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

(71) Applicant: **Tokyo Electron Limited**, Tokyo (JP)

(72) Inventors: **Rui KANEMURA**, Nirasaki City (JP); **Yoshihiro TAKEZAWA**, Nirasaki City (JP); **Keita KUMAGAI**, Nirasaki City (JP); **Keisuke FUJITA**, Nirasaki City (JP)

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(57) **ABSTRACT**

There is provided a film forming method including: supplying a halogen-free silicon raw material gas into a processing container that accommodates a substrate therein in a halogen-free silicon raw material gas supply process; supplying a halogen-containing silicon raw material gas into the processing container in a halogen-containing silicon raw material gas supply process; removing the halogen-containing silicon raw material gas inside the processing container in a halogen-containing silicon raw material gas removal process; and repeating a cycle including a sequence of the halogen-free silicon raw material gas supply process, the halogen-containing silicon raw material gas supply process, and the halogen-containing silicon raw material gas removal process in a continuous manner.

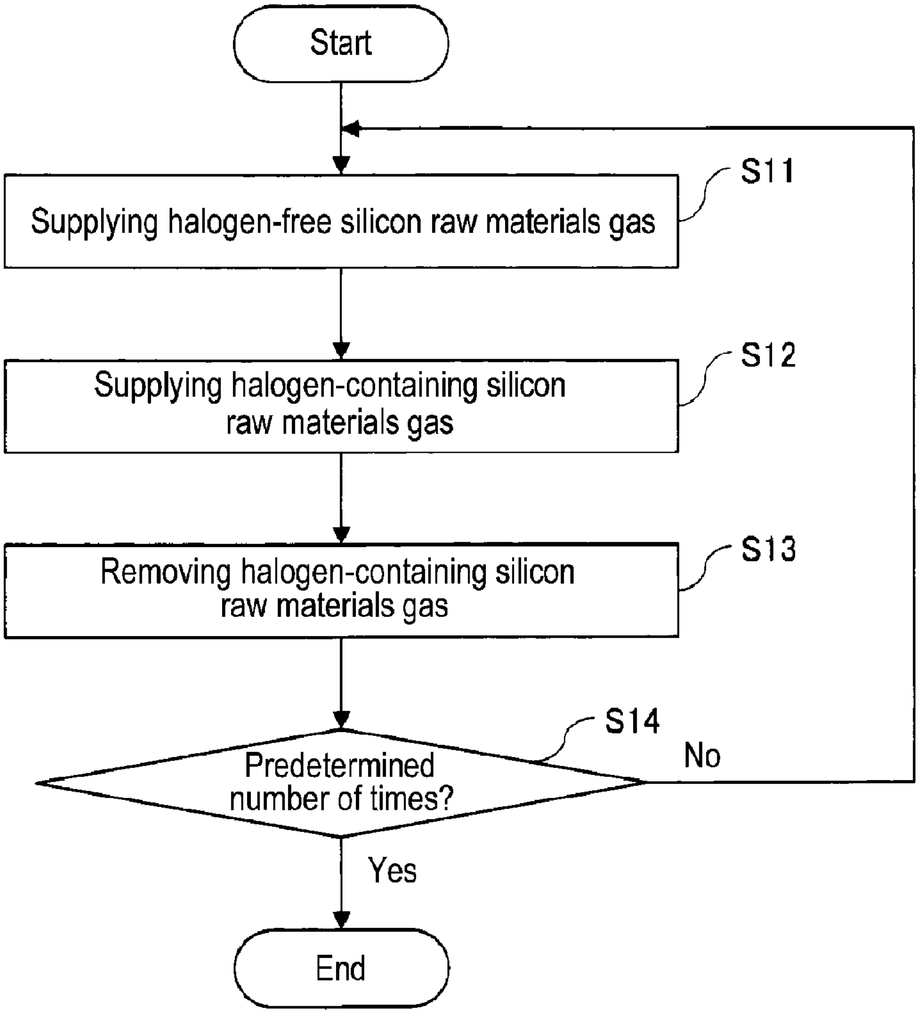


FIG. 1

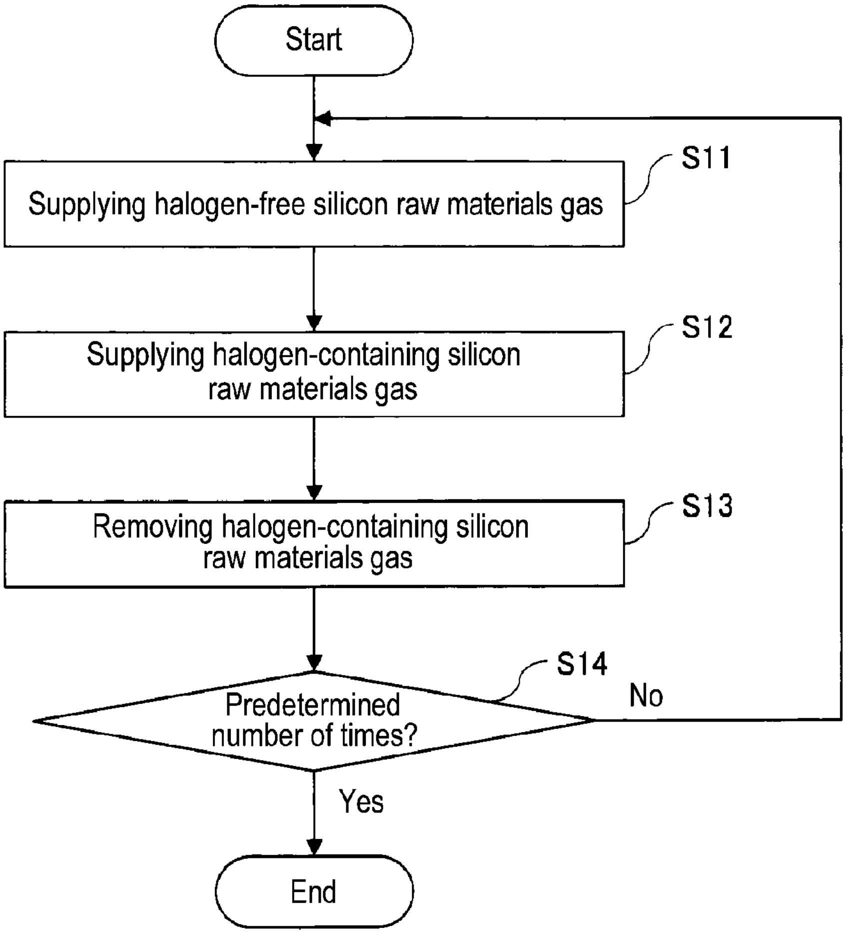

Start
Supplying halogen-free silicon raw materials gas
S11
Supplying halogen-containing silicon raw materials gas
S12
Removing halogen-containing silicon raw materials gas
S13
Predetermined number of times?
S14
No
Yes
End

FIG. 2

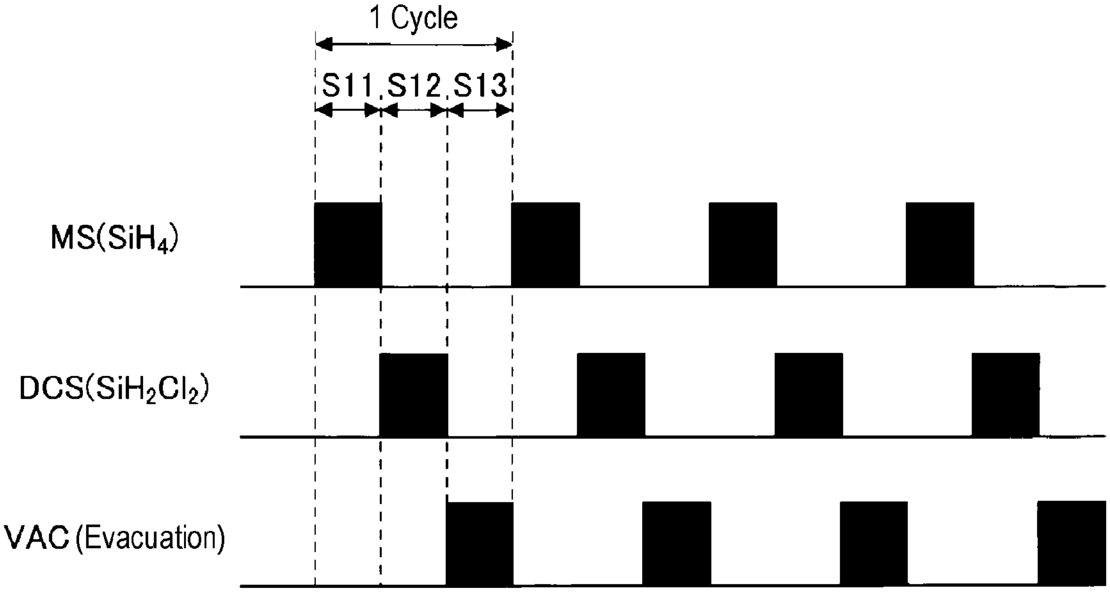

1 Cycle
S11
S12
S13
MS(SiH4)
DCS(SiH2Cl2)
VAC (Evacuation)

FIG. 3

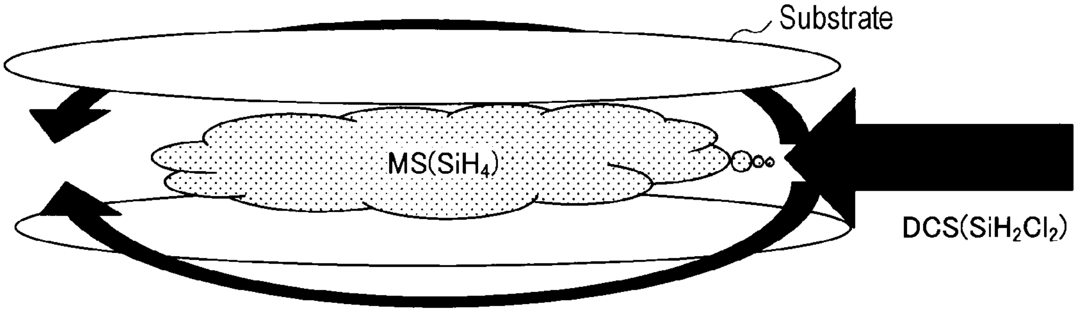


FIG. 4

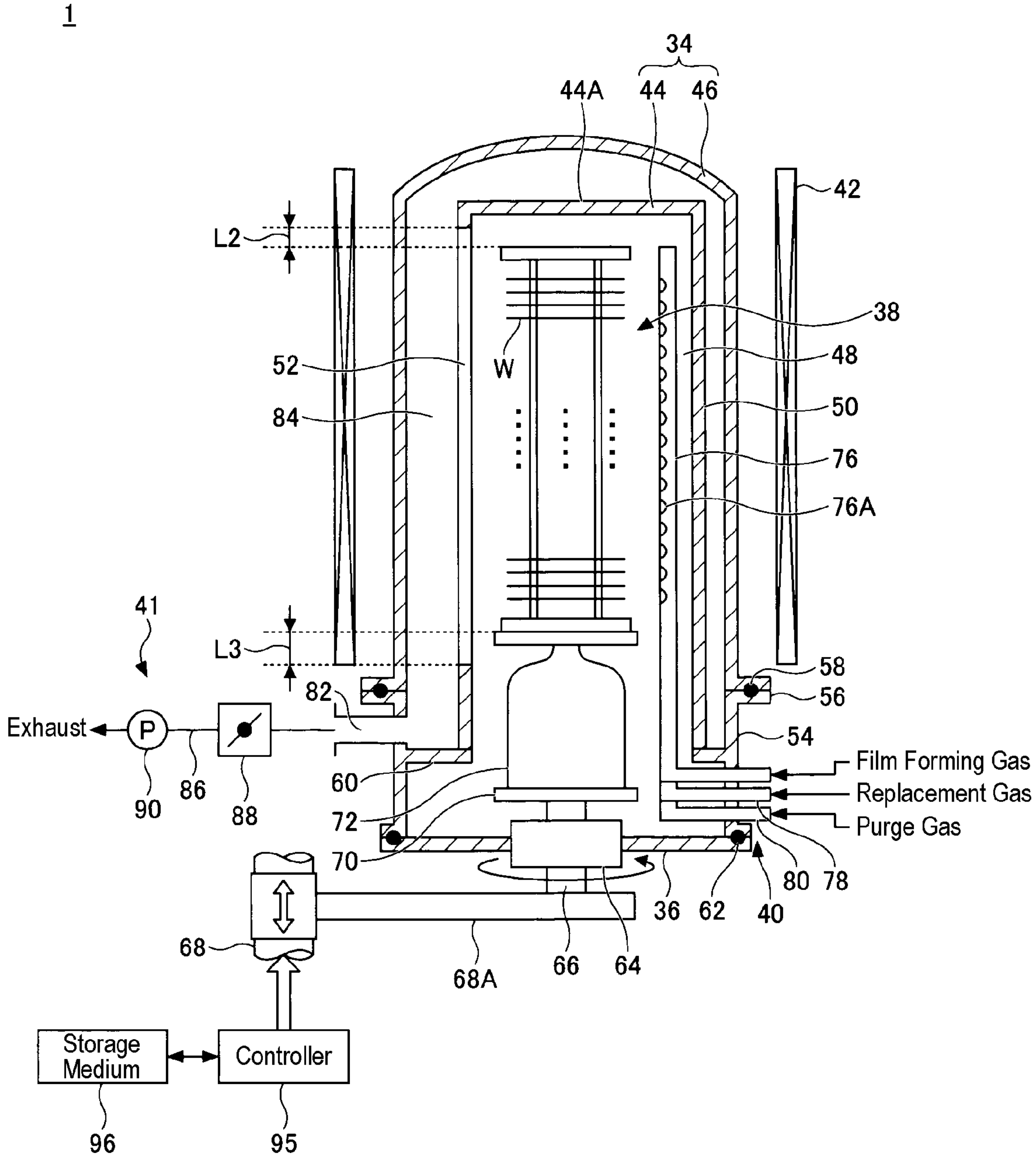

1
34
44A
44
46
42
L2
38
52
W
48
84
50
76
76A
41
L3
58
82
56
Exhaust
P
54
Film Forming Gas
Replacement Gas
Purge Gas
60
90
86
88
72
70
80
78
36
62
40
68
68A
66
64
Storage Medium
Controller
96
95

FIG. 5

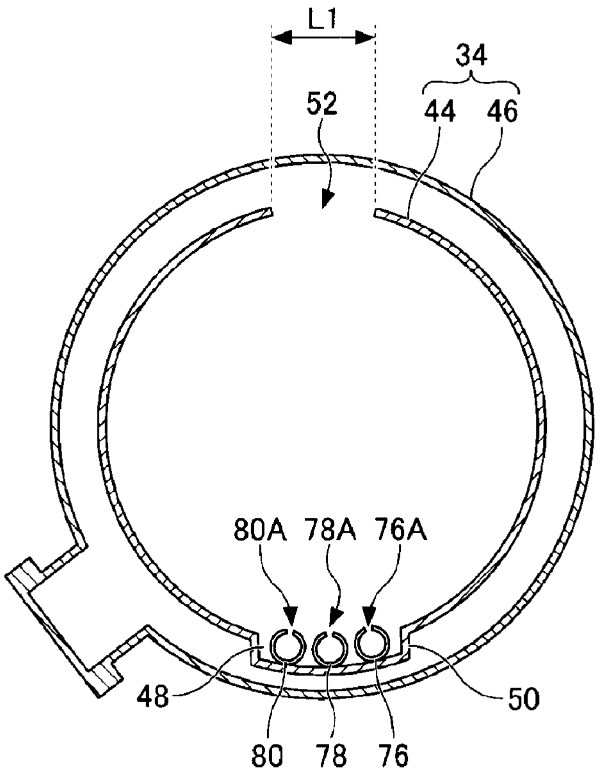


FIG. 6A

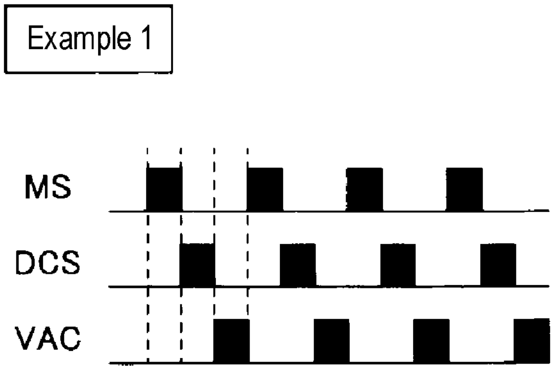


FIG. 6B

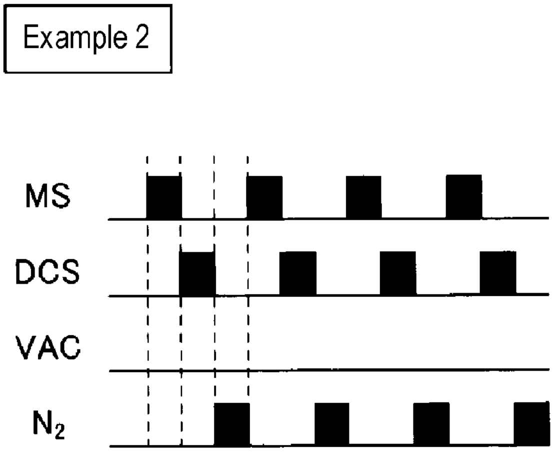


FIG. 6C

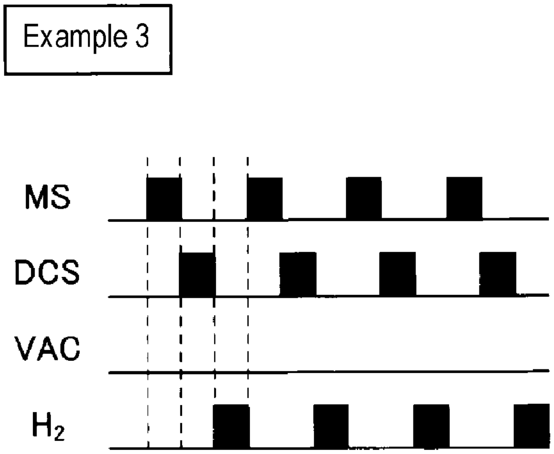


FIG. 6D

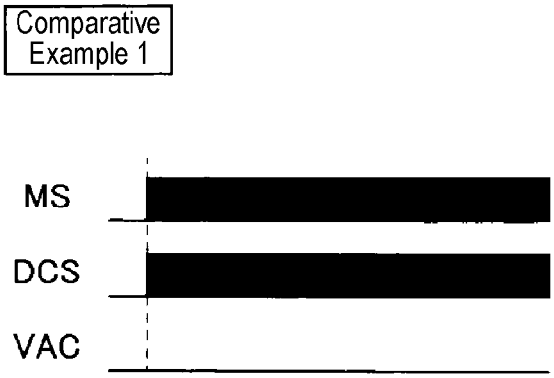


FIG. 6E

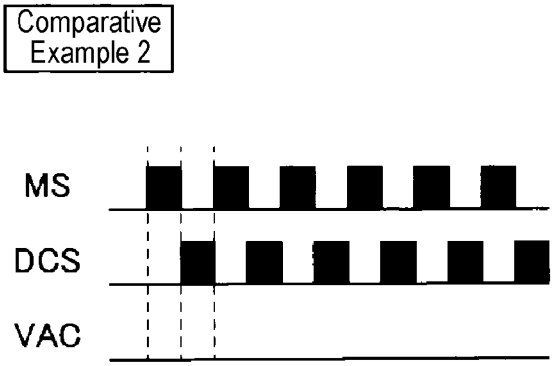


FIG. 6F

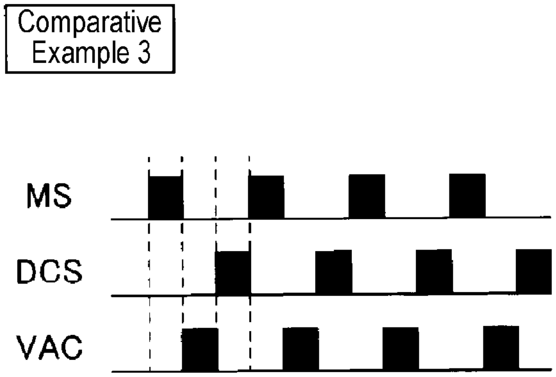


FIG. 6G

Comparative Example 4

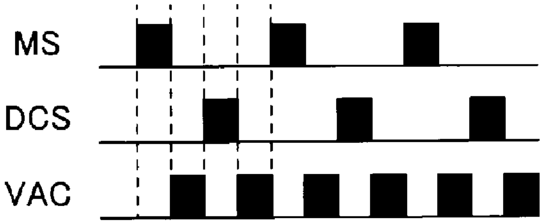


FIG. 6H

Comparative Example 5

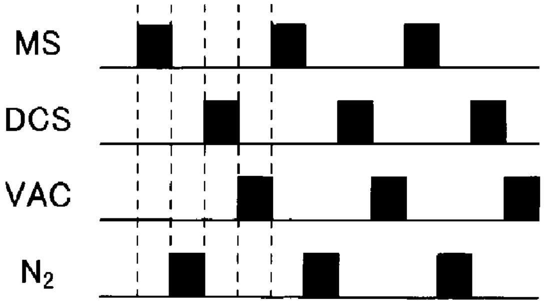


FIG. 7

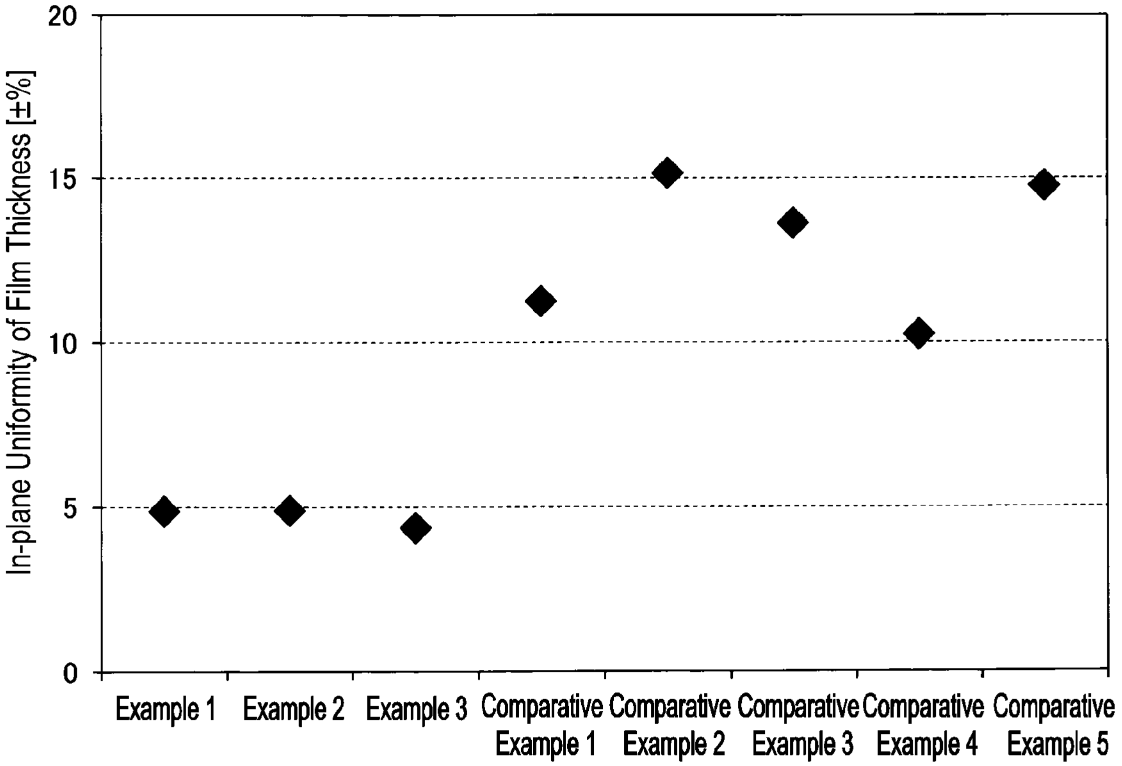
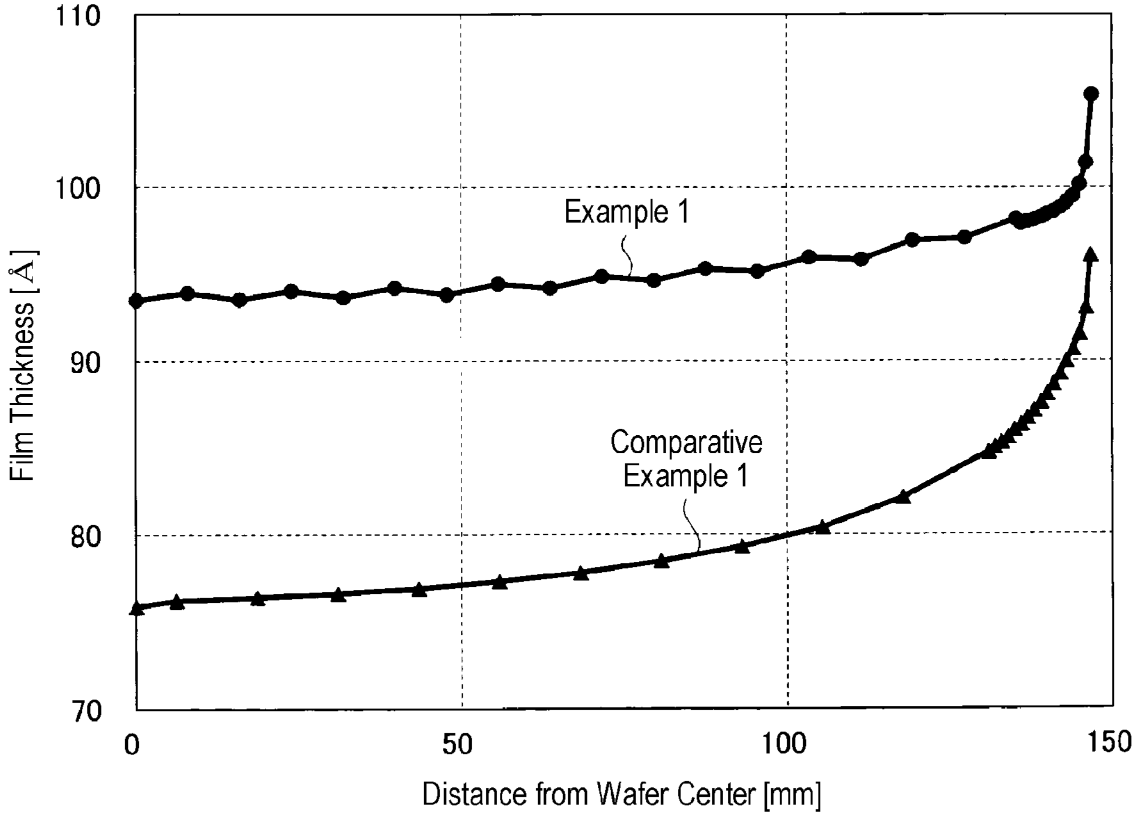

In-plane Uniformity of Film Thickness [±%]
20
15
10
5
0
Example 1
Example 2
Example 3
Comparative Example 1
Comparative Example 2
Comparative Example 3
Comparative Example 4
Comparative Example 5

FIG. 8


110
100
90
80
70
Film Thickness [Å]
Example 1
Comparative Example 1
0
50
100
150
Distance from Wafer Center [mm]

FILM FORMING METHOD AND FILM FORMING APPARATUS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is based upon and claims the benefit of priority from Japanese Patent Application No. 2019-070114, filed on Apr. 1, 2019, the entire contents of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to a film forming method and a film forming apparatus.

BACKGROUND

[0003] There is known a technology for forming a silicon film by supplying a silane-based gas and a silicon-based chlorine-containing compound gas to a substrate having a fine recess formed on the front surface thereof (see, for example, Patent Document 1).

PRIOR ART DOCUMENT

Patent Document

[0004] Patent Document 1: Japanese Laid-Open Patent Publication No. 2017-152426

SUMMARY

[0005] According to one embodiment of the present disclosure, there is provided a film forming method including: supplying a halogen-free silicon raw material gas into a processing container that accommodates a substrate therein in a halogen-free silicon raw material gas supply process; supplying a halogen-containing silicon raw material gas into the processing container in a halogen-containing silicon raw material gas supply process; removing the halogen-containing silicon raw material gas inside the processing container in a halogen-containing silicon raw material gas removal process; and repeating a cycle including a sequence of the halogen-free silicon raw material gas supply process, the halogen-containing silicon raw material gas supply process, and the halogen-containing silicon raw material gas removal process in a continuous manner.

BRIEF DESCRIPTION OF DRAWINGS

[0006] 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.

[0007] FIG. **1** is a flowchart illustrating a film forming method of an embodiment.

[0008] FIG. **2** is a view illustrating a gas supply sequence in the film forming method of the embodiment.

[0009] FIG. **3** is a view for explaining the effects of the film forming method of an embodiment.

[0010] FIG. **4** is a vertical cross-sectional view illustrating an exemplary configuration of a vertical heat treatment apparatus.

[0011] FIG. **5** is a view for explaining a processing container of the vertical heat treatment apparatus of FIG. **4**.

[0012] FIGS. **6**A to **6**H are views for explaining gas supply sequences in Examples and Comparative examples.

[0013] FIG. **7** is a view representing in-plane uniformities of film thickness of silicon films formed on pattern wafers.

[0014] FIG. **8** is a view representing film thickness distributions of silicon films formed on pattern wafers.

DETAILED DESCRIPTION

[0015] Hereinafter, non-limitative exemplary embodiments of the present disclosure will now be described with reference to the accompanying drawings. In all the accompanying drawings, the same or corresponding members or components will be denoted by the same or corresponding reference numerals, and redundant explanations thereof will be omitted. 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.

[Film Forming Method]

[0016] A film forming method according to an embodiment will be described. FIG. **1** is a flowchart illustrating the film forming method according to an embodiment. FIG. **2** is a view illustrating a gas supply sequence in the film forming method of the embodiment.

[0017] As illustrated in FIG. **1**, the film forming method according to an embodiment includes a step of supplying a halogen-free silicon raw material gas (step S**11**), a step of supplying a halogen-containing silicon raw material gas (step S**12**), and a step S**13** of removing the halogen-containing silicon raw material gas. Then, a cycle including a sequence of steps S**11** to S**13** is continuously repeated (step S**14**). Hereinafter, each step will be described.

[0018] First, a substrate is accommodated in a processing container. The halogen-free silicon raw material gas is supplied into the processing container in a state in which the interior of the processing container is depressurized and the substrate is heated (step S**11**). The substrate may be a substrate having a smooth front surface or a substrate having a recess, such as a trench or hole, formed on the front surface thereof. The substrate may be, for example, a semiconductor substrate such as a silicon substrate. In addition, an insulating film, such as a silicon oxide film (SiO_2 film), a silicon nitride film (SiN film) or the like, may be formed on the front surface of the substrate.

[0019] As the halogen-free silicon raw material gas, for example, an aminosilane-based gas or a hydrogenated silicon gas may be used. As the aminosilane-based gas, for example, diisopropylamino silane (DIPAS), trisdimethylamino silane (3DMAS), or bis (tertiary-butylamino) silane (BTBAS) may be used. As the hydrogenated silane gas, for example, SiH_4 (MS), Si_2H_6 (DS), Si_3H_8, or Si_4H_{10} may be used.

[0020] Subsequently, the halogen-containing silicon raw material gas is supplied into the processing container in the state in which the substrate is heated (step S**12**). The step S**12** of supplying the halogen-containing silicon raw material gas is performed continuously after the step S**11** of supplying the halogen-free silicon raw material gas without performing evacuation and purging (gas replacement) inside the processing container. The step **S12** of supplying the halogen-containing silicon raw material gas may be performed continuously, for example, after the step **S11** of supplying the halogen-free silicon raw material gas while keeping the internal pressure of the processing container substantially constant. In addition, the step **S12** of supplying the halogen-containing silicon raw material gas may be performed continuously, for example, after the step **S11** of supplying the halogen-free silicon raw material gas and after changing the setting of the internal pressure of the processing container. In any case, the halogen-containing silicon raw material gas is supplied in the state in which the halogen-free silicon raw material gas remains in the processing container.

[0021] As the halogen-containing silicon raw material gas, for example, a fluorine-containing silicon gas, a chlorine-containing silicon gas, or a bromine-containing silicon gas may be used. As the fluorine-containing silicon gas, for example, SiF_4, $SiHF_3$, SiH_2F_2, or SiH_3F may be used. As the chlorine-containing silicon gas, for example, $SiCl_4$, $SiHCl_3$, SiH_2Cl_2(DCS), SiH_3Cl, or Si_2Cl_6 may be used. As the bromine-containing silicon gas, for example, $SiBr_4$, $SiHBr_3$, SiH_2Br_2, or SiH_3Br may be used.

[0022] Subsequently, the halogen-containing silicon raw material gas in the processing container is removed in the state in which the substrate is heated (step **S13**). In the step **S13** of removing the halogen-containing silicon raw material gas, the interior of the processing container is exhausted by an exhaust device such as a vacuum pump without supplying a processing gas and a purge gas into the processing container. However, a minute amount of purge gas may be supplied into the processing container for the purpose of preventing backflow of gas to a gas supply part, a boat rotation shaft, and the like. The minute amount of purge gas corresponds to, for example, a flow rate smaller than the flow rates of the halogen-free silicon raw material gas and the halogen-containing silicon raw material gas supplied into the processing container in step **S11** and step **S12**, respectively.

[0023] In the step **S13** of removing the halogen-containing silicon raw material gas, gas replacement may be performed by, for example, exhausting the interior of the processing container using an exhaust device such as a vacuum pump or the like while supplying a replacement gas into the processing container. As the replacement gas, for example, an inert gas, H_2 (hydrogen gas), or D_2 (deuterium gas) may be used. Examples of the inert gas may include N_2 and a noble gas, such as He, Ne, or Ar.

[0024] The purpose of the step **S13** of removing the halogen-containing silicon raw material gas is to remove the halogen-containing silicon raw material gas existing in the processing container, specifically on the front surface of the substrate, at the time of starting the step **S11** of supplying the halogen-free silicon raw material gas, which is to be performed after step **S13**. Accordingly, the step **S13** of removing the halogen-containing silicon raw material gas is not limited to the above method as long as it can remove the halogen-containing silicon raw material gas existing on the front surface of the substrate. For example, the step **S13** of removing the halogen-containing silicon raw material gas may be a combination of the evacuation of the interior of the processing container and the supply of the replacement gas into the processing container. In the step **S13** of removing the halogen-containing silicon raw material gas, it is preferable that the halogen-containing silicon raw material gas present on the front surface of the substrate be completely removed, but it is sufficient that most of the halogen-containing silicon raw material gas is removed.

[0025] Subsequently, it is determined whether or not steps **S11** to **S13** have been executed a predetermined number of times (step **S14**). If it is determined that steps **S11** to **S13** have been executed the predetermined number of times, the process ends. Meanwhile, if it is determined that steps **S11** to **S13** have not been performed the predetermined number of times, the process returns to step **S11**. That is, steps **S11** to **S13** are repeated until the predetermined number of times is reached. The predetermined number of times is determined depending a designed thickness of a silicon film to be formed.

[Effects]

[0026] Next, the effects achieved by the film forming method of the embodiment will be described by taking as an example a case where an MS gas is used as the halogen-free silicon raw material gas and a DCS gas is used as the halogen-containing silicon raw material gas. FIG. **3** is a view for explaining the effects obtained by the film forming method of the embodiment.

[0027] For example, in a case where the MS gas and the DCS gas are supplied from the periphery of the substrate substantially parallel to the main surface of the substrate, the film thickness of the central portion of the substrate is likely to be smaller than the thickness of the peripheral portion of the substrate. It is considered that this is caused due to the fact that, when the MS gas and the DCS gas are used, the MS gas greatly contributes to the film formation and the DCS gas plays a role of suppressing the film formation.

[0028] Therefore, in the film forming method of the embodiment, after the step **S11** of supplying the halogen-free silicon raw material gas into the processing container accommodating the substrate, the step **S12** of supplying the halogen-containing silicon raw material gas into the processing container is continuously performed. In other words, after the step **S11** of supplying the halogen-free silicon raw material gas into the processing container accommodating the substrate, the step **S12** of supplying the halogen-containing silicon raw material gas into the processing container is performed without evacuating and purging the interior of the processing container. As a result, as illustrated in FIG. **3**, the DCS gas is supplied into the processing container in step **S12** in the state in which the MS gas supplied into the processing container in step **S11** remains on the front surface of the substrate. Therefore, since the DCS gas is supplied to the peripheral portion of the substrate so as to surround the MS gas remaining in the central portion of the substrate, terminations of chlorine (Cl) to the central portion of the substrate decrease, which makes it is possible to suppress a decrease in film thickness of the central portion of the substrate. As a result, the in-plane uniformity of film thickness is improved.

[0029] In the film forming method of an embodiment, after performing the step **S12** of supplying the halogen-containing silicon raw material gas into the processing container and subsequently performing the step **S13** of removing the halogen-containing silicon raw material gas, the step **S11** of supplying the halogen-free silicon raw material gas into the processing container is performed. Thus, in the state in which the DCS gas supplied into the processing container in step S**12** is discharged from the front surface of the substrate, the MS gas is supplied into the processing container in step S**11**. When the DCS gas stays in the central portion of the substrate, film formation on the central portion of the substrate by the MS gas decreases. However, the present disclosure is capable of suppress such a decrease in film formation. As a result, the in-plane uniformity of film thickness is improved.

[Film Forming Apparatus]

[0030] A film forming apparatus capable of performing the above-described film formation method will be described by taking as an example a batch-type vertical heat treatment apparatus that performs heat treatment on a large number of substrates at once. However, the film forming apparatus is not limited to the batch-type apparatus, and may be, for example, a single-wafer-type apparatus that processes substrates one by one.

[0031] FIG. **4** is a vertical cross-sectional view illustrating an exemplary configuration of the vertical heat treatment apparatus. FIG. **5** is a view for explaining a processing container of the vertical heat treatment apparatus of FIG. **4**.

[0032] As illustrated in FIG. **4**, a vertical heat treatment apparatus **1** includes a processing container **34**, a lid **36**, a wafer boat **38**, a gas supply part **40**, an exhaust part **41**, and a heating part **42**.

[0033] The processing container **34** accommodates the wafer boat **38**. The wafer boat **38** is a substrate holder that holds a large number of semiconductor wafers (hereinafter, referred to as "wafers W") at a predetermined interval in the vertical direction in a shelf-like manner. The processing container **34** has a cylindrical inner tube **44** having a ceiling and a lower opened end, and a cylindrical outer tube **46** having a ceiling and a lower opened end and covering the outside of the inner tube **44**. The inner tube **44** and the outer tube **46** are formed of a heat-resistant material such as quartz, and are arranged in a coaxial relationship with each other to have a double-tube structure.

[0034] A ceiling **44**A of the inner tube **44** is, for example, flat. At one side of the inner tube **44**, a nozzle accommodation portion **48** in which gas supply pipes are accommodated is formed in the longitudinal direction thereof (the vertical direction). For example, as illustrated in FIG. **5**, a portion of the sidewall of the inner tube **44** protrudes outward so as to form a convex portion **50**. The interior of the convex portion **50** is defined as the nozzle accommodation portion **48**. In the sidewall of the inner tube **44** opposite the nozzle accommodation portion **48**, a rectangular opening **52** having a width L**1** is provided in the longitudinal direction thereof (the vertical direction).

[0035] The opening **52** is a gas exhaust port formed so as to be capable of exhausting the gas in the inner tube **44**. A length of the opening **52** is equal to that of the wafer boat **38** or extend upward and downward in the vertical direction to be longer than the length of the wafer boat **38**. That is, an upper end of the opening **52** extends such that it is located at a height equal to or higher than a position corresponding to an upper end of the wafer boat **38**, and a lower end of the opening **52** extends such that it is located at a height equal to or lower than a position corresponding to a lower end of the wafer boat **38**. Specifically, as illustrated in FIG. **4**, a distance L**2** in the height direction between the upper end of the wafer boat **38** and the upper end of the opening **52** falls within a range of about 0 mm to 5 mm A distance L**3** in the height direction between the lower end of the wafer boat **38** and the lower end of the opening **52** falls within a range of about 0 mm to 350 mm.

[0036] A lower end of the processing container **34** is supported by a cylindrical manifold **54** formed of, for example, stainless steel. A flange **56** is formed on an upper end of the manifold **54**. The lower end of the outer tube **46** is installed and supported on the flange **56**. A seal member **58** such as an O-ring is interposed between the flange **56** and the lower end of the outer tube **46** such that the interior of the outer tube **46** is hermetically sealed.

[0037] An annular support portion **60** is provided on an inner wall of an upper portion of the manifold **54**. The lower end of the inner tube **44** is installed and supported on the support portion **60**. The lid **36** is hermetically installed to a lower end opening of the manifold **54** via a sealing member **62** such as an O-ring so as to hermetically close a lower end opening of the processing container **34**, that is, the opening of the manifold **54**. The lid **36** is formed of, for example, stainless steel.

[0038] In the central portion of the lid **36**, a rotary shaft **66** is provided through a magnetic fluid seal **64**. A lower portion of the rotary shaft **66** is rotatably supported by an arm **68**A of an elevating part **68** including a boat elevator.

[0039] A rotary plate **70** is provided at an upper end of the rotary shaft **66**. The wafer boat **38** that holds the wafers W is placed on the rotary plate **70** via a quartz heat-insulating base **72**. Accordingly, by moving the elevating part **68** up and down, the lid **36** and the wafer boat **38** move vertically as a unit, so that the wafer boat **38** can be inserted into and removed from the processing container **34**.

[0040] The gas supply part **40** is provided in the manifold **54**, and introduces gases such as a film-forming gas, a replacement gas, and a purge gas into the inner tube **44**. The gas supply part **40** has a plurality of (e.g., three) gas supply pipes **76**, **78**, and **80** made of quartz. Each of the gas supply pipes **76**, **78**, and **80** is provided within the inner tube **44** in the longitudinal direction thereof. A base end of each gas supply pipe is bent in an L shape and penetrates the manifold **54** while being supported by the manifold **54**.

[0041] As illustrated in FIG. **5**, the gas supply pipes **76**, **78**, and **80** are installed in the nozzle accommodation portion **48** of the inner tube **44** in a row in the circumferential direction. Each gas supply pipe **76**, **78**, or **80** has a plurality of gas holes **76**A, **78**A, or **80**A formed at a predetermined interval in the longitudinal direction. Gases are discharged from the gas holes **76**A, **78**A, or **80**A in the horizontal direction. Thus, the gases are supplied from the peripheries of the wafers W substantially parallel to the main surfaces of the wafers W. The predetermined interval may be set to be equal to the interval between the wafers W supported in the wafer boat **38**. The positions in the height direction are set such that each of the gas holes **76**A, **78**A, and **80**A is located in the middle between vertically adjacent wafers W, so that each gas can be efficiently supplied to spaces between the wafers W. As the types of gases, a film-forming gas, a replacement gas, and a purge gas are used. The gases can be supplied through the respective gas supply pies **76**, **78**, and **80**, as necessary, while the flow rates thereof are controlled. Example of the film-forming gas may include the halogen-free silicon raw material gas and the halogen-containing silicon raw material gas described above. The replacement gas includes, for example, the inert gas, H_2, or D_2 described above.

[0042] A gas outlet **82** is formed in an upper sidewall of the manifold **54** above the support portion **60**, so that the gas in the inner tube **44**, which is exhausted from the opening **52**, can be exhausted through a space portion **84** between the inner tube **44** and the outer tube **46**. In the gas outlet **82**, an exhaust part **41** is provided. The exhaust part **41** has an exhaust passage **86** connected to the gas outlet **82**. A pressure regulation valve **88** and a vacuum pump **90** are sequentially provided in the exhaust passage **86**, so that the interior of the processing container **34** can be evacuated.

[0043] On the outer circumferential side of the outer tube **46**, a cylindrical heating part **42** is provided so as to cover the outer tube **46**. The heating part **42** heats the wafers W accommodated in the processing container **34**.

[0044] The overall operation of the vertical heat treatment apparatus **1** is controlled by a controller **95**. The controller **95** may be, for example, a computer. A computer program that causes the overall operation of the vertical heat treatment apparatus **1** to be performed is stored in a non-transient storage medium **96**. For example, the storage medium **96** may be a flexible disc, a compact disc, a hard disc, flash memory, a DVD or the like.

[0045] An example of the film forming method of forming an amorphous silicon film on each wafer W using the vertical heat treatment apparatus **1** will be described. First, the wafer boat **38** holding the large number of wafers W is loaded into the processing container **34** by the elevating part **68**. The lower end opening of the processing container **34** is hermetically closed and sealed by the lid **36**. Subsequently, the operations of the gas supply part **40**, the exhaust part **41**, the heating part **42**, and the like are controlled by the controller **95** so as to execute the above-described film forming method. Thus, the amorphous silicon film is formed on each wafer W.

[0046] In the case where the halogen-free silicon raw material gas and the halogen-containing silicon raw material gas are supplied from the peripheries of the wafers W substantially in parallel with the main surfaces of the wafers W, a difference between film thickness in the central portion and the peripheral portion of each wafer is prone to occur. In particular, when the large number of wafers W are held at a predetermined interval in the vertical direction in the shelf-like manner, a difference in film thickness occurring between the central portion and the peripheral portion of each wafer increases as the interval decreases. Therefore, in order to reduce the difference in film thickness occurring between the central portion and the peripheral portion of each wafer, a method of increasing the interval is conceivable. However, if the interval is increased, the number of wafers W that are capable of being accommodated in the processing container decreases, which deteriorates productivity.

[0047] Therefore, in the film forming method of the embodiment, after the step S**11** of supplying the halogen-free silicon raw material gas into the processing container **34** accommodating the wafers W, the step S**12** of supplying the halogen-containing silicon raw material gas into the processing container **34** is continuously performed. In other words, after the step S**11** of supplying the halogen-free silicon raw material gas into the processing container **34** accommodating the wafers W, the step S**12** of supplying the halogen-containing silicon raw material gas into the processing container **34** is performed without evacuating and purging the interior of the processing container **34**.

[0048] After performing the step S**12** of supplying the halogen-containing silicon raw material gas into the processing container **34** and subsequently performing the step S**13** of removing the halogen-containing silicon raw material gas inside the processing container **34**, the step S**11** of supplying the halogen-free silicon raw material gas into the processing container **34** is performed. Thus, in the state in which the halogen-contained silicon raw material gas supplied into the processing container **34** in step S**12** is exhausted from the front surfaces of the wafers W, the halogen-free silicon raw material gas is supplied into the processing container **34** in step S**11**. As a result, the in-plane uniformity of film thickness of the silicon film formed on each wafer W is improved. Thus, it is possible to improve the in-plane uniformity of film thickness of the silicon film without increasing the interval. In other words, it is possible to improve the in-plane uniformity of film thickness of the silicon film without deteriorating the productivity.

EXAMPLES

[0049] Next, examples performed to confirm the effects of the film forming method of the embodiment will be described.

[0050] First, wafers (hereinafter, also referred to as "pattern wafers") on each of which a fine uneven pattern having a surface area ratio of 50 times or 30 times was formed was provided. The surface area ratio is a value (A1/A2) obtained by dividing a surface area A1 of a pattern wafer by a surface area A2 of a wafer on which no uneven pattern is formed (hereinafter, also referred to as a "blanket wafer").

[0051] Subsequently, the pattern wafers were accommodated in the processing container **34** of the vertical heat treatment apparatus **1** described above. Predetermined gases were supplied into the processing container **34** according to a gas supply sequence (to be described later) to form silicon films.

[0052] FIGS. **6**A to **6**H are views for explaining gas supply sequences in Examples and Comparative examples. In FIGS. **6**A to **6**H, "MS" represents the supply of the MS gas into the processing container, "DCS" represents the supply of the DCS gas into the processing container, "VAC" represents evacuating the interior of the processing container, "N_2" represents the supply of the N_2 gas into the processing container, and "H_2" represents the supply of the H_2 gas into the processing container. FIGS. **6**A to **6**C represent the gas supply sequences in Examples 1 to 3, respectively, and FIGS. **6**D to **6**H represent the gas supply sequences in Comparative Examples 1 to 5, respectively.

[0053] In Example 1, as represented in FIG. **6**A, a silicon film was formed on the pattern wafer having the surface area ratio of 50 times by repeatedly performing the supply of the MS gas, the supply of the DCS gas, and the evacuation in this order. Processing conditions used in Example 1 are as follows.

[0054] A. Wafer temperature: 470 degrees C.

[0055] B. Processing pressure: 3 Torr (400 Pa)

[0056] C. Flow rate of MS gas: 1,500 sccm

[0057] D. Flow rate of DCS gas: 1,000 sccm

[0058] E. Supply time of MS gas/supply time of DCS gas/evacuation time: 25 seconds/30 seconds/60 seconds

[0059] F. Predetermined number of times: 170 times

[0060] In Example 2, a silicon film was formed on the pattern wafer having the surface area ratio of 30 times under the same conditions as in Example 1, except that gas replacement with the N_2 gas was performed instead of the evacuation in Example 1. That is, in Example 2, as represented in FIG. **6**B, the silicon film was formed on the pattern wafer having the surface area ratio of 30 times by repeating the supply of the MS gas, the supply of the DCS gas, and the supply of the N_2 gas in this order.

[0061] In Example 3, a silicon film was formed on the pattern wafer having the surface area ratio of 30 times under the same conditions as in Example 1, except that gas replacement with the H_2 gas was performed instead of the evacuation in Example 1. That is, in Example 3, as represented in FIG. **6**C, the silicon film was formed on the pattern wafer having the surface area ratio of 30 times by repeating the supply of the MS gas, the supply of the DCS gas, and the supply of the H_2 gas in this order.

[0062] In Comparative example 1, as represented in FIG. **6**D, a silicon film was formed on the pattern wafer having the surface area ratio of 50 times by simultaneously supplying the MS gas and the DCS gas.

[0063] In Comparative example 2, as represented in FIG. **6**E, a silicon film was formed on the pattern wafer having the surface area ratio of 50 times by alternately performing the supply of the MS gas and the supply of the DCS gas in a repetitive manner.

[0064] In Comparative example 3, as represented in FIG. **6**F, a silicon film was formed on the pattern wafer having the surface area ratio of 50 times by repeating the supply of the MS gas, the evacuation, and the supply of the DCS gas in this order.

[0065] In Comparative example 4, as represented in FIG. **6**G, a silicon film was formed on the pattern wafer having the surface area ratio of 50 times by repeating the supply of the MS gas, the evacuation, the supply of the DCS gas, and the evacuation in this order.

[0066] In Comparative example 5, as represented in FIG. **6**H, a silicon film was formed on the pattern wafer having the surface area ratio of 50 times by repeating the supply of the MS gas, the supply of the N_2 gas, the supply of the DCS gas, and the evacuation in this order.

[0067] Subsequently, for each of the silicon films formed in Examples 1 to 3 and Comparative examples 1 to 5, the in-plane uniformity of film thickness of each silicon film was calculated by measuring film thicknesses at a plurality of locations in the plane of the wafer.

[0068] FIG. **7** is a view representing in-plane uniformities of film thicknesses of the silicon films formed on the pattern wafers. In FIG. **7**, the horizontal axis represents Examples 1 to 3 and Comparative examples 1 to 5, and the vertical axis represents in-plane uniformity of film thickness [±%].

[0069] As represented in FIG. **7**, the in-plane uniformities of film thicknesses in Examples 1, 2, and 3 were ±4.87%, ±4.89%, and ±4.37%, respectively. Meanwhile, the in-plane uniformities of film thicknesses in Comparative examples 1 to 5 were ±11.25%, ±15.15%, ±13.63%, ±10.24%, and ±14.76%, respectively. From these results, it can be seen that the gas supply sequences according to Examples 1 to 3 are able to improve the in-plane uniformities of film thicknesses compared with the gas supply sequences according to Comparative examples 1 to 5. That is, it can be said that, by bypassing the evacuation and the gas replacement after the supply of the MS gas and before the supply of the DCS gas, and by removing the DCS gas after the supply of the DCS gas and before the supply of the MS gas, it is possible to improve the in-plane uniformity of film thickness of the silicon film formed on each pattern wafer. That is, it can be said that, by repeating the supply of the MS gas, the supply of the DCS gas, and the removal of the DCS gas in this order, it is possible to improve the in-plane uniformity of film thickness of the silicon film formed on each pattern wafer.

[0070] FIG. **8** is a view representing film thickness distributions in silicon films formed on pattern wafers. In FIG. **8**, the horizontal axis represents a distance [mm] from a wafer center, and the vertical axis represents a film thickness [A] of a silicon film. In FIG. **8**, circle (**0**) marks indicate the measurement results in Example 1, and triangle (**1**) marks represent the measurement results in Comparative example 1.

[0071] As represented in FIG. **8**, it can be seen that the difference in film thickness between the central portion and the peripheral portion of the wafer in Example 1 is smaller than the difference in film thickness between the central portion and the peripheral portion of the wafer in Comparative example 1. That is, by repeating the supply of the MS gas, the supply of the DCS gas, and the evacuation in this order, it is possible to reduce the difference in film thickness between the central portion and the peripheral portion of the silicon film formed on the pattern wafer.

[0072] It should be noted that the embodiments disclosed herein are exemplary in all respects and are not restrictive. The above-described embodiments may be omitted, replaced or modified in various forms without departing from the scope and spirit of the appended claims.

[0073] In the above-described embodiments, the case where the substrate is a semiconductor wafer has been described as an example, but the present disclosure is not limited thereto. For example, the substrate may be a large substrate for a flat panel display (FPD), or a substrate for an EL element or a solar cell.

[0074] According to the present disclosure in some embodiments, it is possible to improve an in-plane uniformity of film thickness.

What is claimed is:

1. A film forming method comprising:

supplying a halogen-free silicon raw material gas into a processing container that accommodates a substrate therein in a halogen-free silicon raw material gas supply process;

supplying a halogen-containing silicon raw material gas into the processing container in a halogen-containing silicon raw material gas supply process;

removing the halogen-containing silicon raw material gas inside the processing container in a halogen-containing silicon raw material gas removal process; and

repeating a cycle including a sequence of the halogen-free silicon raw material gas supply process, the halogen-containing silicon raw material gas supply process, and the halogen-containing silicon raw material gas removal process in a continuous manner.

2. The film forming method of claim **1**, wherein the halogen-free silicon raw material gas and the halogen-containing silicon raw material gas are supplied from a periphery of the substrate.

3. The film forming method of claim **1**, wherein the halogen-free silicon raw material gas and the halogen-containing silicon raw material gas are supplied substantially parallel to a main surface of the substrate.

4. The film forming method of claim **1**, wherein, after the halogen-free silicon raw material gas supply process, the halogen-containing silicon raw material gas supply process is continuously performed without performing an evacuation of an interior of the processing container and a gas replacement inside the processing container.

5. The film forming method of claim **1**, wherein, after the halogen-free silicon raw material gas supply process, the halogen-containing silicon raw material gas supply process is performed in a state in which an internal pressure of the processing container is kept substantially constant.

6. The film forming method of claim **1**, wherein, after the halogen-free silicon raw material gas supply process, the halogen-containing silicon raw material gas supply process is continuously performed while changing setting of an internal pressure of the processing container.

7. The film forming method of claim **1**, wherein the halogen-containing silicon raw material gas removal process includes at least one of performing an evacuation of an interior of the processing container and performing a gas replacement inside the processing container.

8. The film forming method of claim **1**, wherein the halogen-containing silicon raw material gas removal process includes performing an evacuation of an interior of the processing container.

9. The film forming method of claim **1**, wherein the halogen-containing silicon raw material gas removal process includes performing a gas replacement inside the processing container.

10. The film forming method of claim **9**, wherein a gas used for the gas replacement is at least one of an inert gas, a hydrogen gas, and a deuterium gas.

11. The film forming method of claim **1**, wherein the substrate has a recess formed in a surface thereof.

12. The film forming method of claim **1**, wherein the halogen-free silicon raw material gas is a SiH_4 gas, and the halogen-containing silicon raw material gas is a SiH_2Cl_2 gas.

13. The film forming method of claim **1**, wherein a plurality of substrates are accommodated inside the processing container at a predetermined interval in a vertical direction in a shelf-like manner.

14. A film forming apparatus comprising:

a processing container in which a substrate is accommodated;

a gas supply part configured to supply a gas into the processing container; and

a controller,

wherein the controller is configured to control the gas supply part so as to continuously repeat a cycle, the cycle including a sequence of supplying a halogen-free silicon raw material gas into a processing container that accommodates a substrate therein; supplying a halogen-containing silicon raw material gas into the processing container; and removing the halogen-containing silicon raw material gas inside the processing container.

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