SUBSTRATE PROCESSING METHOD AND SUBSTRATE PROCESSING APPARATUS

TECHNICAL FIELD

[0001] The present disclosure relates to a substrate processing method and a substrate processing apparatus.

BACKGROUND

[0002] In manufacturing a semiconductor device, a silicon-containing film, such as a silicon oxide film (SiO_2 film), formed on a surface of a semiconductor wafer serving as a substrate (hereinafter referred to as a "wafer") may be etched. Patent Document 1 describes etching the SiO_2 film by repeatedly performing, in sequence, a first step of supplying a basic gas to the substrate and a second step of supplying a fluorine-containing gas to the wafer, wherein the interior of a processing container in which the substrate is stored is purged after completion of the second step and before commencement of the first step.

[0003] Patent Document 2 describes supplying a process gas including a halogen-containing gas and a basic gas to the wafer to generate a reaction product on a surface of the SiO_2 film, and then reducing the internal pressure of the processing container in which the wafer is stored to 0 to 200 Pa such that a portion of the reaction product remains on the SiO_2 film while another portion thereof is removed. Thereafter, the SiO_2 film is removed by increasing the internal pressure of the processing container and supplying the process gas to the wafer again.

[Prior Art Documents]

[0004] Patent Documents

Patent Document 1: Japanese laid-open publication No. 2021-180281

Patent Document 2: Japanese laid-open publication No. 2021-118250

[0005] The present disclosure provides a technique capable of performing a highly uniform removal process at respective portions within a surface of a substrate when removing a silicon-containing film formed on the surface of the substrate.

SUMMARY

[0006] A substrate processing method in accordance with the present disclosure, includes storing a substrate having a silicon-containing film formed on a surface thereof in a processing container; performing a first operation of supplying a process gas including a halogen-containing gas and a basic gas into the processing container to modify the silicon-containing film and generate a reaction product; performing a second operation of supplying an inert gas into the processing container and exhausting the processing container in a state where supply of the process gas into the processing container is stopped, in order to remove a portion of the reaction product; repeating the first operation and the second operation alternately; and controlling an internal pressure of the processing container to be higher than 200 Pa in each execution of the second operation such that, in a second or subsequent execution of the first operation in the repeating, the process gas is supplied to the substrate on which the reaction product remains.

[0007] According to the present disclosure, it is possible to perform a highly uniform removal process at respective portions within a surface of a substrate when removing a silicon-containing film formed on the surface of the substrate.

BRIEF DESCRIPTION OF DRAWINGS

[0008] FIG. 1 is a longitudinal cross-sectional view illustrating an example of a surface structure of a substrate before an etching process according to an embodiment.

FIG. 2 is an enlarged longitudinal cross-sectional view illustrating a portion of the surface structure of the substrate before the etching process.

FIG. 3A is a view illustrating a change in the surface of a silicon oxide film caused by an etching process according to a comparative embodiment.

FIG. 3B is a view illustrating a change in the surface of the silicon oxide film caused by the etching process according to the comparative embodiment.

FIG. 4A is a view illustrating a change in the surface of a silicon oxide film caused by the etching process according to the embodiment.

FIG. 4B is a view illustrating a change in the surface of the silicon oxide film caused by

the etching process according to the embodiment.

FIG. 4C is a view illustrating a change in the surface of the silicon oxide film caused by the etching process according to the embodiment.

FIG. 4D is a view illustrating a change in the surface of the silicon oxide film caused by the etching process according to the embodiment.

FIG. 5 is a longitudinal cross-sectional view illustrating a substrate processing apparatus according to the embodiment.

FIG. 6 is a time chart illustrating a processing operation in the substrate processing apparatus according to the embodiment.

FIG. 7 is a graph illustrating results of Evaluation Test 1.

FIG. 8 is a graph illustrating results of Evaluation Test 2.

DETAILED DESCRIPTION

[0009] (Surface Layer Structure of Substrate)

FIG. 1 is a longitudinal cross-sectional view illustrating an example of a surface structure of a substrate before an etching process according to an embodiment. As illustrated in FIG. 1, in a surface layer of a wafer W, a large number of protrusions, which are formed of, for example, a polysilicon film 11, are formed on a lower layer film 10 and are arranged in a lateral direction, thereby forming a plurality of recesses. Accordingly, the polysilicon film 11 forms sidewalls of the recesses. A silicon oxide film 12 is formed in each recess. In the present embodiment, etching is performed on each silicon oxide film 12 such that a lower end portion thereof remains. This etching is selectively performed with respect to the polysilicon film 11. In addition, the lower layer film 10 is not illustrated in drawings other than FIG. 1.

[0010] When forming the silicon oxide film 12 in the recess, the silicon oxide film 12 may grow from various locations on the sidewalls of the polysilicon film 11 and join together, thereby forming a seam 13 in a central portion of the silicon oxide film 12 in the lateral direction. The seam 13 is a junction between interfaces of the silicon oxide film 12 or a void formed in the silicon oxide film 12. Hereinafter, a direction from the front surface side toward the back

surface side of the wafer W may also be referred to as a vertical direction or a height direction. The size of the seam 13, such as a length (width) thereof in the lateral direction or a length thereof in the height direction, and a formation position thereof in the height direction vary among the recesses.

[0011] (Comparative Embodiment)

In order to clearly demonstrate the effects of an etching method according to the present disclosure, an etching process according to a comparative embodiment will first be described. FIG. 2 illustrates the wafer W before processing. For purposes of description, it is assumed that two silicon oxide films 12a and 12b are illustrated as the silicon oxide film 12, the seam 13 is not formed in the silicon oxide film 12a, and the seam 13 is formed in the silicon oxide film 12b. In addition, in both the process according to the comparative embodiment and the process according to the embodiment described later, the wafer W is stored in a processing container and is adjusted to a predetermined temperature, and the processes are performed by supplying respective gases into the processing container. During the processing of the wafer W, the interior of the processing container is maintained in a vacuum atmosphere at a desired pressure by adjusting an exhaust amount.

[0012] FIGS. 3A and 3B illustrate changes in the surfaces of the silicon oxide films 12a and 12b caused by the etching process according to the comparative embodiment. First, a process gas is supplied into the processing container. The process gas includes a halogen-containing gas and a basic gas. Specifically, a hydrogen fluoride (HF) gas is supplied as the halogen-containing gas, and an ammonia (NH_3) gas is supplied as the basic gas. Surface portions of the silicon oxide film 12a and 12b that have reacted with the process gas are modified to become ammonium fluoro slicate (AFS), which is a reaction product, thereby forming an AFS layer. This reaction then proceeds, and the thickness of the AFS layer increases.

[0013] When the thickness of the AFS layer is relatively small, the process gas may pass through the AFS layer and modify the silicon oxide films 12a and 12b. However, such passage becomes less likely to occur as the thickness of the AFS layer becomes relatively large. Therefore, after the process gas is supplied for a predetermined time, the supply of the process

gas is stopped, and the internal pressure of the processing container is maintained at a relatively low level. Thereby, the AFS sublimes and the AFS layer is removed, thereby exposing the surfaces of the silicon oxide films 12a and 12b. By alternately repeating the supply of the process gas and the exposure of the surface of the silicon oxide film 12 through removal of the AFS layer, etching for each of the silicon oxide films 12a and 12b proceeds downward (FIG. 3A). In addition, dotted arrows in the drawing indicate sublimated AFS.

[0014] However, when etching proceeds in this manner and the process gas is supplied to a portion of the silicon oxide film 12b where the seam 13 is formed, the process gas travels downward through the seam 13 (specifically, through a void forming the seam 13 or a minute gap between interfaces of the silicon oxide film 12). Then, a portion around the seam 13 is modified to become AFS, and thereafter, the portion sublimates. In other words, etching proceeds further downward in the silicon oxide film 12b than in the silicon oxide film 12a. That is, etching proceeds relatively rapidly at the portion where the seam 13 is formed.

[0015] Accordingly, as illustrated in FIG. 3B, at the end of etching, the amount of etching may differ relatively significantly between the silicon oxide films 12a and 12b (that is, the surface height may differ relatively significantly between the silicon oxide films 12a and 12b). Further, etching is performed in the silicon oxide film 12b such that the seam 13 expands in the lateral direction when the portion around the seam 13 is etched as described above. Therefore, since a central portion in the left-right direction within the recess is etched relatively significantly, variation in surface height among respective portions of the silicon oxide film 12b may become relatively large at the end of etching, as illustrated in FIG. 3B.

[0016] Assuming that a large number of recesses are formed in the wafer W, the width of the seam in the silicon oxide film 12 within the recess, the length thereof in the height direction, and the position thereof in the height direction may differ among the recesses, as described above. Accordingly, although FIGS. 3A and 3B illustrate that variation in the amount of etching occurs between the silicon oxide film 12b in which the seam 13 is formed and the silicon oxide film 12a in which the seam 13 is not formed, the variation in the amount of etching may also occur among the silicon oxide films 12 in which the seam 13 is formed due to differences in the state of such

seams 13.

[0017] (Present Embodiment)

The present embodiment is performed so as to prevent the occurrence of the problems described in the comparative embodiment. A case where the wafer W illustrated in FIG. 2 is processed as in the comparative embodiment will be described by way of example. FIGS. 4A to 4D are views illustrating changes in the surfaces of the silicon oxide films 12a and 12b caused by the etching process according to the present embodiment.

[0018] First, similarly to the comparative embodiment, a HF gas and a NH_3 gas are supplied as a process gas to the wafer W stored in the processing container, which has been exhausted and maintained in a vacuum atmosphere, thereby modifying the surfaces of the silicon oxide films 12a and 12b and forming an AFS layer 14 (FIG. 4A). In addition, the process gas selectively acts on and modifies the silicon oxide film 12, among the polysilicon film 11 forming the sidewalls of the recesses and the silicon oxide film 12. Chain-line arrows in the drawing indicate the process gas.

[0019] Thereafter, the supply of the process gas to the wafer W is stopped. During this stoppage of the supply of the process gas, the processing container is exhausted so that the internal pressure of the processing container is relatively high, specifically, higher than 200 Pa (pressure control step). Meanwhile, a purge gas, which is an inert gas, is supplied so as to remove the process gas remaining in the processing container.

[0020] Since the internal pressure of the processing container is relatively high, rapid sublimation of the AFS layer 14 is prevented. Further, since the wafer W is heated, a small amount of AFS sublimates from a surface layer of the AFS layer 14 to be released into a gas phase in the vicinity of the surface layer. At this state, since a flow of the purge gas is formed in the gas phase in the vicinity of the surface layer, the concentration of AFS in the gas phase decreases. Therefore, sublimation of AFS from the surface layer of the AFS layer 14 is promoted so that the concentration of AFS in the gas phase is maintained in equilibrium. In this way, during the supply of the purge gas, sublimation gradually and continuously proceeds in a surface layer portion of the AFS layer 14. In FIG. 4B, the purge gas is indicated by solid

lines, and vaporized AFS is indicated by dotted lines. Hereinafter, a step of supplying the process gas to form the AFS layer 14 will be referred to as a first step, and a step of maintaining the internal pressure of the processing container higher than 200 Pa and supplying the purge gas to remove the surface layer portion of the AFS layer 14 will be referred to as a second step.

[0021] Before the AFS layer 14 disappears, the supply of the process gas into the processing container is resumed (FIG. 4C). That is, the first step is performed again. Since the thickness of the AFS layer 14 has become smaller than that at the end of the preceding first step as a result of the second step being performed, the process gas passes through the AFS layer 14 and acts on a surface layer of the silicon oxide film 12 below the AFS layer 14, thereby changing the surface layer into AFS. That is, the thickness of the AFS layer 14 increases. Thereafter, the surface layer of the AFS layer 14 is removed by performing the second step again. Subsequently, the first step and the second step are repeatedly performed in sequence, thereby causing etching of the silicon oxide film 12 to proceed downward. In each execution of the first step, the process gas is supplied to the silicon oxide film 12 covered with the remaining AFS layer 14 as in the second execution of the first step described above.

[0022] When etching is advanced by repeatedly performing a cycle composed of the first step and the second step in this manner, etching of the silicon oxide film 12b proceeds downward, and the surface of the AFS layer 14 approaches the portion where the seam 13 is formed, so that the process gas is supplied into the seam 13. Since passage of the process gas is prevented by the AFS layer 14 even in such a state, a large amount of the process gas is prevented from flowing into a deep portion of the seam 13. Further, it is assumed that the formed AFS may flow on the wafer W and a lower portion of the AFS layer 14 may enter the seam 13. FIGS. 4A to 4C illustrate the AFS layer 14 in such a state. In this case, since the thickness of the AFS layer 14 is large at the portion where the seam 13 is formed, the AFS layer 14 may more reliably block passage of the process gas, thereby more reliably preventing the process gas from flowing into the seam 13.

[0023] From the above, during execution of the above-described cycle in the present embodiment, it is prevented that the portion where the seam 13 is formed is etched at a relatively

high rate and that etching proceeds so as to expand the seam 13 in the lateral direction as in the comparative embodiment. As a result, etching proceeds with high uniformity between the silicon oxide films 12a and 12b, and etching also proceeds with high uniformity at respective portions in the recess in which the silicon oxide film 12b is formed.

[0024] After the cycle including the first step and the second step has been repeated a preset number of times, the interior of the processing container is set to a predetermined pressure, and the purge gas is supplied into the processing container, thereby removing the AFS layer 14 from the wafer W and completing the etching. FIG. 4D illustrates the wafer W after completion of the etching.

[0025] FIGS. 4A to 4D illustrate that variation in the amount of etching is prevented between the silicon oxide film 12b in which the seam 13 is formed and the silicon oxide film 12a in which the seam 13 is not formed. The variation in the amount of etching is prevented even among the silicon oxide films 12 in which the seam 13 is formed since the portion where the seam 13 is formed is prevented from being etched at a high rate as described above.

[0026] FIG. 5 is a longitudinal cross-sectional view illustrating a substrate processing apparatus according to the present embodiment. The substrate processing apparatus 1 includes a processing container 21 that contains a processing space in which the wafer W is processed as described above. Reference numeral 22 in the drawing denotes a transfer port for the wafer W that is open in a sidewall of the processing container 21, and is opened and closed by a gate valve 23. A stage 24 on which the wafer W is placed is provided within the processing container 21. The stage 24 is provided with a lift pin (not illustrated), and an upper end of the lift pin protrudes from and retracts into an upper surface of the stage 24. The wafer W is delivered between a substrate transfer mechanism (not illustrated) and the stage 24 via the lift pin.

[0027] A temperature adjuster 25, which is, for example, a heater that performs resistance heating, is embedded in the stage 24, and heats the wafer W placed on the stage 24 to a set temperature of, for example, 80 degrees C or higher. A gas shower head 30 is provided at the upper side within the processing container 21 so as to face the stage 24. The downstream sides

of gas supply paths 31 and 32 are connected to the gas shower head 30. The upstream side of the gas supply path 31 branches to form gas supply paths 31A and 31B, and the upstream side of the gas supply path 32 branches to form gas supply paths 32A and 32B. Then, the upstream sides of the gas supply paths 31A, 31B, 32A and 32B are respectively connected to gas supply sources 41, 42, 43 and 44 via respective flow rate adjusters 35. Each flow rate adjuster 35 includes a valve and a mass flow controller, and performs supply and cutoff of gases supplied from the gas supply sources 41 to 44 to the downstream side and adjusts flow rates thereof.

[0028] The gas supply sources 41, 42, 43 and 44 supply a HF gas, an argon (Ar) gas, a NH_3 gas, and a nitrogen (N_2) gas, respectively, to flow paths connected thereto. In addition, the N_2 gas and the Ar gas constitute the purge gas described above. The respective flow rate adjusters 35 enable switching of the gases supplied from the gas supply sources 41 to 44 into the processing container 21. The gas supply source 41 and the flow rate adjuster 35 for supplying the HF gas in the gas supply path 31A, and the gas supply source 43 and the flow rate adjuster 35 for supplying the NH_3 gas in the gas supply path 32A correspond to a process gas supply mechanism. The gas supply source 42 and the flow rate adjuster 35 for supplying the Ar gas in the gas supply path 31B, and the gas supply source 44 and the flow rate adjuster 35 for supplying the N_2 gas in the gas supply path 32B correspond to an inert gas supply mechanism.

[0029] An upstream end of an exhaust path 51 is connected to the bottom of the processing container 21 and is open to the interior of the processing container 21. A valve V1 and an exhaust mechanism 52 are provided in the exhaust path 51 in this order toward the downstream side, and the exhaust mechanism 52 is configured by, for example, a vacuum pump. The valve V1 is, for example, an Auto Pressure Control (APC) valve, and is capable of changing an opening degree thereof during the processing of the wafer W in accordance with a control signal output from a controller 20, which will be described later, so that the internal pressure of the processing container 21 reaches a preset value.

[0030] The substrate processing apparatus 1 includes the controller 20, which is a computer. The controller 20 includes a program, a memory, and a CPU. The program incorporates instructions (each step) to perform the above-described processing of the wafer W and the

transfer of the wafer W. This program is stored in a non-transitory computer-readable storage medium such as a compact disk, a hard disk, a magneto-optical disk, and a DVD, and is installed in the controller 20. The controller 20 outputs control signals to respective parts of the substrate processing apparatus 1 in accordance with the program, thereby controlling operations of the respective parts. The operations controlled in this manner include, for example, adjustment of the temperature of the stage 24 (i.e., the temperature of the wafer W), an operation of the exhaust mechanism 52, adjustment of the opening degree of the valve V1 (i.e., adjustment of the internal pressure of the processing container 21), and supply and cutoff of the respective gases from the gas supply sources 41 to 44 into the processing container 21 and adjustment of the flow rates thereof by the flow rate adjusters 35.

[0031] Next, a processing operation of the substrate processing apparatus 1 for performing the process described with reference to FIGS. 4A to 4D will be described using the time chart of FIG. 6, which illustrates an operation for two cycles. The time chart of FIG. 6 indicates the timings at which supply and cutoff of the process gas into the processing container 21 are performed and the timing at which the supply amount of the purge gas is changed. The timings of supplying and cutting off the process gas may also be described as the timings of opening and closing the valve of the flow rate adjuster 35, and the timing of changing the supply amount of the purge gas may likewise be described as the timing at which the flow rate of the purge gas is adjusted by the mass flow controller of the flow rate adjuster 35.

[0032] As described with reference to FIGS. 4A to 4D, processing is performed such that the first step of supplying the process gas to the wafer W and the second step of supplying the purge gas in a reduced-pressure atmosphere with a relatively high pressure to remove the AFS are alternately repeated. In each of the first and second steps illustrated here, the interior of the processing container 21 is adjusted to the same pressure P0. In the time chart, the first step is performed during the respective durations from time t1 to time t2 and from time t3 to time t4, and the second step is performed during the respective durations from time t2 to time t3 and from time t4 to time t5. Hereinafter, the duration of the first step in one cycle (i.e., each of the durations from time t1 to time t2 and from time t3 to time t4) may be referred to as a process gas

supply time, and the duration of the second step in one cycle (i.e., each of the durations from time t2 to time t3 and from time t4 to time t5) may be referred to as a purge time. Since the second step is performed so as to prevent exposure of the silicon oxide film 12 as described above, the purge time is set to be relatively short, and thus, the process gas supply time is, for example, longer than the purge time.

[0033] The wafer W illustrated in FIG. 2 is loaded into the processing container 21, is placed on the stage 24, and is heated to the above-described temperature. Then, a HF gas and a NH_3 gas, which serve as the process gas, and an Ar gas and an N_2 gas, which serve as the purge gas, are respectively supplied into the processing container 21, and the opening degree of the valve V1 is adjusted to set the interior of the processing container 21 to pressure P0 (FIG. 4A; time t1 in FIG. 5). The pressure P0 is, for example, 800 Pa (6 Torr) or higher, and more specifically, for example, 1000 Pa (7.5 Torr) to 4000 Pa (30 Torr). The pressure range is higher than the vapor pressure of AFS.

[0034] Next, the supply of the process gas is stopped, and the supply amount of the purge gas is increased (time t2). Thereby, the process gas within the processing container 21 is purged to stop the generation of new AFS, while the surface of the AFS layer 14 is removed, and the removed AFS is discharged together with the purge gas (FIG. 4B). At time t3 when a preset time has elapsed from time t2, the supply of the process gas into the processing container 21 is resumed, and the supply amount of the purge gas is reduced. At this time, removal of the AFS layer 14 is stopped to complete the second step, and a second execution of the first step is started. The same operation as that from time t1 to time t2 is performed during the duration from time t3 to time t4, and the same operation as that from time t2 to time t3 is performed during the duration from time t4 to time t5.

[0035] As an example of the volumetric flow rates per unit time (hereinafter simply referred to as “flow rates”) of the respective gases in the etching process according to the present embodiment, the flow rate of the process gas in the first step is set within a range of 10 sccm to 1000 sccm. For example, the flow rate of the NH_3 gas is set higher than the flow rate of the HF gas. The flow rate of the purge gas in the first step is set within a range of 0 sccm to 10000

sccm. For example, the flow rate of the N_2 gas is set to approximately twice the flow rate of the Ar gas. The flow rate of the purge gas in the second step is set within a range of 10 sccm to 25000 sccm. For example, the flow rate of the N_2 gas is set to approximately twice the flow rate of the Ar gas. Then, the flow rate of the purge gas in the second step is preferably set to approximately twice or more the flow rates of the process gas and the purge gas in the first step.

[0036] (Modifications)

The purge gas in the present embodiment is not necessarily limited to the Ar gas and the N_2 gas, and only one of these gases may be used, or any other inert gas may be used. The process gas is not limited to the HF gas and the NH_3 gas, and may include a halogen-containing gas and a basic gas. The halogen-containing gas is not limited to a fluorine-containing gas, and a halogen-containing gas that contains other halogen molecules such as chlorine (Cl) and bromine (Br) may be used. The same applies to the basic gas.

[0037] Regarding the pressures in the first step and the second step of the present disclosure, it is not an essential condition that the pressures be the same pressure P0, and the pressures may be different from each other and may be appropriately set for each step. Further, in the processing example illustrated in FIG. 6, the supply amount of the purge gas is made different between execution of the first step and execution of the second step, but the supply amount may be the same.

[0038] The surface shape of the wafer W is not limited to the shapes illustrated in FIGS. 1 and 2, and, for example, the polysilicon film 11 may not be provided on the surface of the wafer W, and the silicon oxide film 12 may be uniformly provided. In other words, the present disclosure is not limited to etching the silicon oxide film 12 formed in the recess. However, as described above, the seam 13 is likely to be formed in the silicon oxide film 12 formed within the recess as the film grows. Therefore, the present technique is particularly effective for etching the silicon oxide film 12 formed within the recess. Further, the recess in which the silicon oxide film 12 is formed is not limited to being open upward (i.e., in a thickness direction of the wafer W), and may be open laterally (i.e., in a direction along a main surface of the wafer W).

[0039] Further, the silicon-containing film to be etched is not limited to the silicon oxide film 12,

and may be, for example, a silicon oxynitride film (SiON film). Even when etching the SiON film, AFS may be generated as a reaction product from the SiON film by using the process gas described above, so that the same effects as those obtained when etching the silicon oxide film 12 may be obtained. Further, the silicon-containing film may be a silicon nitride film (SiN film). When etching the SiN film, AFS is generated from the SiN film by supplying a NF_3 gas, a NH_3 gas, and an O_2 gas as the process gas. Thereby, etching may be performed with high uniformity within the surface of the wafer W, similarly to the case of etching the silicon oxide film 12 described above.

[0040] The above-described respective embodiments according to the present disclosure should be considered to be illustrative and not restrictive in all respects. The respective embodiments may be omitted, replaced, modified, and combined in various forms without departing from the scope and spirit of the appended claims.

[0041] [Evaluation Tests]

Hereinafter, evaluation tests performed in relation to the etching process according to the present disclosure will be described.

<Evaluation Test 1>

As Evaluation Test 1, the first step was performed on a plurality of test substrates, each provided with a silicon oxide film having a flat surface, such that the thickness of the AFS layer became a predetermined value. Then, a combination of the internal pressure of the processing container and the flow rate of the purge gas supplied into the processing container was varied for each substrate, and the time until the AFS layer was completely removed from each substrate (hereinafter referred to as a "purge-out time") was measured. The internal pressure of the processing container was set to 1000 Pa (7.5 Torr), 2000 Pa (15 Torr), or 4000 Pa (30 Torr). Tests performed with the pressure set to 1000 Pa, 2000 Pa, and 4000 Pa are referred to as Evaluation Tests 1-1, 1-2, and 1-3, respectively. Further, as a comparative test, for one of the substrates on which the AFS layer was formed as described above, the purge-out time was measured with the valve V1 fully opened so that the internal pressure of the processing container was approximately 0 Torr and the flow rate of the purge gas was 0 sccm.

[0042] FIG. 7 is a graph illustrating results of Evaluation Tests 1-1 to 1-3 and the comparative test, in which the horizontal axis represents the flow rate of the purge gas and the vertical axis represents the purge-out time. As illustrated in the graph, it can be seen from the results of Evaluation Tests 1-1 to 1-3 that the purge-out time increases as the internal pressure of the processing container increases, and also increases as the flow rate of the purge gas decreases. If the purge-out time is too short, it is difficult to leave an appropriate amount of AFS on the silicon oxide film at the end of the second step as described in the embodiment. In the comparative test, it was difficult to leave AFS in such a manner since the purge-out time was as short as 10 seconds. However, Evaluation Tests 1-1 to 1-3 demonstrated that AFS may be left for a relatively long time by appropriately setting the flow rate of the purge gas. Since the internal pressure of the processing container was set to 7.5 Torr or higher in Evaluation Tests 1-1 to 1-3, Evaluation Test 1 demonstrated that it is preferable to set the internal pressure of the processing container to 7.5 Torr or higher. In addition, it is considered, however, that AFS may remain on the substrate for a sufficient time depending on the setting of the flow rate of the purge gas even at a pressure slightly lower than 7.5 Torr. Therefore, it is considered that the internal pressure of the processing container during execution of the second step may, for example, be 800 Pa (6 Torr) or higher.

[0043] <Evaluation Test 2>

As Evaluation Test 2, the etching process according to the present embodiment was performed on a plurality of substrates having the surface layer structure described with reference to FIGS. 1 and 2. In this etching, the purge time was varied for each substrate, and a cycle composed of the first step and the second step was performed 55 times. The purge time was set to 2 seconds, 2.4 seconds, 2.6 seconds, 2.7 seconds, 2.8 seconds, or 3.0 seconds. The substrates after the etching process were evaluated by acquiring SEM images of the surface shape, the amount of etching, and variation in the surface height of the silicon oxide film 12. The amount of etching was obtained by measuring the etching amount at a plurality of positions within one recess, obtaining an average value of the measured values, and then obtaining an average value among a plurality of recesses using the average value. The variation in the surface height of the

silicon oxide film 12 was represented by a 3 σ value calculated from average values obtained among the respective recesses, where each average value was obtained from the heights at a plurality of locations on the surface of the silicon oxide film 12 within one recess. Therefore, variation in the amount of etching among the recesses is indicated by the variation in the surface height of the silicon oxide film 12

[0044] As other processing conditions, the internal pressure of the processing container was set to 4000 Pa (30 Torr), the wafer temperature was set to 130 degrees C, and the process gas supply time was set to 4 seconds. The flow rate of the purge gas in the second step was set to 14800 sccm for the N_2 gas and 6000 sccm for the Ar gas.

[0045] FIG. 8 is a graph illustrating results of Evaluation Test 2. The horizontal axis of the graph represents the purge time [sec], the left vertical axis represents the amount of etching [nm], and the right vertical axis represents the variation in the surface height of the silicon oxide film 12 [nm]. As illustrated in FIG. 8, it was confirmed that the amount of etching increases as the purge time increases. This is considered to be because, as the purge time increases, the amount of AFS remaining on the silicon oxide film 12 at the end of the second step decreases (i.e., the thickness of the AFS layer 14 decreases), and thus, the thickness of the silicon oxide film 12 that is modified and converted into the AFS layer 14 in the subsequent first step increases.

[0046] The variation in the surface height of the silicon oxide film 12 decreased as the purge time decreased within a range of 2.6 seconds or longer, but increased compared with that at the purge time of 2.6 seconds when the purge time was shorter than 2.6 seconds. In other words, the variation in the amount of etching among the recesses was minimized at the purge time of 2.6 seconds. Further, it was confirmed based on the SEM images that the flatness of the surface of the silicon oxide film 12 within the recesses was also highest when the purge time was set to 2.6 seconds. When the purge time is long within a range of 2.6 seconds or longer, the amount of AFS remaining on the silicon oxide film 12 during execution of the first step is small (i.e., the thickness of the AFS layer 14 is small). Therefore, it is presumed that the variation in the surface height of the silicon oxide film 12 increased because the etching rate became higher at the portion where the seam 13 was formed, as described in the comparative embodiment. It is

considered that, when the purge time is shorter than 2.6 seconds, the variation occurred because the amount of AFS remaining on the silicon oxide film 12 during execution of the first step was excessively large (i.e., the thickness of the AFS layer 14 was excessively large), and thus, the passage of the process gas was excessively inhibited in some of the recesses.

As described above, it was confirmed from Evaluation Test 2 that there is an appropriate range for the purge time. Although the appropriate purge time may be affected by, e.g., the surface shape, the volume of the processing space, the wafer temperature, and the process gas supply conditions, it is considered that the purge time may be 30 seconds or less, and even if it is longer, may be 1 minute or less since the purge time was as short as 2.6 seconds in this evaluation test.

EXPLANATION OF REFERENCE NUMERALS

[0047] W: wafer, 12: silicon oxide film, 14: AFS layer, 21: processing container

WHAT IS CLAIMED IS:

1. A substrate processing method comprising:

storing a substrate having a silicon-containing film formed on a surface of the substrate in a processing container;

performing a first operation of supplying a process gas including a halogen-containing gas and a basic gas into the processing container to modify the silicon-containing film and generate a reaction product;

performing a second operation of supplying an inert gas into the processing container and exhausting the processing container in a state where supply of the process gas into the processing container is stopped, in order to remove a portion of the reaction product;

repeating the first operation and the second operation alternately; and

controlling an internal pressure of the processing container to be higher than 200 Pa in each execution of the second operation such that, in a second or subsequent execution of the first operation in the repeating, the process gas is supplied to the substrate on which the reaction product remains.

2. The substrate processing method of Claim 1, wherein, in the controlling the internal pressure, the internal pressure of the processing container is controlled to 800 Pa or higher.

3. The substrate processing method of Claim 2, wherein the silicon-containing film is a silicon oxide film.

4. The substrate processing method of Claim 3, wherein the halogen-containing gas is a hydrogen fluoride gas and the basic gas is an ammonia gas.

5. The substrate processing method of Claim 4, wherein the silicon-containing film is formed in a recess formed in the substrate, and

wherein the first operation selectively modifies the silicon-containing film such that the silicon-containing film is selectively removed, among a sidewall of the recess and the silicon-containing film, in the second operation.

6. The substrate processing method of Claim 5, wherein before the process gas is supplied, the silicon-containing film includes a void or a junction between interfaces of the silicon-containing film.

7. A substrate processing apparatus comprising:

a processing container configured to store a substrate having a silicon-containing film formed on a surface thereof;

a process gas supply mechanism configured to supply a process gas including a halogen-containing gas and a basic gas into the processing container;

an inert gas supply mechanism configured to supply an inert gas into the processing container;

an exhaust mechanism configured to exhaust the processing container; and

a controller configured to output a control signal so as to implement a process including: a first operation of supplying the process gas into the processing container to modify the silicon-containing film and generate a reaction product; a second operation of supplying an inert gas into the processing container and exhausting the processing container in a state where supply of the process gas into the processing container is stopped, in order to remove a portion of the reaction product; repeating the first operation and the second operation alternately; and controlling an internal pressure of the processing container to be higher than 200 Pa in each execution of the second operation such that, in a second or subsequent execution of the first operation in the repeating, the process gas is supplied to the substrate on which the reaction product remains.

8. The substrate processing apparatus of Claim 7, wherein, in the controlling, the internal pressure of the processing container is controlled to 800 Pa or higher during the second operation.