



US 20090090384A1

(19) **United States**

(12) **Patent Application Publication**

**You et al.**

(10) **Pub. No.: US 2009/0090384 A1**

(43) **Pub. Date: Apr. 9, 2009**

(54) **CLEANING METHOD OF APPARATUS FOR DEPOSITING METAL CONTAINING FILM**

(76) Inventors: **Dong-Ho You**, Kyungki-do (KR);  
**Ki-Hoon Lee**, Kyungki-do (KR);  
**Yu-Min Jung**, Daejeon (KR)

Correspondence Address:  
**LADAS & PARRY LLP**  
224 SOUTH MICHIGAN AVENUE, SUITE 1600  
CHICAGO, IL 60604 (US)

(21) Appl. No.: **12/301,051**  
(22) PCT Filed: **Jan. 22, 2007**  
(86) PCT No.: **PCT/KR07/00366**  
§ 371 (c)(1),  
(2), (4) Date: **Nov. 17, 2008**

(30) **Foreign Application Priority Data**

May 29, 2006 (KR) ..... 10-2006-0047915

**Publication Classification**

(51) **Int. Cl.**  
**C25F 3/12** (2006.01)  
(52) **U.S. Cl.** ..... **134/1.1; 134/2**

(57) **ABSTRACT**

Provided is a cleaning method of an apparatus for depositing a metal containing film using a metal organic (MO) source. A fluorine (F)-containing gas and a carbon (C)-eliminating gas are supplied to a reactor of the apparatus so that in-situ cleaning can be performed. A solid by-product is not generated in the method, and after a predetermined quantity of wafers is processed, in-situ cleaning can be performed without exposing the reactor to the air such that productivity of the apparatus is maximized.

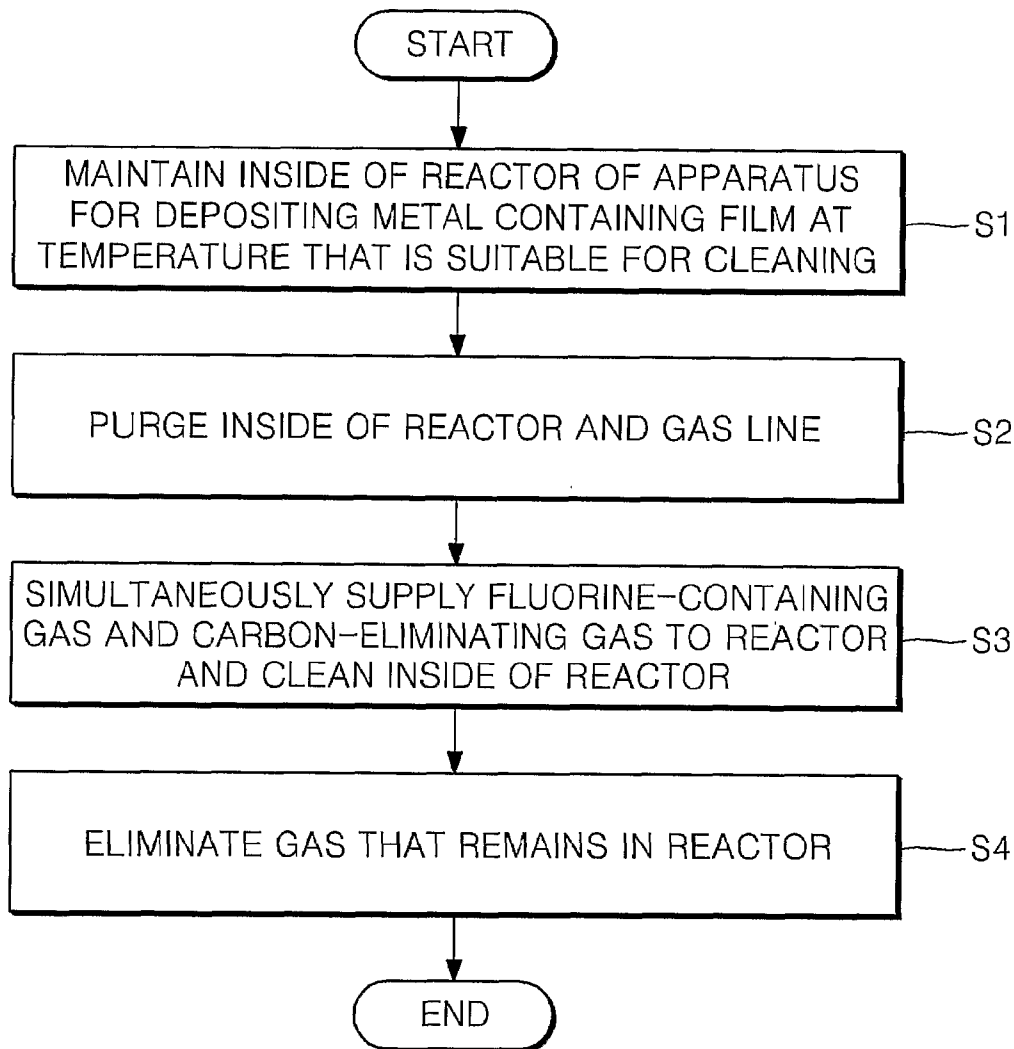


FIG. 1

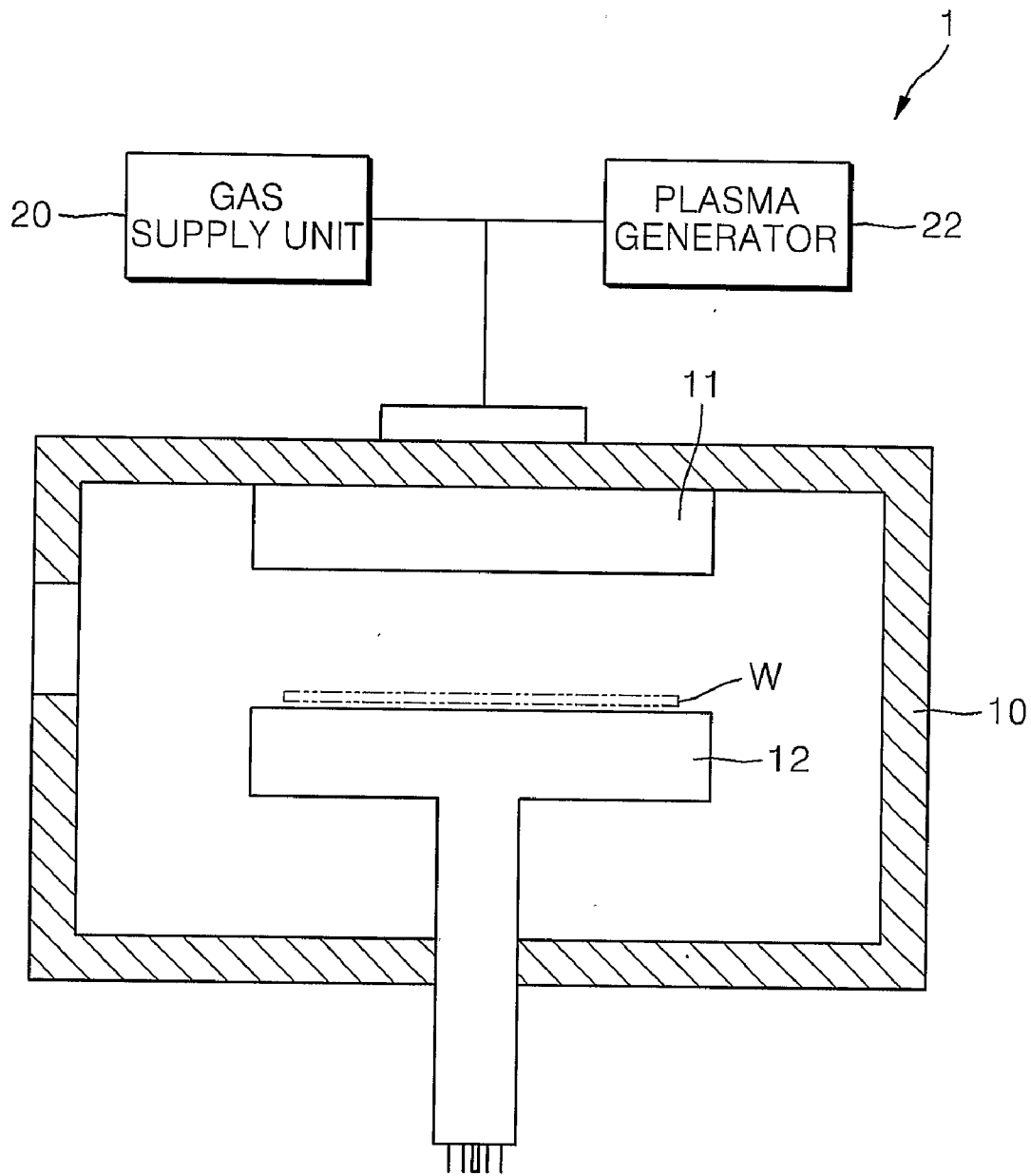


FIG. 2

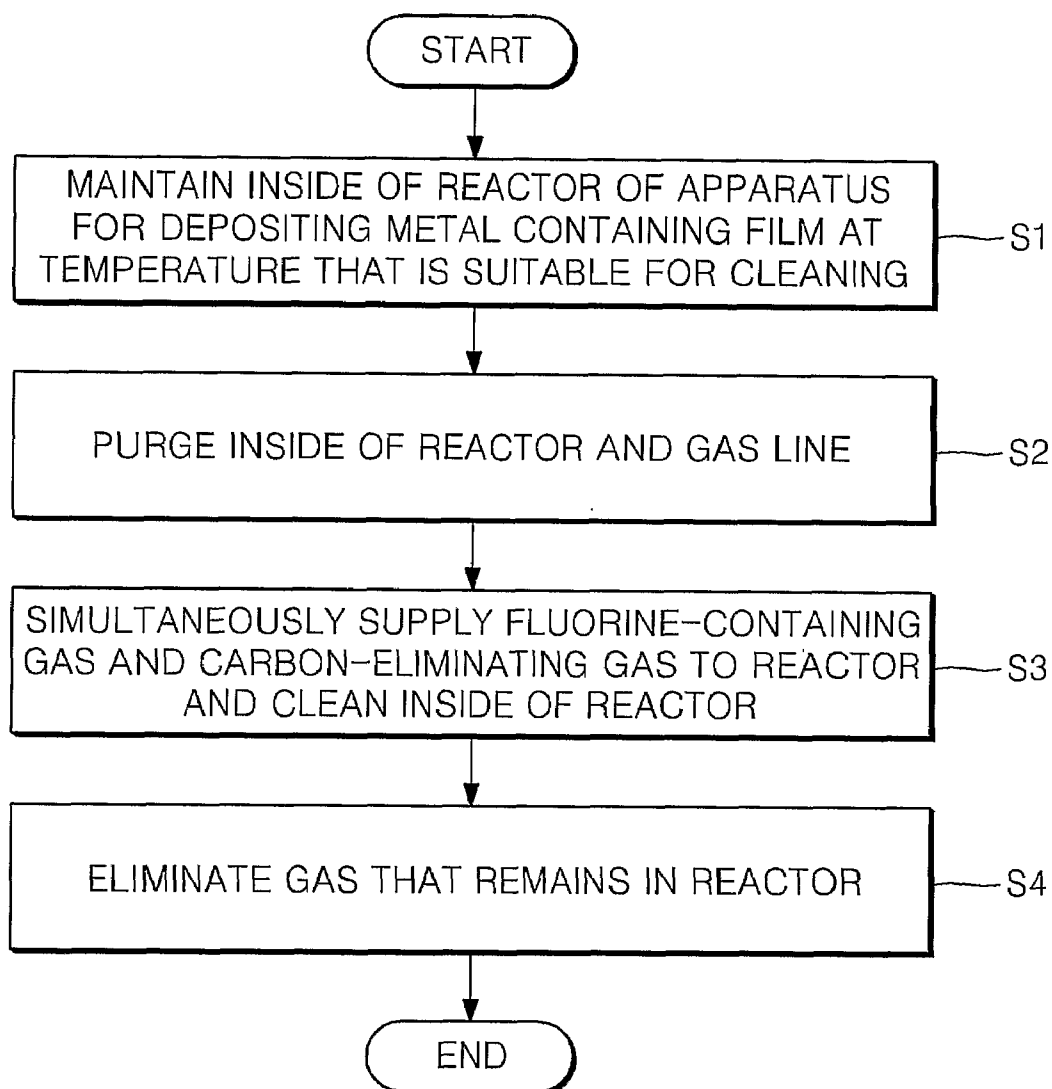


FIG. 3

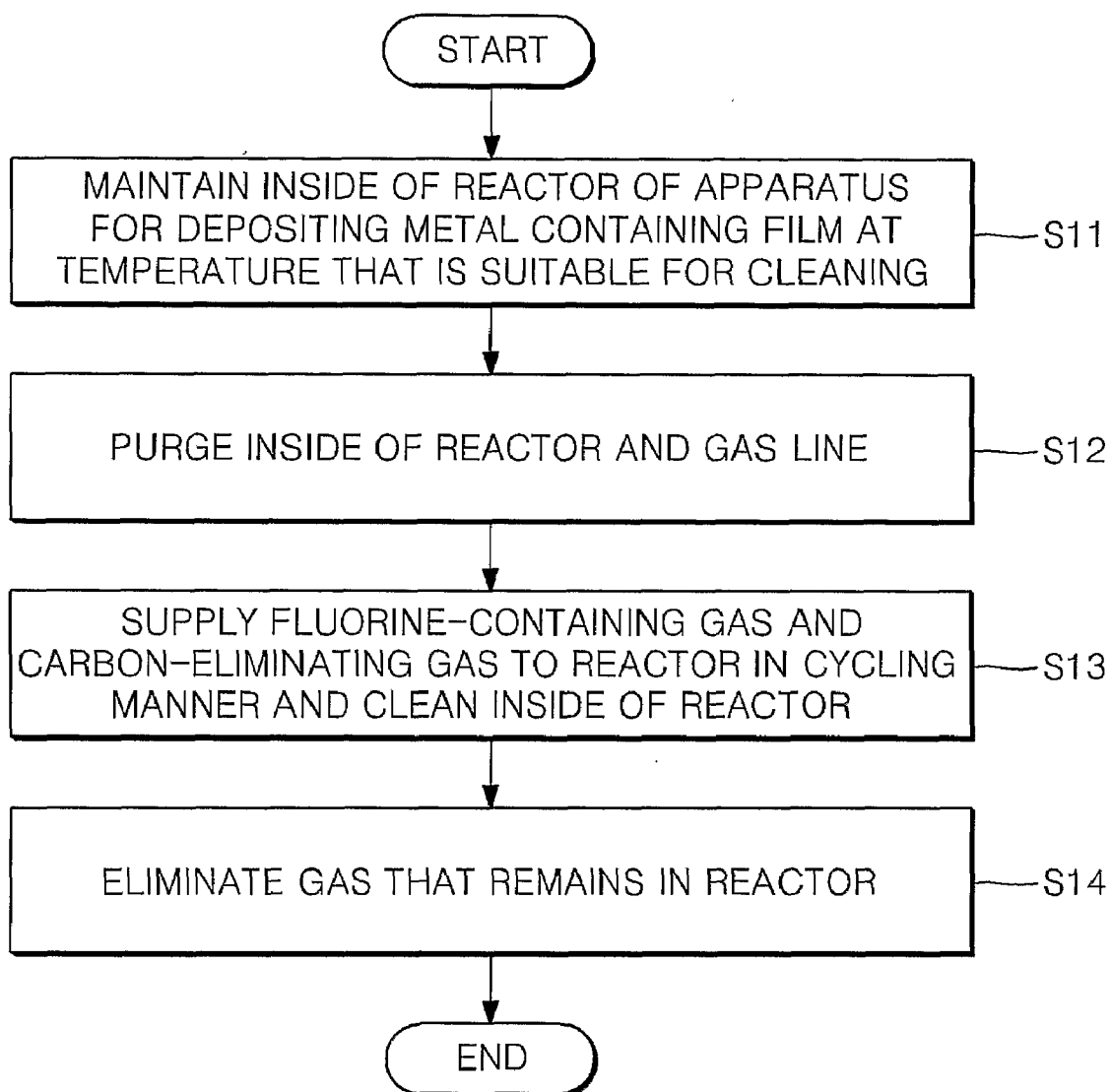


FIG. 4

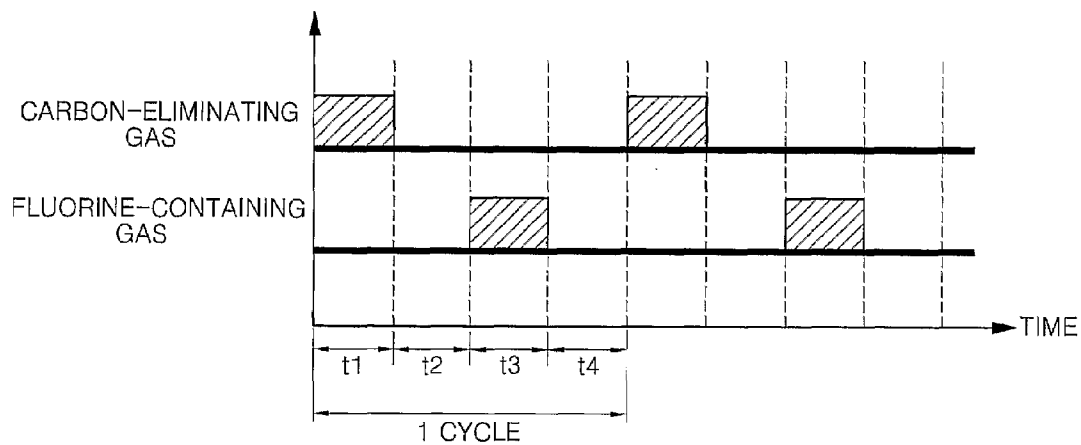


FIG. 5

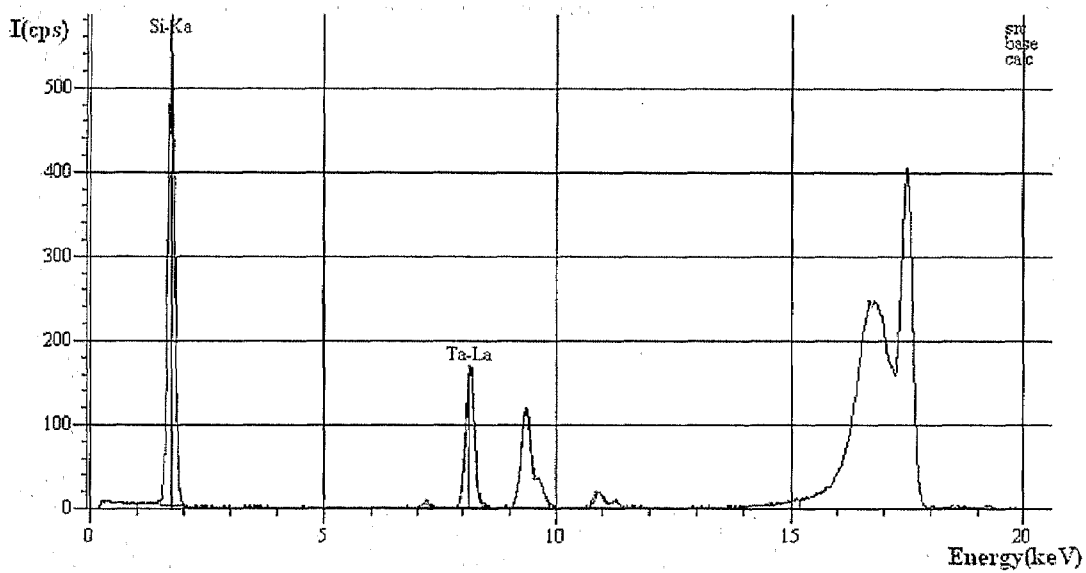


FIG. 6

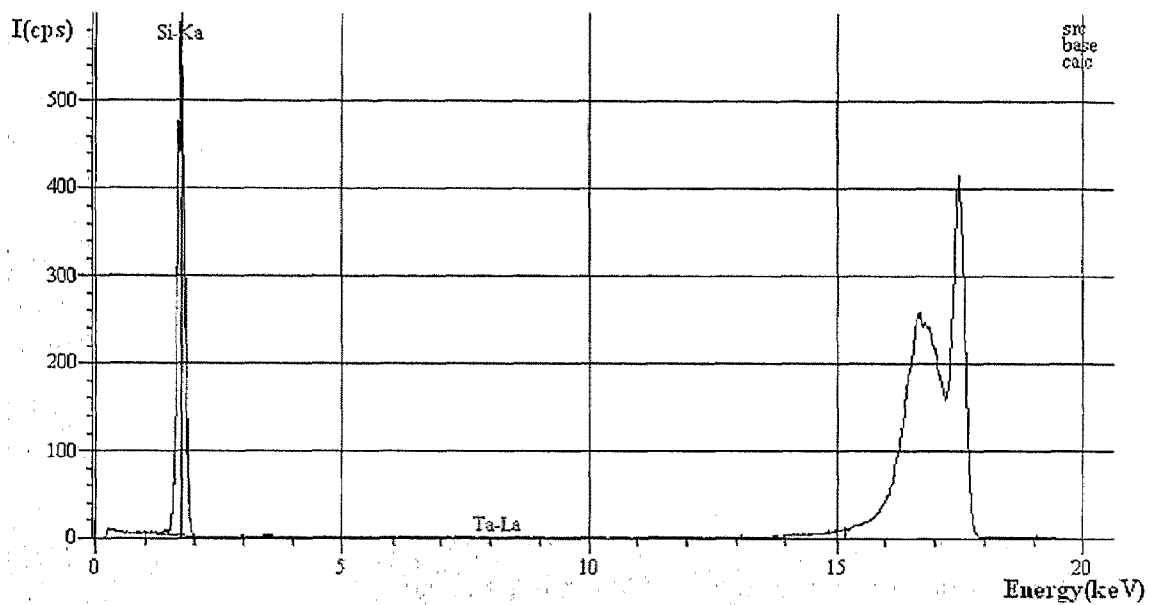


FIG. 7

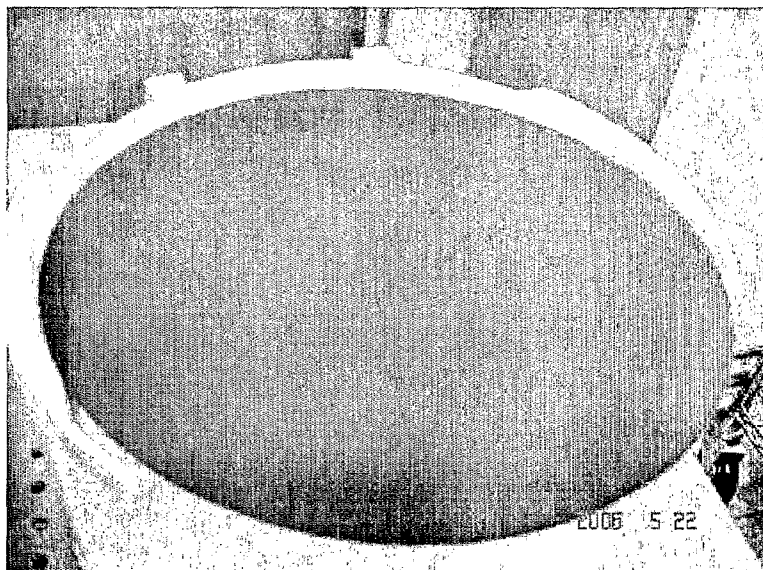
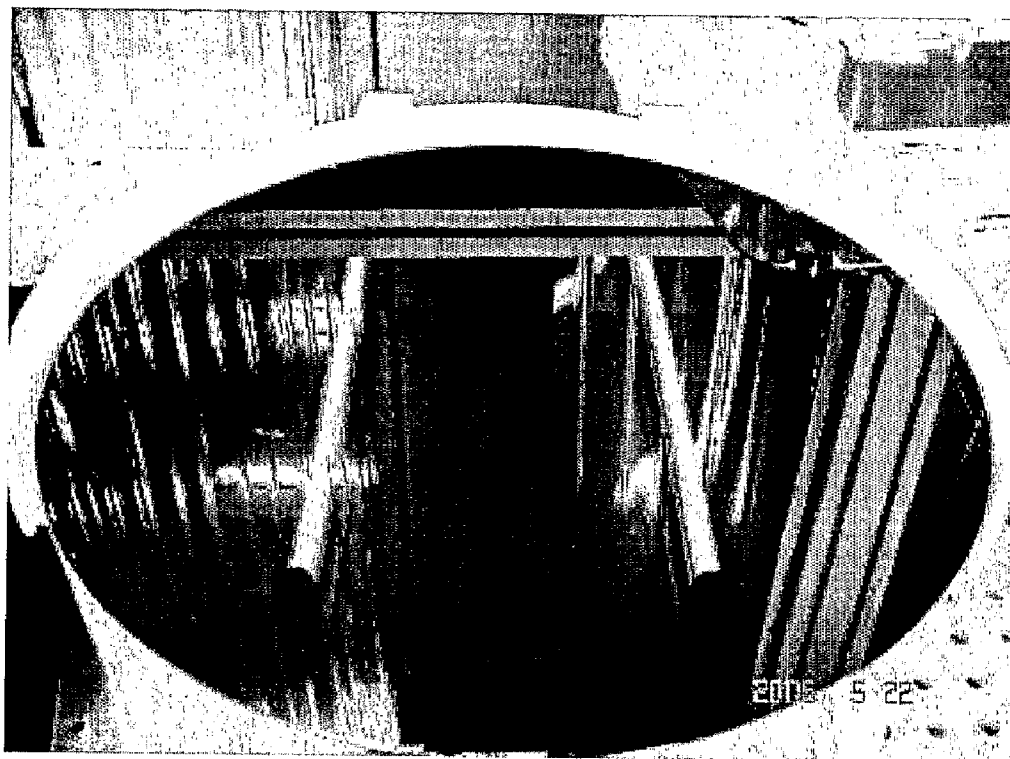


FIG. 8



## CLEANING METHOD OF APPARATUS FOR DEPOSITING METAL CONTAINING FILM

### TECHNICAL FIELD

[0001] The present invention relates to a cleaning method of an apparatus for fabricating a semiconductor, and more particularly, to a cleaning method of a reactor of an apparatus for depositing a metal containing film using a metal organic (MO) source.

### BACKGROUND ART

[0002] In general, semiconductor devices are fabricated using a plurality of unit processes, such as an ion implantation process, a thin film deposition process, a diffusion process, a photolithography process, and an etching process. The thin film deposition process of the unit processes is an essential process in which improvements in reproducibility and reliability for fabricating a semiconductor device are required.

[0003] A thin film of a semiconductor device is deposited on a wafer using sputtering, evaporation, chemical vapor deposition (CVD) or atomic layer deposition (ALD). A thin film deposition apparatus for performing these methods generally includes a reactor, a gas line for supplying various gases into the reactor, and a wafer block on which the wafer is seated.

[0004] However, while a thin film-depositing process is performed using the thin film deposition apparatus, a reaction product generated during the thin film-depositing process is accumulated (attached) on inner walls of the reactor as well as on the surface of a semiconductor thin film. Since the thin film deposition apparatus for semiconductor mass production processes a large quantity of wafers, if a semiconductor fabrication process is consecutively performed in the state where the reaction product is attached to the inside of the reactor, characteristics of a film may be changed. As the most representative example, a change of a film resistance value, a change of thickness, and particles generated when the reaction product is peeled off. These particles cause defects in a deposition process and are attached to the wafer, resulting in lowering of the yield of a semiconductor device.

[0005] As such, in conventional semiconductor fabrication methods, the thin film deposition apparatus is paused after a process of a predetermined quantity of wafers before a change of a film occurs, and the reactor is exposed to the air, thereby separating the reactor from each of elements inside the reactor. After foreign substances deposited in the reactor and each of elements are cleaned using volatile materials such as alcohol, the separated reactor is again assembled to each of elements. Generally, this cleaning method is referred to ex-situ cleaning. In ex-situ cleaning, productivity in semiconductor fabrication is greatly reduced and there are additional problems such as the occurrence of a change point of equipment.

[0006] A different method of cleaning methods of a thin film deposition apparatus is a cleaning method, so-called in-situ cleaning, by which the thin film deposition apparatus is not paused and deposition materials inside a reactor are eliminated using a corrosive gas without exposing the reactor to the air. For example, a perfluorized compound gas, such as  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_8$ ,  $\text{CHF}_3$  or  $\text{SF}_6$ , or  $\text{NF}_3$  as a cleaning gas for an apparatus for depositing a film, such as silicon (Si), a

silicon oxide ( $\text{SiO}_x$ ), and a silicon nitride ( $\text{SiN}_x$ ), is implanted into the reactor and the films are eliminated.

### TECHNICAL PROBLEM

[0007] In particular, in order to improve step coverage for a product having a high aspect ratio as a semiconductor device is highly integrated, CVD or ALD is recently used in a metal or metal nitride process. There is no method of effectively in-situ cleaning a metal containing film yet. In addition, a metal organic (MO) source is usually used as a metal source when a metal containing film is deposited. The MO source contains carbon (C) and therefore, an effective cleaning method is particularly required.

### TECHNICAL SOLUTION

[0008] The present invention provides a cleaning method of an apparatus for depositing a metal containing film using a metal organic (MO) source.

[0009] According to an aspect of the present invention, there is provided a cleaning method of an apparatus for depositing a metal containing film using an MO (metal organic) source, the method comprising supplying a fluorine (F)-containing gas and a carbon (C)-eliminating gas to a reactor and cleaning an inside of the reactor without a pause of the apparatus and without exposing the reactor to the air.

[0010] The fluorine (F)-containing gas may be one selected from the group consisting of  $\text{NF}_3$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CF}_4$ ,  $\text{CHF}_3$ , and a combination thereof. The carbon (C)-eliminating gas may be an oxygen (O)-containing gas or hydrogen (H)-containing gas. The carbon (C)-eliminating gas may be one selected from the group consisting of  $\text{O}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{NH}_3$ ,  $\text{H}_2$ , and a combination thereof. The fluorine (F)-containing gas and the carbon (C)-eliminating gas may be simultaneously supplied to the reactor or may be supplied in a cycling manner.

### ADVANTAGEOUS EFFECTS

[0011] The present invention provides a method of in-situ cleaning an apparatus for depositing a metal containing film using an MO source. Since the MO source contains carbon (C), when a reactor is cleaned using only a corrosive gas used as a general cleaning gas, carbon (C) and fluorine (F) that remain in the reactor react with each other, fluorocarbon is formed, a solid by-product is generated so that the reactor cannot be completely cleaned. In the present invention, a metal by-product in the reactor is eliminated using a fluorine (F)-containing gas, and the reactor can be cleaned by additionally using a carbon (C)-eliminating gas without generation of a by-product of a solid ingredient. Therefore, after a process of a predetermined quantity of wafers is performed, in-situ cleaning can be performed without a pause of the apparatus and without exposing the reactor to the air so that productivity of the apparatus can be maximized.

### DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 illustrates an apparatus for depositing a metal containing film for performing a cleaning method according to an embodiment of the present invention.

[0013] FIG. 2 is a flowchart illustrating a cleaning method of the apparatus for depositing a metal containing film according to an embodiment of the present invention.

[0014] FIG. 3 is a flowchart illustrating a cleaning method of the apparatus for depositing a metal containing film according to another embodiment of the present invention.



[0015] FIG. 4 illustrates a sequence for supplying a cleaning gas in the cleaning method of FIG. 2.

[0016] FIG. 5 shows an X-ray fluorescence spectrometry (XRF) intensity curve of an experimental wafer before the cleaning method according to the present invention is performed.

[0017] FIG. 6 shows an XRF intensity curve of an experimental wafer after the cleaning method according to the present invention is performed.

[0018] FIG. 7 shows a photograph of an experimental wafer presented as a comparative example.

[0019] FIG. 8 shows a photograph of an experimental wafer after the cleaning method according to the present invention is performed.

#### BEST MODE

[0020] The present invention will now be described more fully with reference to the accompanying drawings, in which exemplary embodiments of the invention are shown. The invention may, however, be embodied in many different forms and should not be construed as being limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the concept of the invention to those skilled in the art.

[0021] First, a cleaning method according to the present invention can be used in cleaning of an apparatus for depositing a metal containing film of FIG. 1.

[0022] The apparatus of FIG. 1 includes a reactor 10 having an internal space, a wafer block 12 which is installed in the internal space of the reactor 10 to ascend and descend and on which a wafer W is disposed, and a shower head 11 which sprays a gas so that a thin film can be deposited on the wafer W disposed on the wafer block 12.

[0023] The apparatus 1 deposits a metal containing film such as a metal film or a metal nitride film on a semiconductor wafer W, such as a silicon wafer or a liquid crystal display (LCD) glass substrate, using a metal organic (MO) source and further includes a gas supply unit 20 which supplies a source gas, an inert gas for a process, and a cleaning gas to the reactor 10 through a gas line. In the cleaning method according to the present invention, the cleaning gas includes a fluorine (F)-containing gas and a carbon (C)-eliminating gas.

[0024] The fluorine (F)-containing gas may be  $\text{NF}_3$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CF}_4$ ,  $\text{CHF}_3$  or a combination thereof. The carbon (C)-eliminating gas may be an oxygen (O)-containing gas or hydrogen (H)-containing gas. The carbon (C)-eliminating gas may be one selected from the group consisting of  $\text{O}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{NH}_3$ ,  $\text{H}_2$ , and a combination thereof. Thus, this cleaning gas can be supplied through the gas supply unit 20 during a cleaning process. The cleaning gas may be simultaneously supplied to the reactor 10 or may be supplied in a cycling manner. For example, the carbon (C)-eliminating gas is firstly supplied to the reactor 10 to eliminate a metal by-product in the reactor 10, and then, the fluorine (F)-containing gas is supplied to the reactor 10 to clean the reactor 10 without generation of a solid by-product. The procedure may be repeated more than once, which will be described in detail in the following embodiments.

[0025] The cleaning gas can be plasmatized to maximize cleaning efficiency. In this case, the cleaning gas may be plasmatized by using a remote plasma and may be supplied to the reactor 10. Alternatively, the cleaning gas may be supplied to the reactor 10 in the state where direct plasma is generated

into the reactor 10 and may be plasmatized. A method for plasmatizing the cleaning gas depends on types of apparatuses. In a type using a remote plasma illustrated in FIG. 1, the cleaning gas is plasmatized by a remote plasma generator 22 before the cleaning gas reaches the shower head 11. In a type using a direct plasma, a direct plasma generator is provided outside the reactor 10. The applied plasma may be low frequencies of 300-500 KHz and/or high frequencies of 13.56-21.12 MHz at a power of 50-2000 W.

[0026] Next, specific embodiments of a method of cleaning the reactor 10 of the apparatus 1 of FIG. 1 will be described.

#### FIRST EMBODIMENT

[0027] FIG. 2 is a flowchart illustrating a cleaning method of the apparatus for depositing a metal containing film according to an embodiment of the present invention.

[0028] Referring to FIGS. 1 and 2, the inside of the reactor 10 of the apparatus 1 is maintained at temperature that is suitable for cleaning, as in operation s1 of FIG. 2. For example, when a metal nitride, such as TaN or TaCN, as a metal containing film is deposited by the apparatus 1, the temperature of elements to be cleaned, such as the shower head 11 and the wafer block 12, is maintained at 450° C. during a cleaning process. This is because the temperature is made the same as a TaN process temperature so that deposition and cleaning processes can be performed without any change of temperature. The cleaning process can be performed at approximately 250-500° C.

[0029] Next, the inside of the reactor 10 and a gas line are purged, as in optional operation s2 of FIG. 2. This is because, when a residual gas exists in the inside of the reactor 10 and the gas line, a severe reaction or a large amount of particles are prevented from occurring during a subsequent cleaning gas supply process. When this problem does not occur, the purging operation s2 may be omitted. A purge gas may be an inert gas, for example, Ar or  $\text{N}_2$ .

[0030] Of course, operations s1 and s2 may be performed in reverse order.

[0031] Next, a fluorine (F)-containing gas and a carbon (C)-eliminating gas are simultaneously supplied into the reactor 10 so that the inside of the reactor 10 can be cleaned without a pause of the apparatus 1, as in operation s3 of FIG. 2. In this case, pressure inside the reactor 10 ranges from 0.3 torr to 10 torr. As pressure inside the reactor 10 decreases, cleaning efficiency increases. The reactor 10 is maintained under pressure of approximately 0.5-4 torr. A time required for the cleaning operation s3 depends on degree of contamination of the reactor 10 or may be varied whether the film deposition process has been performed by 500 times or 1000 times. Although the time required for the cleaning operation s3 varies according to specific process conditions, films are eliminated at rate of approximately 1000 Å/min. Thus, if 200 Å film deposition process is performed by 1000 times, the reactor 10 is cleaned for 200 minutes.

[0032] When a metal nitride, such as TaN or TaCN, is deposited by the apparatus 1, the fluorine (F)-containing gas may be  $\text{NF}_3$  and the carbon (C)-eliminating gas may be  $\text{H}_2$ . When the remote plasma generator 22 operates, if the cleaning gas is plasmatized and is supplied into the reactor 10, cleaning efficiency can be more maximized. A gas for plasma generation may be Ar. As described previously, the cleaning gas may be supplied into the reactor 10 in the state where direct plasma is generated in the reactor 10, according to types of apparatuses.

[0033] Since the MO source contains carbon (C), when cleaning is performed using only a corrosive gas such as fluorine (F) used as a general cleaning gas, carbon (C) and fluorine (F) that remain in the reactor 10 react with each other and form fluorocarbon and a solid by-product is generated so that the reactor 10 cannot be completely cleaned. However, if the carbon (C)-eliminating gas is additionally supplied to the reactor 10 as in the present invention, the reactor 10 can be effectively cleaned without generation of a by-product of a solid ingredient.

[0034] If the cleaning operation s3 is finished, operation s4 of eliminating a gas that remains in the reactor 10 is performed. For example, the inside of the reactor 10 is purged for a long time or is processed using plasma that has no reaction and has a sputtering effect, such as H<sub>2</sub>, Ar or N<sub>2</sub> plasma. Operation s4 is also an optional operation.

#### SECOND EMBODIMENT

[0035] FIG. 3 is a flowchart illustrating a cleaning method of the apparatus for depositing a metal containing film according to another embodiment of the present invention.

[0036] The cleaning method according to the second embodiment is similar to that of the first embodiment and is different from that of the first embodiment in that cleaning gas supply is performed in a cycling manner.

[0037] Referring to FIGS. 1 and 3, the inside of the reactor 10 of the apparatus 1 is maintained at temperature that is suitable for cleaning, as in operation s11 of FIG. 3. Next, as in optional operation s12, the inside of the reactor 10 and a gas line are purged. Of course, operations s11 and s12 may be performed in reverse order. Regarding operations s11 and s12, the description of operations s1 and s2 of FIG. 2 can be cited.

[0038] Next, a cleaning gas is supplied into the reactor 10 and the inside of the reactor 10 is cleaned, as in operation s13. In this case, a gas supply sequence in a cycling manner as illustrated in FIG. 4 will be referred to.

[0039] Referring to FIG. 4, firstly, a carbon (C)-eliminating gas is supplied to the reactor 10 in operation t1. The supply of the carbon (C)-eliminating gas is stopped after a predetermined time elapses in operation t2. Next, the fluorine (F)-containing gas is supplied to the reactor 10 in operation t3. The supply of the fluorine (F)-containing gas is stopped after a predetermined time elapses in operation t4. A gas supply cycle comprised of operations t1 through t4 is repeated more than once and the inside of the reactor 10 is cleaned. Here, operations t2 and t4 may have substantially a maintenance time of 0. In detail, the supply of the carbon (C)-eliminating gas may be stopped and simultaneously, the fluorine (F)-containing gas may be supplied to the reactor 10, and the supply of the fluorine (F)-containing gas may be stopped and simultaneously, the carbon (C)-eliminating gas may be supplied to the reactor 10.

[0040] If the cleaning operation s13 is finished, operation s14 of eliminating a gas that remains in the reactor 10 is performed. Regarding operation s14, the description of operation s4 of FIG. 2 can be cited.

#### EXPERIMENTAL EXAMPLE

[0041] A plasma enhanced (PE)-tetraethylorthosilicate (TEOS) film was deposited on a wafer to a thickness of 1000 Å. Then a TaN film was deposited to a thickness of 800-1000 Å on the PE-TEOS film in a reactor of an apparatus for

depositing a metal containing film. And a cleaning method according to the present invention was performed without a pause of the apparatus. As a cleaning gas, NF<sub>3</sub> was used as a fluorine (F)-containing gas and H<sub>2</sub> was used as a carbon (C)-eliminating gas. Like in the first embodiment, the fluorine (F)-containing gas and the carbon (C)-eliminating gas were simultaneously supplied into the reactor. Ar was used as a gas for plasma generation.

[0042] FIG. 5 shows an X-ray fluorescence spectrometry (XRF) intensity curve of an experimental wafer before it is cleaned in the state where the TaN film is deposited on the PE-TEOS film to a thickness of 800 Å. Referring to FIG. 5, a peak corresponding to the PE-TEOS film as an oxide and a peak corresponding to the TaN film are simultaneously observed.

[0043] FIG. 6 shows an XRF intensity curve of an experimental wafer after the cleaning method according to the present invention is performed. Referring to FIG. 6, the peak corresponding to the PE-TEOS film as an oxide is observed but the peak corresponding to the TaN film is not observed. In detail, the TaN film on the experimental wafer is effectively eliminated by the cleaning method according to the present invention and there are no remainders. Thus, in the cleaning method according to the present invention, it can be construed that the TaN film deposited on inner walls of the reactor can be effectively eliminated.

[0044] FIG. 7 shows a photograph of an experimental wafer presented as a comparative example. The wafer is cleaned using only NF<sub>3</sub> as a fluorine (F)-containing gas without a carbon (C)-eliminating gas in the state where a TaN film is deposited on a PE-TEOS film to a thickness of 1000 Å. As shown in the photograph, the surface of the wafer is very opaque. This is because carbon (C) that is separated from an MO source reacts with fluorine (F) in NF<sub>3</sub> as a cleaning gas, fluorocarbon is formed and a solid by-product generated in this way is attached to the surface of the wafer. Thus, it can be construed that the reactor cannot be completely cleaned without the carbon (C)-eliminating gas.

[0045] FIG. 8 shows a photograph of an experimental wafer after the cleaning method according to the present invention is performed. In detail, NF<sub>3</sub> and H<sub>2</sub> are used together. In contrast with FIG. 7, the wafer appears to be a clean mirror surface. Thus, the reactor can be completely cleaned by using a carbon (C)-eliminating gas without generation of a by-product of a solid ingredient.

[0046] In the embodiments and the experimental example, cleaning of an apparatus for depositing a film containing tantalum, such as TaN or TaCN, has been described. However, the cleaning method according to the present invention can be applied to cleaning of an apparatus for depositing a film containing other metal, for example, tungsten, such as BW, WSi<sub>x</sub>, or WN. The cleaning method according to the present invention can be applied to the case where elements in a film except carbon (C) is basically eliminated using only fluorine (F).

[0047] While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those skilled in the art that various changes in forms and details may be made therein without departing from the spirit and scope of the invention as defined by the following claims.

#### INDUSTRIAL APPLICABILITY

[0048] According to the present invention, an apparatus for depositing a metal containing film using an MO source can be

effectively cleaned. A metal by-product in a reactor is eliminated using a fluorine (F)-containing gas and a carbon (C)-eliminating gas is additionally used so that the reactor can be cleaned without generation of a by-product of a solid ingredient. Accordingly, after a predetermined quantity of wafers is processed, in-situ cleaning can be performed without a pause of the apparatus such that productivity of the apparatus is maximized.

1. A cleaning method of an apparatus for depositing a metal containing film using an MO (metal organic) source, the method comprising

simultaneously supplying a fluorine (F)-containing gas and a carbon (C)-eliminating gas to a reactor and cleaning an inside of the reactor without a pause of the apparatus.

2. The cleaning method of claim 1, wherein the gases are plasmatized using a remote plasma and are supplied to the reactor.

3. The cleaning method of claim 1, wherein the gases are supplied to the reactor in the state where direct plasma is generated in the reactor and are plasmatized.

4. The cleaning method of claim 1, wherein the fluorine (F)-containing gas is one selected from the group consisting of  $\text{NF}_3$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CF}_4$ ,  $\text{CHF}_3$ , and a combination thereof.

5. The cleaning method of claim 1, wherein the carbon (C)-eliminating gas is an oxygen (O)-containing gas or hydrogen (H)-containing gas.

6. The cleaning method of claim 1, wherein the carbon (C)-eliminating gas is one selected from the group consisting of  $\text{O}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{NH}_3$ ,  $\text{H}_2$ , and a combination thereof.

7. A cleaning method of an apparatus for depositing a metal containing film using an MO (metal organic) source, the method comprising

supplying a fluorine (F)-containing gas and a carbon (C)-eliminating gas to a reactor and cleaning an inside of the reactor without a pause of the apparatus,

wherein the cleaning of the inside of the reactor repeats a gas supply cycle more than once, the gas supply cycle comprising:

supplying the carbon (C)-eliminating gas to the reactor;

stopping supply of the carbon (C)-eliminating gas;

supplying the fluorine (F)-containing gas to the reactor; and

stopping supply of the fluorine (F)-containing gas.

8. The cleaning method of any one of claims 1 through 7, wherein the metal containing film is one of TaN and TaCN, the fluorine (F)-containing gas is  $\text{NF}_3$  and the carbon (C)-eliminating gas is  $\text{H}_2$ .

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