as to supply the second precursor gas. Then, the first gas supply part **16** supplies the second precursor gas and injects the second precursor gas toward the substrate W (step **S1103**). The second precursor gas may be, for example, a gas including a carbon-containing nitriding agent. Thus, a SiCN film is formed on the substrate W.

**[0154]** During the rotation at which the second precursor gas is supplied, the control part **70** causes the plasma generation part **22** to supply a third gas (an oxygen-containing gas) to the plasma region, namely the second region **R2** (step **S1104**). At the next rotation of the mounting table **14**, the first gas supply part **16** is caused to supply the purge gas to the first region **R1** and the plasma generation part **22** is caused to supply the purge gas to the plasma region (step **S1105**).

**[0155]** Subsequently, the control part **70** determines whether the processes of steps **S1101** to **S1105** have been performed a predetermined number of times (step **S1106**). If the control part **70** determines that the processes of steps **S1101** to **S1105** have not been performed a predetermined number of times (if "No" at step **S1106**), the flow comes back to step **S1101** to repeat the processes. On the other hand, if it is determined that the processes of steps **S1101** to **S1105** have been performed a predetermined number of times (if "Yes" at step **S1106**), the control part **70** causes the

plasma generation part **22** to supply the modifying gas, thereby performing a plasma cure (step S**1107**). At the next rotation, the purge gas is supplied to both the first region R**1** and the second region R**2** (step S**1108**). Then, the control part **70** determines whether the plasma cure has been performed a predetermined number of times (step S**1109**). If it is determined that the plasma cure has not been performed a predetermined number of times (if "No" at step S**1109**), the control part **70** controls the film forming apparatus **10** so as to perform the process of step S**1101** again. On the other hand, if it is determined that the plasma cure has been performed a predetermined number of times (if "Yes" at step S**1109**), the control part **70** terminates the processes. In this way, a SiOCN film is formed on the substrate W.

**[0156]** FIG. **13** is a schematic view for explaining the flow of another example of the film forming process of the SiOCN film implemented in the film forming apparatus **10** according to the first embodiment. The processes illustrated in FIG. **13** differ from the processes illustrated in FIG. **11** in that the second precursor gas and the oxygen-containing gas (the third gas) are supplied during the same rotation. The processes (1), (2) and (4) to (6) illustrated in FIG. **13** are the same as the processes (1), (2) and (6) to (8) illustrated in FIG. **11**. Hereinafter, descriptions on the same processes as the processes illustrated in FIG. **11** will be omitted.

**[0157]** In the processes illustrated in FIG. **13**, the Si precursor gas is supplied and the purge operation is performed by the processes (1) and (2), thereby forming a Si film. At the next rotation, the gas including a carbon-containing nitriding agent is supplied to the first region R**1** and the Ar gas and the $O_2$ gas are supplied to the second region R**2** ((3) in FIG. **13**). Even at this time, by operating the second gas supply part **20** and the exhaust part **18** disposed in the first region R**1**, the first region R**1** and the second region R**2** are separated from each other so that the gas existing in the first region R**1** and the gas existing in the second region R**2** are not mixed with each other. Then, at the next rotation, the purge gas is supplied to both the first region R**1** and the second region R**2**, thereby removing the residual gas ((4) in FIG. **13**).

**[0158]** In the processes illustrated in FIG. **13**, the processes (1) to (4) are first performed N cycles, thereby forming a SiOCN film. Thereafter, a plasma cure is performed ((5) in FIG. **13**). By virtue of the plasma cure, the atoms not sufficiently adsorbed in the processes (1) to (4) are removed while leaving only the sufficiently-bonded atoms. Thereafter, the first region R**1** and the second region R**2** are purged with an Ar gas ((6) in FIG. **13**). If the number of times of the plasma cure fails to reach a predetermined number of times, the flow comes back to the process (1) to repeat the formation process of the SiOCN film. As described above, even in the processes illustrated in FIG. **13**, by repeating the film forming process while removing the weakly-bonded atoms, it is possible to strengthen the bonds between the atoms included in the film and to improve the film quality.

**[0159]** Furthermore, in the first embodiment, the rotation speed of the mounting table **14** when performing the film forming process may be adjusted depending on the process contents. For example, in the film forming process of the SiOCN film illustrated in FIG. **11**, the rotation speed of the mounting table **14** may be adjusted so that the processes (1), (2) and (4) to (8) are performed during one rotation of 12 seconds and the process (3) is performed during one rotation of 18 seconds. This makes it possible to reliably perform the process at every rotation and to reliably proceed to the process at the next rotation.

Effects of the First Embodiment

**[0160]** As described above, the film forming method according to the first embodiment is directed to a film forming method for forming a nitride film on a workpiece substrate accommodated within a process vessel. The film forming method according to the first embodiment includes a first reaction step of supplying a first precursor gas to the workpiece substrate accommodated within the process vessel, a second reaction step of supplying a second precursor gas to the workpiece substrate accommodated within the process vessel, and a modifying step of generating plasma of a modifying gas just above the workpiece substrate by supplying the modifying gas into the process vessel and supplying microwaves from an antenna into the process vessel, and plasma-processing, by the plasma thus generated, a surface of the workpiece substrate subjected to the first and second reaction steps using the first and second precursor gases. In this way, a film is formed by independently injecting two kinds of precursor gases toward the substrate. Thereafter, plasma of the modifying gas is generated. The workpiece is exposed to the plasma thus generated. Thus, among the materials existing within the film thus generated, a weakly-bonded material can be removed while leaving only a strongly-bonded material. This makes it possible to improve the film quality of a nitride film as formed. Furthermore, by modifying the film with the plasma, it is possible to realize modification while suppressing damage to the film. In addition, the probability of adsorption of the respective materials to the substrate and the modification using the plasma can be realized at a desired level by adjusting the process conditions.

**[0161]** Furthermore, in the film forming method according to the first embodiment, the first precursor gas contains silicon and the second precursor gas contains carbon atoms and nitrogen atoms. Thus, a SiCN film can be formed by the film forming method. It is possible to leave strongly-bonded carbon atoms while removing carbon atoms weakly bonded to silicon. Furthermore, by performing the modifying process with the plasma, it is possible to expect the improvement of a bonding state of carbon atoms.

**[0162]** Furthermore, in the film forming method according to the first embodiment, the modifying step is performed once each time when the first reaction step and the second reaction step are repeatedly performed a predetermined number of times. Thus, by additionally performing the first reaction step and the second reaction step using the first and second precursor gases after the weakly-bonded material is removed by the modifying step, it is possible to adjust the amount of the materials contained in the film and to improve the bonding state of the materials within the film. Furthermore, by adjusting the number of repetition times of the first reaction step and the second reaction step and adjusting the number of performing times of the modifying step, it is possible to easily adjust the film quality.

**[0163]** Furthermore, the film forming method according to the first embodiment further includes a third reaction step of supplying a third gas to the workpiece substrate accommodated within the process vessel and a removal step of purging a mechanism for supplying the first precursor gas, the second precursor gas and the third gas, which is per-

formed after the first reaction step, the second reaction step and the third reaction step but before the modifying step. Thus, a material differing from the material for forming a film on the substrate at the first reaction step and the second reaction step can be supplied to the substrate at the third reaction step. Furthermore, the gases used in forming a film at the first reaction step, the second reaction step and the third reaction step are purged before performing the modifying step. This makes it possible to prevent different kinds of gases from being mixed with each other and to prevent the plasma of the modifying gas from being mixed with other gases. It is therefore possible to easily perform a film forming process using plural kinds of gases.

**[0164]** Furthermore, in the film forming method according to the first embodiment, the first precursor gas contains one of monochlorosilane, dichlorosilane, trichlorosilane, tetrachlorosilane and hexachlorodisilane. This makes it possible to form a Si film on the substrate at the first reaction step. In addition, by using, for example, carbon, nitrogen or oxygen as the material for forming a film on the substrate at the second reaction step and the third reaction step, it is possible to form a SiOCN film, a SiCN film or the like.

**[0165]** Furthermore, in the film forming method according to the first embodiment, the second precursor gas is supplied into the process vessel together with ammonia. Thus, for example, in the case where a gas including a carbon-containing nitriding agent is used as the second precursor gas, it is possible to increase the deposition rate while maintaining the deposition temperature at a low temperature. Particularly, even if the internal vapor pressure of the process vessel is low and the gas flow rate is low, it is possible to increase the deposition rate and to enhance the production efficiency. Furthermore, since the deposition is performed by allowing silicon to be adsorbed at the first reaction step and by introducing nitrogen or carbon together with ammonia at the second reaction step, it is possible to prevent different kinds of gases from being mixed with each other and to prevent generation of an undesired reaction.

**[0166]** Furthermore, in the film forming method according to the first embodiment, the second precursor gas is pyrolyzed at a temperature of 200 degrees C. or more and 550 degrees C. or less. This makes it possible to reduce a deposition temperature and to reduce a thermal budget.

**[0167]** Furthermore, in the film forming method according to the first embodiment, the modifying gas may be a mixed gas of $NH_3$ and $H_2$. This makes it possible to easily perform the modification of a film using a mechanism of related art for performing a plasma generation process.

**[0168]** Furthermore, the film forming apparatus according to the first embodiment is a semi-batch-type film forming apparatus. Therefore, as compared with a batch-type apparatus in which multiple substrates are simultaneously processed, it is possible to reduce an in-plane or inter-plane variation of the film thickness or the film composition. Furthermore, as compared with a single-substrate-type apparatus in which substrates are processed one by one, the semi-batch-type film forming apparatus can improve the productivity. In addition, since a mechanism for supplying plural kinds of gases is installed in the shower head, it is possible to easily realize ternary deposition while preventing different gases from being unintentionally mixed with each other.

## Second Embodiment

**[0169]** In the first embodiment, the film forming method is realized by the semi-batch-type film forming apparatus including one shower head and three plasma generation parts (antennas). Next, as a second embodiment, a film forming apparatus including two shower heads and two plasma generation parts (antennas) will be described.

**[0170]** In the first embodiment, plural kinds of precursor gases are supplied from one shower head. Mixing of gases is prevented by installing the gas supply/exhaust mechanism. Furthermore, by allowing the plasma generation parts to supply the Ar gas and the $O_2$ gas, the reaction process using plural kinds of gases and the modifying process using plasma are realized by one shower head and three plasma generation parts.

**[0171]** In contrast, in the second embodiment, two shower heads are installed so that different precursor gases can be supplied from different shower heads. Furthermore, by forming the two shower heads at different sizes, the adsorption/reaction time of the materials included in the respective precursor gases is adjusted. Thus, the size of a space for adsorption or reaction process can be adjusted by adjusting the size of the shower heads depending on the vapor pressure used in processing the respective materials or the time required in adsorption or reaction of the respective materials.

**[0172]** Furthermore, in the second embodiment, structures for supplying a purge gas are provided between the two shower heads and around the two shower heads to prevent the gases supplied from the two shower heads from being mixed with each other. Furthermore, the structures prevent plasma of a modifying gas from entering a region to which gases are supplied from the two shower heads.

[One Example of a Configuration of Film Forming Apparatus **100** according to the Second Embodiment]

**[0173]** A film forming apparatus **100** according to a second embodiment will be described.

**[0174]** The configuration of the film forming apparatus **100** according to the second embodiment is substantially the same as the configuration of the film forming apparatus **10** according to the first embodiment. Hereinafter, descriptions will be made on the points differing from the film forming apparatus **10** according to the first embodiment.

**[0175]** FIG. **14** is a sectional view illustrating one example of the film forming apparatus **100** according to the second embodiment. FIG. **15** is a top view illustrating one example of the film forming apparatus **100** according to the second embodiment. FIG. **16** is a plan view illustrating one example of a state in which a top portion of a process vessel is removed from the film forming apparatus **100** illustrated in FIG. **15**. FIG. **14** shows a cross section taken along line A-A in FIGS. **15** and **16**. FIG. **17** is a view illustrating one example of an arrangement of injection holes of a shower head provided in the film forming apparatus **100** according to the second embodiment. FIG. **18** is a view for explaining the relationship between the arrangement of the injection holes of the shower head and the quality of films as formed. FIG. **19** is a schematic sectional view illustrating a configuration of two shower heads in the film forming apparatus **100** according to the second embodiment. The film forming apparatus **100** illustrated in FIGS. **14** to **19** includes a process vessel **112** and a mounting table **114**. The film forming apparatus **100** further includes first gas supply parts **116**A and **116**B, exhaust parts **118**A and **118**B, a second gas supply part **120** and plasma generation parts **122**.

**[0176]** As illustrated in FIG. **14**, the film forming apparatus **100** is substantially identical in configuration with the film forming apparatus **10**. However, as illustrated in FIGS. **15** to **19**, the film forming apparatus **100** includes two plasma generation parts **122** (antennas **122***a*) and two units U**1** and U**2**, namely two shower heads, for supplying precursor gases. Hereinafter, the term "two shower heads" refer to the entire structure formed by the units U**1** and U**2**.

**[0177]** Referring to FIG. **14**, the process vessel **112** of the film forming apparatus **100** includes a lower member **112***a* and an upper member **112***b*. The film forming apparatus **100** further includes the mounting table **114** disposed within a process chamber C defined by the process vessel **112**. The mounting table **114** is rotationally driven about an axis X by a drive mechanism **124**. The drive mechanism **124** includes a drive device **124***a* such as a motor or the like and a rotary shaft **124***b*. The drive mechanism **124** is installed in the lower member **112***a* of the process vessel **112**.

**[0178]** The unit U**1** provided with an injection part **17***a* (see FIG. **17**) and the unit U**2** provided with an injection part **17***b* (see FIG. **17**) are installed in the process chamber C defined within the process vessel **112**. The units U**1** and U**2** are one example of shower heads. Details of the units U**1** and U**2** will be described later.

**[0179]** The film forming apparatus **100** further includes a plurality of plasma generation parts **122** disposed in the process vessel **112**. Each of the plasma generation parts **122** includes an antenna **122***a* disposed above the process vessel **112** and configured to output microwaves. In the example illustrated in FIGS. **14** to **16**, the film forming apparatus **100** includes two plasma generation parts **122** and two antennas **122***a*. However, the number of plasma generation parts **122** and the number of the antennas **122***a* are not limited to two but may be one or three or more.

**[0180]** As illustrated in FIG. **16**, the film forming apparatus **100** includes a mounting table **114** having a plurality of substrate mounting regions **114***a* formed on the upper surface thereof. The mounting table **114** is a substantially disc-shaped member. The substrate mounting regions **114***a* for holding substrates W are formed on the upper surface of the mounting table **114** (six substrate mounting regions **114***a* are formed in the example illustrated in FIG. **16**).

**[0181]** As illustrated in FIG. **16**, the process chamber C includes a first region R**1** and a second region R**2** arranged along the circumferential direction about the axis X. The substrates W mounted in the substrate mounting regions **114***a* sequentially pass through the first region R**1** and the second region R**2** upon rotation of the mounting table **114**. The first region R**1** corresponds substantially to a position where the units U**1** and U**2** are disposed. Furthermore, the second region R**2** corresponds substantially to a position where the plasma generation parts **122** are disposed.

**[0182]** The film forming apparatus **100** includes a gate valve G installed in the outer edge of the process vessel **112**. Furthermore, the film forming apparatus **100** includes an exhaust port **122***h* formed under the outer edge of the mounting table **114**. An exhaust device **152** is connected to the exhaust port **122***h* so as to maintain the internal pressure of the process chamber C at a target pressure.

**[0183]** The film forming apparatus **100** includes plasma generation parts **122** installed in apertures AP of the upper member **112***b* existing above the second region R**2** so as to face the upper surface of the mounting table **114**. Each of the plasma generation parts **122** includes an antenna **122***a* and a coaxial waveguide **122***b* configured to supply microwaves and a modifying gas to the antenna **122***a*. For example, three apertures AP are formed in the upper member **112***b*. The film forming apparatus **100** includes, for example, two plasma generation parts **122**. The plasma generation parts **122** supplies a modifying gas and microwaves to the second region R**2**, thereby generating plasma of the modifying gas in the second region R**2**.

**[0184]** A gas supply source **262***g* of a modifying gas is connected to the upper end of an inner conductor **262***a* of the coaxial waveguide **122***b* via a valve **262***v* and a flow rate control part **262***c* such as a mass flow controller or the like. The modifying gas supplied from the valve **262***v* to the coaxial waveguide **122***b* is injected to the second region R**2**. The film forming apparatus **100** further includes a waveguide **260** and a microwave generator **268**.

**[0185]** Furthermore, a modifying gas is also supplied from a modifying gas supply part **122***c* to the second region R**2**. The modifying gas supply part **122***c* includes injection parts **150***b*. For example, the injection parts **150***b* are installed inside the upper member **112***b* of the process vessel **112** so as to extend around the apertures AP. The injection parts **150***b* inject the modifying gas supplied from the gas supply source **150***g* toward the second region R**2**. The gas supply source **150***g* of the modifying gas is connected to the injection parts **150***b* via a valve **150***v* and a flow rate control part **150***c* such as a mass flow controller or the like. The film forming apparatus **100** further includes a control part **170**.

**[0186]** Unless specifically mentioned otherwise, the respective components of the film forming apparatus **100** have the same configurations and functions as those of the corresponding components of the film forming apparatus **10** of the first embodiment.

[One Example of the Configuration of a Shower Head According to the Second Embodiment]

**[0187]** The configuration of the shower head according to the second embodiment will be further described with reference to FIGS. **17** to **19**. As illustrated in FIG. **17**, the shower head according to the second embodiment includes two shower heads, namely units U**1** and U**2**, which supply gases to the first region R**1**. All the cross sections of the units U**1** and U**2** taken along a radial direction passing the axis X of the mounting table **114** have the shape illustrated in FIG. **14**. The units U**1** and U**2** are disposed along the circumferential direction (rotation direction) of the mounting table **114** as illustrated in FIG. **19**.

**[0188]** As illustrated in FIG. **19**, similar to the unit U of the first embodiment, each of the units U**1** and U**2** has a structure in which a first member, a second member, a third member and a fourth member are stacked one above another. However, unlike the unit U of the first embodiment, the units U**1** and U**2** are configured by first members, second members and third members differing from each other and are connected by a common fourth member.

**[0189]** In the unit U**1**, a second member M**2***a* is disposed on a first member M**1***a* provided with injection holes **116***h* communicating with a process space through which the substrates W pass. A space into which precursor gases are supplied is formed between the first member M**1***a* and the second member M**2***a*. Furthermore, a third member M**3***a* is disposed on the second member M**2***a*. A space communicating with the process space through which the substrates W pass is formed between the second member M**2***a* and the

third member M**3**$a$. An exhaust port **118**$a$ is formed by the portion in which the space formed between the second member M**2**$a$ and the third member M**3**$a$ communicates with the process space. As illustrated in FIG. **14**, the exhaust port **118**$a$ is connected to an exhaust device **134**A such as a vacuum pump or the like.

**[0190]** Similarly, in the unit U**2**, a second member M**2**$b$ is disposed on a first member M**1**$b$ provided with injection holes **116**$h$ communicating with a process space through which the substrates W pass. A space into which precursor gases are supplied is formed between the first member M**1**$b$ and the second member M**2**$b$. Furthermore, a third member M**3**$b$ is disposed on the second member M**2**$b$. A space communicating with the process space through which the substrates W pass is formed between the second member M**2**$b$ and the third member M**3**$b$. An exhaust port **118**$b$ is formed by the portion in which the space formed between the second member M**2**$b$ and the third member M**3**$b$ communicates with the process space. As illustrated in FIG. **14**, the exhaust port **118**$b$ is connected to an exhaust device **134**B such as a vacuum pump or the like.

**[0191]** A fourth member M**4**$ab$ is disposed so as to cover the third member M**3**$a$ constituting the unit U**1** and the third member M**3**$b$ constituting the unit U**2**. The fourth member M**4**$ab$ is a member common to the units U**1** and U**2**. Spaces into which a purge gas is supplied are formed between the third member M**3**$a$ and the fourth member M**4**$ab$ and between the third member M**3**$b$ and the fourth member M**4**$ab$.

**[0192]** Next, flow routes of precursor gases supplied from the units U**1** and U**2** will be described with reference to FIG. **14**. Although the cross-sectional structure of the unit U**2** is illustrated in FIG. **14**, the cross-sectional structure of the unit U**1** is the same as the cross-sectional structure of the unit U**2**. In FIG. **14**, reference symbols of components of the unit U**1** are indicated in parentheses in the case where the units U**1** and U**2** include different corresponding components.

**[0193]** The unit U**1** includes the first gas supply part **116**A independent from the unit U**2**. As illustrated in FIG. **14**, the first gas supply part **116**A includes an inner gas supply part **1161**A, a middle gas supply part **1162**A and an outer gas supply part **1163**A. The inner gas supply part **1161**A, the middle gas supply part **1162**A and the outer gas supply part **1163**A are identical in configuration with the first inner gas supply part **161**, the first middle gas supply part **162** and the first outer gas supply part **163** of the first embodiment, respectively. The first gas supply part **116**A extends through the fourth member M**4**$ab$ and the third member M**3**$a$ and supplies a first precursor gas (indicated by "A" in FIG. **19**) from the injection holes **116**$h$ into the process space of the first region R**1** through a gas flow path communicating with spaces formed between the third member M**3**$a$ and the second member M**2**$a$ and between the third member M**3**$a$ and the first member M**1**$a$.

**[0194]** The unit U**1** further includes an exhaust part **118**A independent from the unit U**2**. The configuration of the exhaust part **118**A is the same as the configuration of the exhaust part **18** of the first embodiment. The exhaust part **118**A includes the aforementioned exhaust device **134**A. The exhaust part **118**A extends through the fourth member M**4**$ab$ and the third member M**3**$a$. The exhaust part **118**A exhausts the gas existing within the process space from the exhaust port **118**$a$ through a gas flow path communicating with a space formed between the third member M**3**$a$ and the second member M**2**$a$.

**[0195]** The unit U**1** further includes the second gas supply part **120** common to the unit U**2**. The second gas supply part **120** is the same as the second gas supply part **20** of the first embodiment. However, the gas flow paths formed within the units U**1** and U**2** differ from the gas flow path formed within the unit U of the first embodiment. As illustrated in FIG. **19**, the second gas supply part **120** extends through the fourth member M**4**$ab$ and injects a purge gas (indicated by "P" in FIG. **19**) from injection holes **120**$a$, **120**$b$ and **120**$ab$ into the process space (the first region R**1**) through gas flow paths formed between the fourth member M**4**$ab$ and the third member M**3**$a$ and between the fourth member M**4**$ab$ and the third member M**3**$b$.

**[0196]** The unit U**2** includes the first gas supply part **116**B independent from the unit U**1**. As illustrated in FIG. **14**, the first gas supply part **116**B includes an inner gas supply part **1161**B, a middle gas supply part **1162**B and an outer gas supply part **1163**B. The inner gas supply part **1161**B, the middle gas supply part **1162**B and the outer gas supply part **1163**B are identical in configuration with the first inner gas supply part **161**, the first middle gas supply part **162** and the first outer gas supply part **163** of the first embodiment, respectively. The first gas supply part **116**B extends through the fourth member M**4**$ab$ and the third member M**3**$b$ and supplies a second precursor gas (indicated by "B" in FIG. **19**) into the process space of the first region R**1** through a gas flow path communicating with spaces formed between the third member M**3**$b$ and the second member M**2**$b$ and between the third member M**3**$b$ and the first member M**1**$b$.

**[0197]** The unit U**2** further includes the exhaust part **118**B independent from the unit U**1**. The configuration of the exhaust part **118**B is the same as the configuration of the exhaust part **18** of the first embodiment. The exhaust part **118**B includes the aforementioned exhaust device **134**B. The exhaust part **118**B extends through the fourth member M**4**$ab$ and the third member M**3**$b$. The exhaust part **118**B exhausts the gas existing within the process space from an exhaust port **118**$b$ through a gas flow path communicating with a space formed between the third member M**3**$b$ and the second member M**2**$b$.

**[0198]** The unit U**2** further includes the second gas supply part **120** common to the unit U**1**.

**[0199]** As described above, the unit U**1** as a supply system for supplying the first precursor gas and the unit U**2** as a supply system for supplying the second precursor gas are provided independently of each other, thereby preventing mixing of gases. Furthermore, the exhaust ports **118**$a$ and **118**$b$ of the exhaust part **118**A and the exhaust part **118**B are disposed between the space into which the first precursor gas is supplied from the injection hole **116**$h$ of the unit U**1** and the space into which the second precursor gas is supplied from the injection hole **116**$h$ of the unit U**2**. Thus, the first precursor gas supplied from the unit U**1** is exhausted by the exhaust part **118**A and the second precursor gas supplied from the unit U**2** is exhausted by the exhaust part **118**B. Accordingly, the first precursor gas and the second precursor gas are exhausted through different exhaust ports and are prevented from being mixed with each other.

**[0200]** Furthermore, the second gas supply part **120** for supplying the purge gas is installed in common to the units U**1** and U**2**, thereby supplying the purge gas so as to

surround the entirety of the units U**1** and U**2**. That is to say, as illustrated in FIG. **19**, the purge gas is injected toward the process space from between the fourth member M**4***ab* and the third member M**3***a* and from between the fourth member M**4***ab* and the third member M**3***b* (from the injection holes **120***a* and **120***b*). The exhaust ports **118***a* and **118***b* are respectively disposed closer to the centers of the respective units than the injection holes **120***a* and **120***b* from which the purge gas is injected. Thus, the residual first precursor gas and the residual second precursor gas are exhausted from the exhaust ports **118***a* and **118***b*. The purge gas is drawn inward from the outer peripheries of the respective units and is exhausted together with the respective precursor gases.

**[0201]** Thus, it is possible to prevent the first and second precursor gases supplied from the two shower heads from flowing out of the first region R**1**. Furthermore, it is possible to prevent the plasma generated in the second region R**2** from entering the first region R**1**. Since the purge gas is supplied by installing the second gas supply part **120** common to the units U**1** and U**2**, it is possible to prevent the plasma from entering the space formed between the units U**1** and U**2**.

[One Example of Arrangement of Injection Holes of Two Shower Heads]

**[0202]** Referring back to FIG. **17**, one example of an arrangement of the injection holes of the two shower heads will be further described. The unit U**1** includes the injection part **17***a* and the unit U**2** includes the injection part **17***b*. The injection part **17***a* includes an inner injection part **171***a*, a middle injection part **172***a* and an outer injection part **173***a*. The injection part **17***b* includes an inner injection part **171***b*, a middle injection part **172***b* and an outer injection part **173***b*. The injection parts **17***a* and **17***b* are substantially identical in configuration with each other. However, as illustrated in FIG. **17**, the inner injection part **171***a*, the middle injection part **172***a* and the outer injection part **173***a* are separated from one another by linear partitions (elastic members) (see **161***b*, **162***b* and **163***b* in FIG. **6**), whereas the inner injection part **171***b*, the middle injection part **172***b* and the outer injection part **173***b* are separated from one another by curved partitions (elastic members).

**[0203]** First, descriptions will be made on the injection part **17***a* of the unit U**1**. Each of the inner injection part **171***a*, the middle injection part **172***a* and the outer injection part **173***a* of the injection part **17***a* includes a plurality of injection holes **116***h* (see FIG. **14**). In the unit U**1**, the first precursor gas is injected from the inner injection part **171***a*, the middle injection part **172***a* and the outer injection part **173***a* into the first region R**1** through the inner gas supply part **1161**A, the middle gas supply part **1162**A and the outer gas supply part **1163**A. As illustrated in FIG. **19**, the first precursor gas supplied from a gas supply source passes through the gas supply path extending through the fourth member M**4***ab*, the third member M**3***a* and the second member M**2***a* and reaches the space formed between the first member M**1***a* and the second member M**2***a*. Then, the first precursor gas is supplied from the space formed between the first member M**1***a* and the second member M**2***a* to the injection holes **116***h* formed in the first member M**1***a* and is injected toward the first region R**1**. As illustrated in FIG. **14**, the flow spaces of the gas supplied from the inner gas supply part **1161**A, the middle gas supply part **1162**A and the outer gas supply part **1163**A are separated from one another by the elastic member installed between the first member M**1***a* and the second member M**2***a*. Thus, by controlling the flow rate control parts installed in the respective gas supply parts, it is possible to supply the gases at different flow rates from the inner injection part **171***a*, the middle injection part **172***a* and the outer injection part **173***a*.

**[0204]** Subsequently, descriptions will be made on the injection part **17***b* of the unit U**2**. Each of the inner injection part **171***b*, the middle injection part **172***b* and the outer injection part **173***b* of the injection part **17***b* includes a plurality of injection holes **116***h* (see FIG. **14**). In the unit U**2**, the second precursor gas is injected from the inner injection part **171***b*, the middle injection part **172***b* and the outer injection part **173***b* into the first region R**1** through the inner gas supply part **1161**B, the middle gas supply part **1162**B and the outer gas supply part **1163**B. As illustrated in FIG. **19**, the second precursor gas supplied from a gas supply source passes through the gas supply path extending through the fourth member M**4***ab*, the third member M**3***b* and the second member M**2***b* and reaches the space formed between the first member M**1***b* and the second member M**2***b*. Then, the second precursor gas is supplied from the space formed between the first member M**1***b* and the second member M**2***b* to the injection holes **116***h* formed in the first member M**1***b* and is injected toward the first region R**1**. As illustrated in FIG. **14**, the flow spaces of the gas supplied from the inner gas supply part **1161**B, the middle gas supply part **1162**B and the outer gas supply part **1163**B are separated from one another by the elastic member installed between the first member M**1***b* and the second member M**2***b*. Thus, by controlling the flow rate control parts installed in the respective gas supply parts, it is possible to supply the gases at different flow rates from the inner injection part **171***b*, the middle injection part **172***b* and the outer injection part **173***b*.

[Arrangement Angle and Shape of Elastic Member]

**[0205]** As illustrated in FIG. **17**, the inner injection part **171***a*, the middle injection part **172***a* and the outer injection part **173***a* are partitioned by the elastic members having a substantially linear shape. The elastic members are disposed so as to obliquely intersect a straight line extending in the radial direction of the substantially-circular mounting table **114** from the axis X of the film forming apparatus **100**. Descriptions will be made on the reason why the longitudinal direction of the elastic members is disposed at an angle inclined with respect to the radial direction of the mounting table **114**.

**[0206]** FIGS. **18**A to **18**D are views for explaining the relationship between the arrangement of the injection holes of the shower head and the quality of a film as formed. At the left side in each of FIGS. **18**A to **18**D, there is illustrated an example of arrangement of the inner injection part, the middle injection part and the outer injection part. Furthermore, at the right side in each of FIGS. **18**A to **18**D, there is illustrated the relationship between the number of injection holes (gas holes) passing through the respective radial positions on the substrate W and the respective radial positions on the substrate W in the case where the arrangement of the injection parts illustrated at the left side is employed.

**[0207]** Referring first to FIG. **18**A, the elastic members are disposed so that the longitudinal direction of the elastic members intersects the radial direction of the mounting table **114** at a right angle. In the example illustrated in FIG. **18**A,

the radial length of the inner injection part is about 45 mm, the radial length of the middle injection part is about 200 mm, and radial length of the outer injection part is about 45 mm. In this case, as indicated by arrows in the right graph of FIG. **18**A, little injection holes exist in the radial positions where the elastic members are disposed. For that reason, when the substrate W passes under the unit U**1**, the precursor gas is not sufficiently injected to the radial positions of the substrate W corresponding to the elastic members.

**[0208]** Referring to FIG. **18**B, the elastic members are disposed so that the longitudinal direction of the elastic members extends obliquely at about 5 degrees with respect to the direction perpendicular to the radial direction of the mounting table **114**. In this case, as compared with the example illustrated in FIG. **18**A, the positions on the substrate W, above which the injection holes do not pass, are reduced. However, as indicated by an arrow in FIG. **18**B, the position through which the injection holes do not pass still exists.

**[0209]** Referring to FIG. **18**C, the elastic members are disposed so that the longitudinal direction of the elastic members extends obliquely at about 10 degrees with respect to the direction perpendicular to the radial direction of the mounting table **114**. In this case, the positions on the substrate W, above which the injection holes do not pass, are eliminated. The precursor gas is injected from the injection holes in all the positions on the substrate W.

**[0210]** Referring to FIG. **18**D, the elastic members are disposed so that the longitudinal direction of the elastic members extends obliquely at about 15 degrees with respect to the direction perpendicular to the radial direction of the mounting table **114**. In this case, the positions on the substrate W, above which the injection holes do not pass, are eliminated. However, the number of injection holes passing above the positions on the substrate W decreases in the radial outermost position (the position indicated by an arrow in FIG. **18**D).

**[0211]** As described above, the amount of the precursor gas injected on the substrate W varies depending on the arrangement angle of the elastic members. Thus, the flow rate of the gas injected from each of the inner injection part, the middle injection part and the outer injection part is adjusted and the shape of the injection parts is determined by adjusting the arrangement angle or the shape of the elastic members. In the second embodiment, the injection part **17***a* of the unit U**1** has the shape illustrated in FIG. **18**C so that the precursor gas can be injected on the substrate W in all the radial positions.

[Difference Between Injection Part of Unit U1 and Injection Part of Unit U2]

**[0212]** In the second embodiment, the injection part **17***a* of the unit U**1** and the injection part **17***b* of the unit U**2** are formed with different sizes, and the shapes and arrangement directions of the elastic members within the injection parts **17***a* and **17***b* are made to be different from each other.

**[0213]** In the second embodiment, the unit U**1** supplies and injects the first precursor gas, and the unit U**2** supplies and injects the second precursor gas. Depending on the properties of the gases introduced as the first precursor gas and the second precursor gas, there may be a case where different reaction time periods are required in order to enable the molecules of the precursor gases to be sufficiently adsorbed onto the substrate W. Thus, in order to ensure that the molecules of the precursor gases used in deposition are adsorbed onto the substrate W at a desired amount, the sizes of the units U**1** and U**2** are adjusted. By doing so, the time period during which the substrate W is exposed to the precursor gases is adjusted.

**[0214]** For example, it is assumed that the first precursor gas supplied from the unit U**1** is sufficiently adsorbed onto the substrate W even when the reaction time is short and further that the second precursor gas supplied from the unit U**2** is not sufficiently adsorbed onto the substrate W unless the reaction time of the second precursor gas is set longer than the reaction time of the first precursor gas. In this case, the unit U**2** is formed to become larger than the unit U**1** so that the molecules of the respective precursor gases are sufficiently adsorbed onto the substrate W.

**[0215]** If the elastic members have the same shape in the case where the sizes of the units U**1** and U**2** are made different as described above, there may be a case where, due to the difference in the rotation angles of the respective units, the number of the injection holes in the respective positions of the substrate W is not necessarily set at a desired number. For example, if the elastic members are formed of substantially linear members as illustrated in FIGS. **18**A to **18**D, even when the injection part is configured as in the left diagram of FIG. **18**A, the number of injection holes deviates from the right graph of FIG. **18**A as the rotation angle of the unit grows larger. In view of this point, in the second embodiment, the elastic members of the unit U**2**, which is a larger one of the two units, are formed in a curved shape as illustrated in FIG. **17**.

**[0216]** The shape of the elastic members of the units U**1** and U**2** is not necessarily limited to the shape illustrated in FIG. **17**. For example, the size of the units U**1** and U**2** may be changed depending on the properties of the precursor gases used. For example, the unit U**2** may be formed at a size five times or six times larger than the size of the unit U**1**. For example, the unit U**2** may be formed in a semicircular shape. In this case, the number of the plasma generation part (antenna) may be one.

[One Example of the Flow of a Film Forming Process According to the Second Embodiment (in the Case of SiCN Film)]

**[0217]** FIG. **20** is a flowchart illustrating one example of a film forming process of a SiCN film implemented in the film forming apparatus **100** according to the second embodiment. As illustrated in FIG. **20**, in the case of forming a SiCN film on the substrate W, the substrate W is first mounted in each of the substrate mounting regions **114***a* and then the operation of the film forming apparatus **100** is started. The control of the film forming apparatus **100** using the control part **170** is started. As the mounting table **114** rotates, the substrate W is moved into the first region R**1**. The first gas supply part **116**A of the unit U**1** supplies the first precursor gas to the first region R**1** (step S**1701**). The first precursor gas may be, for example, a Si precursor gas such as DCS or the like. Thus, a Si film is formed on the substrate W.

**[0218]** Subsequently, the substrate W passes under the unit U**1** and passes through a region between the units U**1** and U**2**. At this time, the purge gas is injected from the second gas supply part **120** onto the substrate W. The purge gas thus injected is drawn and exhausted by the exhaust port **118***a* of the exhaust part **118**A of the unit U**1** and the exhaust port

**118**_b_ of the exhaust part **118**B of the unit U**2**. Then, the substrate W passes under the unit U**2**. At this time, the first gas supply part **116**B of the unit U**2** supplies the second precursor gas to the first region R**1** (step S**1702**). The second precursor gas may be, for example, a gas including a carbon-containing nitriding agent. Thus, a SiCN film is formed on the substrate W. As described in the first embodiment, a gas including a 1H-1,2,3-triazole may be used as the second precursor gas.

**[0219]** Then, the control part **170** of the film forming apparatus **100** determines whether steps **S1701** and **S1702** have been performed a predetermined number of times (step S**1703**). If it is determined that the steps S**1701** and S**1702** have not been performed a predetermined number of times (if "No" at step S**1703**), the control part **170** continues to rotate the mounting table **114** so that the substrate W passes through the second region R**2** and comes back to the first region R**1**, thereby repeating steps S**1701** and S**1702**.

**[0220]** On the other hand, if it is determined that the steps S**1701** and S**1702** have been performed a predetermined number of times (if "Yes" at step S**1703**), the control part **170** causes the plasma generation part **122** to perform a plasma supply process in the second region R**2** through which the substrate W passes. First, the control part **170** controls the plasma generation part **122** so as to supply a modifying gas and microwaves ("plasma-on" at step S**1704**). Then, plasma of the modifying gas is generated by the plasma generation part **122** and is radiated into the second region R**2**. The substrate W passing through the second region R**2** is exposed to the plasma of the modifying gas, whereby a plasma cure is performed (step S**1705**). After the substrate W passes through the second region R**2**, the control part **170** determines whether the processes of steps S**1704** and S**1705** have been performed a predetermined number of times (step S**1706**). If it is determined that the processes of steps S**1704** and S**1705** have not been performed a predetermined number of times (if "No" at step S**1706**), the control part **170** rotates the mounting table **114** and returns the substrate W to the first region R**1**. Thus, the flow comes back to the process of step S**1701**. On the other hand, if it is determined that the processes of steps S**1704** and S**1705** have been performed a predetermined number of times (if "Yes" at step S**1706**), the control part **170** terminates the processes. Thus, a modified SiCN film is formed on the substrate W.

**[0221]** FIG. **21** is a schematic view for explaining the flow of one example of the film forming process of the SiCN film implemented in the film forming apparatus **100** according to the second embodiment. In the example illustrated in FIG. **21**, the unit U**1** of the film forming apparatus **100** is formed at such a size as to occupy a region having a rotation angle of about 30 degrees, and the unit U**2** is formed at such a size as to occupy a region having a rotation angle of about 180 degrees. DCS is used as the first precursor gas. A gas including a carbon-containing nitriding agent and ammonia are used as the second precursor gas. Furthermore, the film forming apparatus **100** includes one plasma generation part **122**.

**[0222]** In this film forming apparatus **100**, the substrate W is first moved into the first region R**1** along with the rotation of the mounting table **114**. Then, DCS is injected toward the substrate W by the first gas supply part **116**A of the unit U**1** disposed above the first region R**1** (corresponding to step S**1701** in FIG. **20**). Thus, a Si film is formed on the substrate W.

**[0223]** Then, the substrate W is moved to under the unit U**2**. The first gas supply part **116**B of the unit U**2** injects a mixed gas of a gas including a carbon-containing nitriding agent and ammonia toward the substrate W (corresponding to step S**1702** in FIG. **20**). Thus, a SiCN film is formed on the substrate W. If the substrate W has not passed through the first region R**1** a predetermined number of times (if "No" at step S**1703** in FIG. **20**), the control part **170** rotates the mounting table **114** so that the substrate W passes through the second region R**2**. At this time, the plasma generation part **122** does not perform the supply of plasma of the modifying gas. Then, the control part **170** allows the substrate W to come back to the first region R**1**. Thereafter, the control part **170** causes the unit U**1** to supply DCS and causes the unit U**2** to supply a gas including a carbon-containing nitriding agent and ammonia, thereby continuously performing the formation of the SiCN film. On the other hand, if the formation on the substrate W of the SiCN film in the first region R**1** has been performed a predetermined number of times (if "Yes" at step S**1703** in FIG. **20**), the control part **170** causes the plasma generation part **122** to start generation of plasma of the modifying gas at the timing at which the substrate W is moved into the second region R**2** (step S**1704** in FIG. **20**). Then, the plasma generation part **122** has the substrate W exposed to the plasma of the modifying gas, thereby performing modification (plasma cure) of the SiCN film formed on the substrate W over a predetermined number of times (step S**1705** in FIG. **20**). If the plasma cure is performed a predetermined number of times with respect to one substrate W, the process is completed. In the example illustrated in FIG. **21**, for example, the mounting table **114** is rotated N times so that the processes of steps S**1701** to S**1705** are performed N cycles.

**[0224]** Furthermore, while supplying the first precursor gas and the second precursor gas, the supply of the purge gas from the second gas supply part **120** and the exhaust using the exhaust parts **118**A and **118**B are continuously performed.

**[0225]** As described above, in the film forming method of the SiCN film according to the second embodiment, it is possible to perform three processes, namely the deposition using the first precursor gas, the deposition using the second precursor gas and the plasma cure, by rotating the mounting table **114** once. Furthermore, the process of performing the plasma cure after the deposition using the first and second precursor gases is performed a predetermined number of times and then repeating the deposition using the first precursor gas and the deposition using the second precursor gas, can be easily performed by the on/off control of the plasma generation part **122**. Furthermore, by the supply of the purge gas using the second gas supply part **120** and the exhaust using the exhaust parts **118**A and **118**B, it is possible to prevent the plasma of the modifying gas from moving into a region between the units U**1** and U**2**. Similarly, it is possible to prevent the first precursor gas and the second precursor gas from being mixed with each other. Furthermore, the reaction time of the precursor gases can be adjusted by adjusting the sizes of the units U**1** and U**2**. This makes it possible to realize deposition using the molecules or atoms included in the precursor gases at a desired amount.

In addition, by setting the performing frequency of the plasma cure in association with the number of times of formation of the SiCN film, it is possible to adjust the amount of molecules or atoms removed by the plasma cure.

[One Example of the Flow of a Film Forming Process According to the Second Embodiment (in the Case of SiOCN Film)]

**[0226]** FIG. **22** is a flowchart illustrating one example of a film forming process of a SiOCN film implemented in the film forming apparatus **100** according to the second embodiment. FIG. **23** is a schematic view for explaining the flow of one example of the film forming process of the SiOCN film implemented in the film forming apparatus **100** according to the second embodiment.

**[0227]** As illustrated in FIG. **22**, in the case of forming a SiOCN film on the substrate W, the substrate W is first mounted in each of the substrate mounting regions **114***a* and then the operation of the film forming apparatus **100** is started. That is to say, the control of the film forming apparatus **100** using the control part **170** is started. As the mounting table **114** makes rotation, the substrate W is moved into the first region R**1**. At this time, in the first gas supply part **116**A of the unit U**1**, the respective valves and the respective flow rate controllers are controlled so that the first precursor gas is supplied to the first region R**1**. Then, the first precursor gas is supplied by the first gas supply part **116**A and is injected toward the substrate W (step S**1901**). The first precursor gas may be, for example, a Si precursor gas such as DCS or the like. Thus, a Si film is formed on the substrate W.

**[0228]** The substrate W passes under the unit U**1** and enters a region between the units U**1** and U**2**. At this time, the purge gas is supplied from the second gas supply part **120** and is injected onto the substrate W. Furthermore, the first precursor gas and the second precursor gas are exhausted by the exhaust parts **118**A and **118**B, respectively. The purge gas is also exhausted. Thus, the excessive molecules or atoms adhering to the substrate W are removed. In addition, the plasma or the like is prevented from moving into a region between the units U**1** and U**2**.

**[0229]** Subsequently, the substrate W passes under the unit U**2**. At this time, in the first gas supply part **116**B of the unit U**2**, the respective valves and the respective flow rate controllers are controlled so that the second precursor gas is supplied to the first region R**1**. Then, the second precursor gas is supplied by the first gas supply part **116**B and is injected toward the substrate W (step S**1902**). The second precursor gas may be, for example, a mixed gas of a gas including a carbon-containing nitriding agent and ammonia. Thus, a SiCN film is formed on the substrate W.

**[0230]** Thereafter, the substrate W passes through the first region R**1** and then enters the second region R**2**. At this time, the plasma generation part **122** is controlled so as to supply a third gas without supplying microwaves. The term "third gas" refers to an oxygen-containing gas such as, for example, a mixed gas of an Ar gas and an $O_2$ gas. Then, the oxygen-containing gas is injected toward the substrate W by the plasma generation part **122** (step S**1903**). Thus, a SiOCN film is formed on the substrate W.

**[0231]** After the substrate W passes through the second region R**2**, the control part **170** determines whether the processes of steps S**1901** to S**1903** have been performed a predetermined number of times (step S**1904**). If it is determined that the processes of steps S**1901** to S**1903** have not been performed a predetermined number of times (if "No" at step S**1904**), the control part **170** further rotates the mounting table **114** and sends the substrate W to the first region R**1** again, thereby repeating the processes from step S**1901**. On the other hand, if it is determined that the processes of steps S**1901** to S**1903** have been performed a predetermined number of times (if "Yes" at step S**1904**), the control part **170** causes the unit U**1**, the unit U**2** and the plasma generation part **122** to supply the purge gas, thereby performing a purge operation (step S**1905**). For example, an Ar gas may be used as the purge gas.

**[0232]** Subsequently, at the timing at which the substrate W enters the second region R**2**, the plasma generation part **122** is caused to generate plasma of a modifying gas, thereby performing a plasma cure (step S**1906**). The plasma cure is performed by, for example, using an Ar gas as the modifying gas. Alternatively, $N_2$, $H_2$, $NH_3$, He or a mixed gas thereof may be used as the modifying gas.

**[0233]** Then, the unit U**1**, the unit U**2** and the plasma generation part **122** supply the purge gas to perform a purge operation (step S**1907**).

**[0234]** Then, the control part **170** determines whether the plasma cure has been performed a predetermined number of times (step S**1908**). If it is determined that the plasma cure has not been performed a predetermined number of times (if "No" at step S**1908**), the control part **170** sends the substrate W to the first region R**1** again, thereby repeating the processes from step S**1901**. If it is determined that the plasma cure has been performed a predetermined number of times (if "Yes" at step S**1908**), the control part **170** terminates the processes.

**[0235]** The film forming process of the SiOCN film will be further described with reference to FIG. **23**. In the process illustrated in FIG. **23**, DCS is used as the first precursor gas, and a mixed gas of a gas including a carbon-containing nitriding agent and ammonia is used as the second precursor gas. If the process is started as illustrated in (1) in FIG. **23**, the supply of DCS, the supply of a mixed gas of a gas (C+N) including a carbon-containing nitriding agent and ammonia, and the supply of an oxygen-containing gas ($Ar+O_2$) are performed at the first rotation. That is to say, a SiOCN film is formed by rotating the mounting table **114** once. Furthermore, if the same process is repeated a predetermined number of times by rotating the mounting table **114**, it is possible to produce a SiOCN film having a desired thickness. In the example illustrated in FIG. **23**, the SiOCN film is produced by rotating the mounting table **114** N times.

**[0236]** After the process illustrated in (1) in FIG. **23** is performed N times, a purge operation illustrated in (2) in FIG. **23** is performed using the unit U**1**, the unit U**2** and the plasma generation part **122**. At the next rotation, the plasma generation part **122** is controlled to generate plasma of a modifying gas, thereby performing a plasma cure ((3) in FIG. **23**). Then, at the next rotation, a purge operation is performed using the unit U**1**, the unit U**2** and the plasma generation part **122** ((4) in FIG. **23**). Then, the process illustrated in (1) in FIG. **23** is repeated again.

(Modifications)

**[0237]** In the second embodiment, the Ar gas and the $O_2$ gas are supplied into the second region R**2** using the gas supply mechanism of the plasma generation part **122**. The timing at which the Ar gas as the purge gas is independently

supplied and the timing at which the $O_2$ gas is supplied in order to form the SiOCN film on the substrate W are controlled by the control signal transmitted from the control part **170**. However, the present disclosure is not limited thereto. The plasma generation part **122** may be configured to include a shower head similar to those of the units U**1** and U**2** so that the Ar gas and the $O_2$ gas are supplied from the shower head.

(Modification—Adjustment of Process Order)

**[0238]** In the aforementioned embodiments, when forming the SiCN film, the first precursor gas (the Si precursor gas) and the second precursor gas (the gas including a carbon-containing nitriding agent or the like) are injected toward the substrate in the named order. Thereafter, the plasma cure is performed. Furthermore, when forming the SiOCN film, the first precursor gas (the Si precursor gas), the second precursor gas (the gas including a carbon-containing nitriding agent or the like) and the third gas (the $O_2$ gas) are injected toward the substrate in the named order. Thereafter, the plasma cure is performed. However, the present disclosure is not limited to this order. Various kinds of gases may be supplied in other orders.

**[0239]** For example, when forming the SiCN film, the second precursor gas (the gas including a carbon-containing nitriding agent or the like) may be first injected toward the substrate. Thereafter, the first precursor gas (the Si precursor gas) may be injected toward the substrate. After repeating this cycle a predetermined number of times, a plasma cure may be performed. The process is repeated in this order.

**[0240]** Examples of a method of changing a process order may include the following methods.

**[0241]** First, descriptions will be made on a case where the SiCN film is formed using the film forming apparatus **10** according to the first embodiment. For example, in the process procedure illustrated in FIG. **9**, at the first rotation of the mounting table ((1) in FIG. **9**), the second precursor gas (C+N) is supplied instead of the first precursor gas (DCS). Then, at the second rotation, the purge gas is supplied (similar to (2) in FIG. **9**). Then, at the third rotation ((3) in FIG. **9**), the first precursor gas (DCS) is supplied. Then, at the fourth rotation, the purge gas is supplied (similar to (4) in FIG. **9**). In the case of the film forming apparatus **10** according to the first embodiment, by changing the supply order of the gases supplied from the shower head, it is possible to change the process order.

**[0242]** Similarly, in the case of forming the SiOCN film using the film forming apparatus **10** according to the first embodiment, the film forming apparatus **10** may be controlled so as to change the supply order of the first precursor gas (the Si precursor gas), the second precursor gas (C+N) and the third gas (the $O_2$ gas). For example, the second precursor gas may be supplied in the process (1) illustrated in FIG. **11** and the first precursor gas may be supplied in the process (3). Furthermore, the film forming apparatus **10** may be controlled so as to change the process order in such a way that the processes (5) and (6) illustrated in FIG. **11** are performed before the processes (1) to (4). For example, various kinds of gases may be supplied in the order of the first precursor gas (the Si precursor gas), the third gas (the $O_2$ gas) and the second precursor gas (C+N). Furthermore, various kinds of gases may be supplied in the order of the second precursor gas (C+N), the first precursor gas (the Si precursor gas) and the third gas (the $O_2$ gas). Moreover, various kinds of gases may be supplied in the order of the third gas (the $O_2$ gas), the second precursor gas (C+N) and the first precursor gas (the Si precursor gas).

**[0243]** In the case of forming the SiCN film using the film forming apparatus **100** according to the second embodiment, the process order may be change in the following manner. Hereinafter, descriptions will be made with reference to FIG. **21**.

**[0244]** First, in the case of forming the SiCN film using the film forming apparatus **100** according to the second embodiment, the control part **170** controls the film forming apparatus **100** so as to initially perform the process of supplying the second precursor gas from the unit U**2**. Then, by rotating the mounting table clockwise in FIG. **21**, it is possible to supply the gases in the order of the second precursor gas, the third gas and the first precursor gas. Then, a plasma cure is performed after a predetermined number of rotations (a predetermined number of cycles).

**[0245]** Furthermore, instead of changing the gas supply timings, the rotation direction of the mounting table may be reversed. That is to say, in FIG. **21**, the mounting table may be rotated counterclockwise rather than clockwise. Then, the gas supply timings are adjusted so that a desired gas is initially supplied to the substrate W. By doing so, it is possible to supply the gases to the substrate W in the order of the first precursor gas (the Si precursor gas supplied from the unit U**1**), the third gas (the $O_2$ gas supplied to the second region R**2**) and the second precursor gas (C+N supplied from the unit U**2**). Furthermore, the gases may be supplied to the substrate W in the order of the third gas, the second precursor gas and the first precursor gas. Moreover, the gases may be supplied to the substrate W in the order of the second precursor gas, the first precursor gas and the third gas. A plasma cure is performed after rotating the mounting table a desired number of times.

**[0246]** Furthermore, the positions of the units U**1** and U**2** of the film forming apparatus **100** may be reversed. That is to say, by interchanging the positions of the units U**1** and U**2** in FIG. **21**, the supply order of the first precursor gas and the second precursor gas when the mounting table is rotated clockwise may be reversed. If the supply timings of various kinds of gases are adjusted after reversing the positions of the units U**1** and U**2** in this way, it is possible to change the supply order of the first precursor gas, the second precursor gas and the third gas.

Effects of the Second Embodiment

**[0247]** As described above, the film forming apparatus according to the second embodiment includes: a process vessel divided into a plurality of regions along a circumferential direction in which workpiece substrates are moved about an axis by the rotation of a mounting table configured to hold the workpiece substrates and installed to rotate about the axis so that the workpiece substrates can move around the axis; a first shower head disposed to face the mounting table and configured to supply a first precursor gas to a first region among the plurality of regions of the process vessel; a second shower head disposed to face the mounting table and configured to supply a second precursor gas to a second region adjoining the first region among the plurality of regions of the process vessel; and a plasma generation part disposed to face the mounting table and configured to generate plasma of a modifying gas just above the workpiece substrates by supplying the modifying gas to a third

region among the plurality of regions of the process vessel and supplying microwaves from an antenna to the third region. Thus, after a film is formed on the substrate by supplying different gases from the two shower heads, the film quality can be improved by the plasma of the modifying gas. Furthermore, after a film forming process is performed by installing the two shower heads in two adjoining regions among the plurality of regions of the process vessel, a modifying process using the plasma is performed in a region differing from the two regions. Thus, if the substrates are rotated by the rotation of the mounting table, it is possible to continuously perform the film forming process and the modifying process. This makes it possible to realize efficient deposition.

**[0248]** Furthermore, in the aforementioned film forming apparatus, the first shower head may be formed smaller than the second shower head. One of the first and second precursor gases requiring a longer reaction time is supplied from a larger one of the two shower heads. The other precursor gas is supplied from a smaller one of the two shower heads. Thus, the shower heads can be properly used depending on the properties of the precursor gases. It is therefore possible to realize an efficient film forming process.

**[0249]** Furthermore, the aforementioned film forming apparatus further includes a gas supply/exhaust mechanism configured to supply a purge gas between the first and second shower heads and around the first and second shower heads so as to prevent the plasma from moving into a space between the first and second shower heads. This makes it possible to prevent plasma of a modifying gas from entering the first region where the first and second shower heads are disposed.

**[0250]** Furthermore, in the aforementioned film forming apparatus, the first shower head is configured to supply a first precursor gas containing silicon and the second shower head is configured to supply a second precursor gas containing carbon atoms and nitrogen atoms. Thus, by rotating the mounting table while supplying different gases from different shower heads, it is possible to efficiently produce a SiCN film.

**[0251]** Furthermore, in the aforementioned film forming apparatus, the plasma generation part includes a first gas supply part configured to supply an oxygen gas to the third region and a second gas supply part configured to, after the supply of the oxygen gas, supply a purge gas to remove the oxygen gas. For example, an Ar gas is supplied as the purge gas. Thus, a SiOCN film can be formed on the substrate by allowing the plasma generation part to supply the oxygen gas without supplying microwaves. After the SiOCN film is formed, the purge gas is supplied to remove the oxygen gas. This enables the plasma generation part to efficiently perform a plasma cure.

**[0252]** Furthermore, in the aforementioned film forming apparatus, each of the first and second shower heads is divided into a plurality of regions, in which flow rates of an injected gas are independently controlled, radially outward from the axis of the process vessel by linear members or curved members extending along a circumferential direction of the process vessel. An inclination angle of the linear members or the curved members of the first shower head with respect to a radial direction of the process vessel is larger than an inclination angle of the linear members or the curved members of the second shower head with respect to the radial direction of the process vessel. By adjusting the flow rates of the gas supplied from the shower head in conformity with the radial positions of the shower head in this way, it is possible to sufficiently inject the gas toward the substrate in all the radial positions. Furthermore, by changing the arrangement angle of the members partitioning the shower head in conformity with the size of the shower head, it is possible to finely adjust the amount of the injected gas in the respective radial positions.

**[0253]** Furthermore, in the film forming apparatus and the film forming method according to the second embodiment, it is possible to achieve the same effects as those of the first embodiment. For example, in the second embodiment, after the SiOCN film is formed into a predetermined thickness, a plasma cure is performed to remove weakly-bonded carbon atoms and to improve the bonding state of the carbon atoms. Thereafter, a process of producing a SiOCN film is performed again. This makes it possible to improve the bonding state of molecules included in the SiOCN film and to improve the quality of a film as formed.

**[0254]** Furthermore, in the film forming apparatus according to the second embodiment, the first precursor gas is supplied from the first shower head and the second precursor gas is supplied from the second shower head. The plasma generation part supplies a mixed gas of Ar and $O_2$ and supplies a modifying gas and microwaves for a plasma cure. Thus, by rotating the mounting table once, it is possible to realize the supply of the first precursor gas, the supply of the second precursor gas and the supply of $O_2$ with respect to the substrate. Furthermore, by converting the gas supplied from the plasma generation part to a modifying gas and supplying microwaves, plasma of the modifying gas is generated. Thus, each time when the production process of the SiOCN film is repeatedly performed a predetermined number of times, a plasma cure can be performed at the next rotation. This makes it possible to easily produce the SiOCN film.

## Example 1

### When a Gas Including a Carbon-Containing Nitriding Agent is Used as a Second Precursor Gas

**[0255]** Hereinafter, as Example 1, descriptions will be made on a SiCN film obtained in the case where the aforementioned film forming process is performed using hexachlorodisilane (HCD) as a first precursor gas and using a gas including 1H-1,2.3-triazole as a second precursor gas. The SiCN film is obtained by, for example, performing steps S**701** to S**704** illustrated in FIG. **8** or steps S**1701** to S**1702** illustrated in FIG. **20** a predetermined number of times.

**[0256]** In Example 1, the process conditions used in a process of producing a Si film by supplying the first precursor gas (HCD) are as follows.

**[0257]** HCD flow rate: 100 sccm

**[0258]** Deposition time 0.5 min (per one cycle)

**[0259]** Deposition temperature: 550 degrees C.

**[0260]** Deposition pressure: 133.32 Pa (1 Torr)

**[0261]** Furthermore, the conditions of a process of producing a SiCN film by supplying a second precursor gas (a gas including 1H-1,2,3-triazole as a carbon-containing nitriding agent) are as follows.

**[0262]** Triazole flow rate: 100 sccm

**[0263]** Process time: 0.5 min (per one cycle)

**[0264]** Process temperature: 550 degrees C.

**[0265]** Process pressure: 133.32 Pa (1 Torr)

**[0266]** In Example 1, a SiCN film is produced by, for example, performing steps **S701** to **S704** illustrated in FIG. **8** a predetermined number of times. The atomic composition of the SiCN film thus formed is illustrated in FIG. **24**. FIG. **24** is a view illustrating the atomic composition of the SiCN film of Example 1. In FIG. **24**, as a reference example, there is illustrated an atomic composition of a SiCN film formed by a thermal atomic layer deposition (ALD) method using a deposition temperature of 630 degrees C., using dichlorosilane (DCS) as a Si precursor gas, using $NH_3$ as a nitriding agent and using ethylene ($C_2H_4$) as carbonizing agent.

**[0267]** As illustrated in FIG. **24**, the atomic composition of the SiCN film according to the reference example is represented by N=41.9 at %, Si=47.6 at % and C=10.5 at %. According to the reference example, C is added in an amount smaller than the amount of Si or N. According to the reference example, the SiCN film is a Si-rich or N-rich SiCN film.

**[0268]** In contrast, the atomic composition of the SiCN film of Example 1 is represented by N=30.5 at %, Si=30.6 at % and C=38.4 at %. The SiCN film is formed as a C-rich SiCN film in which the amount of C is larger than the amount of Si or N. Furthermore, a small amount of chlorine (Cl) of 0.5 at % is detected from the SiCN film. The chlorine (Cl) originates from HCD which is a Si precursor gas.

**[0269]** As described above, according to the SiCN film of Example 1, as compared with the reference example, it is possible to produce a C-rich SiCN film in which the amount of C is larger than the amount of Si or N. The additional amount of C can be adjusted by adjusting the flow rate of 1H-1,2,3-triazole. That is to say, by performing the process of FIG. **8** or the like using the aforementioned carbon-containing nitriding agent, it is possible to more broadly control the additional amount of C than in the reference example. For example, the additional amount of C affects the chemical resistance of the SiCN film. The broad controllability of the additional amount of C means that it is possible to form a SiCN film whose chemical resistance is higher than that of the reference example.

**[0270]** According to the embodiment, a modifying process is performed with respect to the C-rich SiCN film using plasma, thereby removing easily-desorbed C. Thereafter, the adsorption and nitriding of Si and the addition of C are performed. This makes it possible to improve the quality of the SiCN film while adjusting the addition amount of C.

**[0271]** FIG. **25** is a view for explaining an etching rate of the SiCN film of Example 1. In FIG. **25**, there are illustrated ratios of etching rates of SiN films and SiCN films when 0.5% DHF is used as an etchant and when an etching rate of a thermal $SiO_2$ film is used as a reference value of 1.0 (100%).

**[0272]** First, the etching rates of the SiN films will be described.

**[0273]** The etching rate against 0.5% DHF of the SiN film formed by a plasma ALD method using a deposition temperature of 500 degrees C., using DCS as a Si precursor gas and using $NH_3$ as a nitriding agent is 0.47 (47%) when compared with the reference value and is approximately one half of the etching rate of the thermal $SiO_2$ film. However, if the deposition temperature is reduced to 450 degrees C., the etching rate against 0.5% DHF is changed to 1.21 (121%) when compared with the reference value and is higher than the etching rate of the thermal $SiO_2$ film. Thus, it cannot be said that the SiN film formed by the plasma ALD method is superior in chemical resistance, particularly in the resistance against 0.5% DHF.

**[0274]** Furthermore, according to a SiN film formed by a thermal ALD method using a deposition temperature of 630 degrees C., using DCS as a Si precursor gas and using $NH_3$ as a nitriding agent, the etching rate against 0.5% DHF is 0.19 (19%) when compared with the reference value and can be improved to become about ⅕ of the etching rate of the thermal $SiO_2$ film. The deposition temperature of the SiN films formed by the thermal ALD method illustrated in FIG. **25** is 630 degrees C. which is higher than the deposition temperature, 450 to 500 degrees C., of the SiN films formed by the plasma ALD method illustrated in FIG. **25**. Thus, under a general theory which is not based on the comparison made at the same temperature, it is preferred that the deposition temperature is set high in order to increase the chemical resistance of the SiN films. Furthermore, it may be considered that the thermal ALD method is more advantageous than the plasma ALD method. As is apparent in FIG. **25**, the SiN films formed by the thermal ALD method at a high temperature of 630 degrees C. are higher in the resistance against 0.5% DHF than the SiN films formed by the plasma ALD method at a low temperature of 450 to 500 degrees C.

**[0275]** Furthermore, according to a C-added SiCN film formed by a thermal ALD method using a deposition temperature of 630 degrees C., using DCS as a Si precursor gas and using $NH_3$ as a nitriding agent, the etching rate against 0.5% DHF is 0.03 (3%) when compared with the reference value. That is to say, the SiN film formed by the thermal ALD method is higher in the chemical resistance than the SiN film formed by the plasma ALD method.

**[0276]** According to the SiCN film of Example 1, the etching rate against 0.5% DHF is equal to or lower than a measurement limit value which falls below 0.03 (3%). The result obtained is that the SiCN film of example 1 is hardly etched by 0.5% DHF. Moreover, the deposition temperature of the SiCN film of Example 1 is 550 degrees C. which is lower than 630 degrees C.

**[0277]** As described above, the SiCN film of Example 1 is higher in chemical resistance than the SiCN film formed by the thermal ALD method using DCS as a Si precursor gas and using $NH_3$ as a nitriding agent.

**[0278]** FIG. **26** is a view for explaining the relationship between the deposition temperature of the SiCN film of Example 1 and the deposition rate thereof. As illustrated in FIG. **26**, the plasma ALD method using DCS as a Si precursor gas and using $NH_3$ as a nitriding agent is capable of achieving a deposition rate of 0.02 nm/min or more even under a low deposition temperature and is, therefore, advantageous in low temperature deposition.

**[0279]** Furthermore, the thermal ALD method using DCS as a Si precursor gas and using $NH_3$ as a nitriding agent is capable of achieving a practical deposition rate of 0.06 to 0.07 nm/min when the deposition temperature is 600 degrees C. However, if the deposition temperature is reduced to 550 degrees C., the deposition rate decreases to about 0.01 nm/min. In the thermal ALD method using DCS as a Si precursor gas and using $NH_3$ as a nitriding agent, it is hard to form a SiN film if the deposition temperature falls below 500 degrees C. However, if HCD rather than DCS is used as the Si precursor gas, it is possible to ameliorate the reduction of the deposition rate in the low temperature deposition.

[0280] According to the SiCN film of Example 1, it is possible to achieve a deposition rate of 0.07 to 0.08 nm/min when the deposition temperature is 550 degrees C. Even if the deposition temperature is reduced to 450 degrees C., it is possible to achieve a deposition rate of 0.05 to 0.06 nm/min Particularly, the deposition rate in a temperature range of 200 degrees C. or more and 550 degrees C. or less is as good as the deposition rate of the plasma ALD method.

[0281] As described above, according to the SiCN film of Example 1, even when the deposition is performed under a low temperature, for example, in a temperature range of 200 degrees C. or more and 550 degrees C. or less, without using plasma, it is possible to achieve a deposition rate which is equivalent to the deposition rate achieved in the case of using plasma. One of the reasons is as follows.

[0282] As illustrated in FIG. 27, the 1,2,3-triazole-based compound includes a "N═N—N" bond within a five-member ring. The "N═N" portion in the "N═N—N" bond tends to be decomposed to become nitrogen ($N_2$, N≡N). Thus, the 1,2,3-triazole-based compound, unlike the usual ring-opening cleavage, has a tendency to undergo cleavage and decomposition at a plurality of points. That is to say, the 1,2,3-triazole-based compound generates "N≡N". Thus, an electronically unsaturated state occurs within the compound. A decomposition product obtained as a result of cleavage and decomposition of the 1,2,3-triazole-based compound is active. For that reason, even when the deposition temperature is low and falls within a temperature range of, for example, 200 degrees C. or more and 550 degrees C. or less, it is possible to nitride a Si film and, ultimately, to add C.

[0283] Thus, even when the deposition temperature is reduced, it is possible to form the SiCN film of Example 1 while maintaining a high deposition rate.

[0284] In the case where the gas including a carbon-containing nitriding agent is used, the nitriding and the C adding can be simultaneously performed during the same step using one kind of compound. This is because the 1,2,3-triazole-based compound contains N atoms and C atoms. Thus, a step of carbonizing a Si film or a SiN film becomes unnecessary. This is advantageous in enhancing the throughput.

[0285] According to the present disclosure in some embodiments, it is possible to produce a high-performance film while realizing low-temperature deposition.

[0286] 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 film forming method for forming a nitride film on a workpiece substrate accommodated within a process vessel, comprising:

performing a first reaction of supplying a first precursor gas to the workpiece substrate accommodated within the process vessel;

performing a second reaction of supplying a second precursor gas to the workpiece substrate accommodated within the process vessel;

performing a modification of generating plasma of a modifying gas just above the workpiece substrate by supplying the modifying gas into the process vessel and supplying microwaves from an antenna into the process vessel, and plasma-processing, by the plasma thus generated, a surface of the workpiece substrate subjected to the first and second reactions using the first and second precursor gases.

**2**. The method of claim **1**, wherein the first precursor gas contains silicon and the second precursor gas contains carbon atoms and nitrogen atoms.

**3**. The method of claim **1**, wherein the modification is performed once each time when the first and second reactions are repeatedly performed a predetermined number of times.

**4**. The method of claim **1**, further comprising:

performing a third reaction of supplying a third gas to the workpiece substrate accommodated within the process vessel; and

performing a removal of purging a mechanism for supplying the first precursor gas, the second precursor gas and the third gas, the removal being performed after the first reaction, the second reaction and the third reaction but before the modification.

**5**. The method of claim **4**, wherein the third gas contains oxygen atoms.

**6**. The method of claim **1**, wherein the first precursor gas contains one of monochlorosilane, dichlorosilane, trichlorosilane, tetrachlorosilane and hexachlorodisilane.

**7**. The method of claim **1**, wherein the second precursor gas is supplied into the process vessel together with ammonia.

**8**. The method of claim **1**, wherein the second precursor gas is pyrolyzed at a temperature of 200 degrees C. or more and 550 degrees C. or less.

**9**. The method of claim **1**, wherein the modifying gas is a mixed gas of $NH_3$ and $H_2$.

**10**. A film forming apparatus, comprising:

a process vessel divided into a plurality of regions along a circumferential direction in which workpiece substrates are moved about an axis by a rotation of a mounting table, the mounting table being configured to hold the workpiece substrates and installed to rotate about the axis so that the workpiece substrates move around the axis;

a first shower head disposed to face the mounting table and configured to supply a first precursor gas to a first region among the plurality of regions of the process vessel;

a second shower head disposed to face the mounting table and configured to supply a second precursor gas to a second region adjoining the first region among the plurality of regions of the process vessel; and

a plasma generation part disposed to face the mounting table and configured to generate plasma of a modifying gas just above the workpiece substrates by supplying the modifying gas to a third region among the plurality of regions of the process vessel and supplying microwaves from an antenna to the third region.

**11**. The apparatus of claim **10**, wherein the first shower head is smaller in size than the second shower head.

**12**. The apparatus of claim **10**, further comprising:

a gas supply/exhaust mechanism configured to supply a purge gas between the first and second shower heads and around the first and second shower heads so as to prevent the plasma from moving into a space between the first and second shower heads.

**13**. The apparatus of claim **10**, wherein the first shower head is configured to supply the first precursor gas containing silicon and the second shower head is configured to supply the second precursor gas containing carbon atoms and nitrogen atoms.

**14**. The apparatus of claim **10**, wherein the plasma generation part includes a first gas supply part configured to supply an oxygen gas to the third region and a second gas supply part configured to, after the supply of the oxygen gas, supply a purge gas to remove the oxygen gas.

**15**. The apparatus of claim **10**, wherein each of the first and second shower heads is divided into a plurality of regions, in which flow rates of an injected gas are independently controlled, radially outward from the axis of the process vessel by linear members or curved members extending along the circumferential direction of the process vessel, and

an inclination angle of the linear members or the curved members of the first shower head with respect to a radial direction of the process vessel is larger than an inclination angle of the linear members or the curved members of the second shower head with respect to the radial direction of the process vessel.

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