

POST-FILM-FORMATION PROCESSING METHOD AND SUBSTRATE PROCESSING APPARATUS

TECHNICAL FIELD

[0001] The present disclosure relates to a post-film-formation processing method and a substrate processing apparatus.

BACKGROUND

[0002] In logic ICs as semiconductor devices, titanium (Ti) silicides and nickel (Ni) silicides, for example, are used as contact materials for sources and drain. However, since contacts have become smaller with a progress of device miniaturization in recent years, a resistance of the contacts tends to increase. Therefore, use of zirconium (Zr) silicides, which are low-resistance metals, as a contact material has been studied in order to reduce the resistance of the contacts.

[0003] Zirconium silicides are formed on a wafer, which is a silicon-based semiconductor substrate, by performing a thermal treatment on a zirconium film formed by a sputtering method, a vapor deposition method, or an ion plating method (*see*, for example, Patent Document 1). The zirconium film is formed on the wafer by, for example, supplying a raw material gas as a raw material of the zirconium film into a chamber made of aluminum, and generating plasma from the raw material gas in the chamber.

[Prior Art Document]

Patent Document

[0004] Patent Document 1: International Patent Application Publication No. 2007/063908

SUMMARY

[0005] The technology according to the present disclosure suppresses occurrence of metal contamination and adhesion of particles with respect to a zirconium film formed on a substrate.

[0006] Some embodiments of the present disclosure provide a post-film-formation processing

method of performing processing on a chamber having a processing space into which a processing gas containing zirconium chloride is supplied in a state where a substrate is accommodated in the processing space and in which a film formation process of forming a film formed of zirconium on the substrate is performed, at least a portion of the chamber exposed to the processing space being formed of a material containing aluminum, the method including: a processing gas discharge process of stopping supply of the processing gas after the film formation process and discharging the processing gas from the processing space; and a hydrogen nitride-based gas supply process of supplying a hydrogen nitride-based gas into the processing space after the processing gas discharge process.

[0007] According to the present disclosure, it is possible to suppress occurrence of metal contamination and adhesion of particles with respect to a zirconium film formed on a substrate.

BRIEF DESCRIPTION OF DRAWINGS

[0008] FIG. 1 is a schematic vertical cross-sectional view illustrating an example of a substrate processing apparatus according to the present disclosure.

FIG. 2 is a block diagram illustrating an example of a hardware configuration of the substrate processing apparatus illustrated in FIG. 1.

FIG. 3 is a graph illustrating an example of a comparison of occurrence of metal contamination between the substrate processing apparatus illustrated in FIG. 1 and a conventional substrate processing apparatus.

FIG. 4 is a graph illustrating an example of a comparison of the number of particles adhering to a wafer between the substrate processing apparatus illustrated in FIG. 1 and the conventional substrate processing apparatus.

FIG. 5 is a graph illustrating an example of a relationship between a product of a partial pressure of a hydrogen nitride-based gas and a supply time of the hydrogen nitride-based gas and an aluminum atom distribution, which is an index of occurrence of metal contamination, in the substrate processing apparatus illustrated in FIG. 1.

FIG. 6A is a flowchart illustrating an example of processes executed in the substrate

processing apparatus illustrated in FIG. 1.

FIG. 6B is a flowchart illustrating an example of processes executed in the substrate processing apparatus illustrated in FIG. 1.

FIG. 6C is a flowchart illustrating an example of processes executed in the substrate processing apparatus illustrated in FIG. 1.

FIG. 6D is a flowchart illustrating an example of processes executed in the substrate processing apparatus illustrated in FIG. 1.

DETAILED DESCRIPTION

[0009] As described above, in a technique of Patent Document 1, zirconium films are sequentially formed on a plurality of wafers, respectively. However, when zirconium chloride gas is used as a film formation gas, chlorine may remain in an interior of a chamber as the formation of the zirconium film on each wafer is repeated. This chlorine reacts with aluminum of the chamber to produce an aluminum chloride, and the aluminum chloride adheres to the zirconium film on the wafer as metallic foreign substances, thereby causing a problem of metal contamination. Further, when the formation of the zirconium film on each wafer is repeated, a zirconium film or a zirconium chloride film may also be formed on an inner wall of the chamber. When these films are finely fragmented and peeled off from the inner wall of the chamber, there is also a problem in that they adhere, as particles, to the zirconium film on the wafer.

[0010] In contrast, according to a technique of the present disclosure, after the formation of the zirconium film, a hydrogen nitride-based gas is supplied to the interior of the chamber to suppress occurrence of metal contamination and adhesion of particles with respect to the zirconium film on the wafer.

[0011] Hereinafter, one embodiment of the technique according to the present disclosure will be described with reference to the drawings. However, a configuration described in the following embodiment is merely illustrative and is not intended to limit the present disclosure. For example, each component included in the configuration may be replaced with any component capable of exerting a similar function. Further, arbitrary components may be added.

[0012] FIG. 1 is a schematic vertical cross-sectional view illustrating an example of a substrate processing apparatus according to the present disclosure. A substrate processing apparatus 1 illustrated in FIG. 1 is an apparatus that performs a film formation process of forming a film formed of zirconium (Zr) on a wafer (substrate) W. The substrate processing apparatus 1 includes a Zr film formation chamber 2, a stage 3, a shower head 4, a processing gas supply 5, a radio frequency power supply 6, and an exhaust system 7. The Zr film formation chamber 2 has a substantially cylindrical shape, and a processing space U, which is an internal space of the chamber, is depressurized. The wafer W is accommodated in the processing space U. Further, a Zr film formation process by plasma CVD is performed in the processing space U where the wafer W is accommodated. In addition, a volume of the processing space U may be, for example, 15 L or more and 30 L or less, and more specifically 20 L or more and 25 L or less. With this configuration, it is possible to secure, for example, an installation space for the stage 3 and an entry space for an arm (not illustrated) that loads and unloads the wafer W with respect to the processing space U without excess or deficiency. Further, at least a portion of the Zr film formation chamber 2 exposed to the processing space U (for example, the cross-hatched portion in FIG. 1) is formed of a material containing aluminum (Al). Hereinafter, the portion formed of the Al-containing material is referred to as an "aluminum-made portion 23." In addition, a temperature of the aluminum-made portion 23 during the film formation process may be 200 degrees C or lower even with a heat input from plasma. With this configuration, it is possible to prevent the aluminum-made portion 23 from being softened during the film formation process.

[0013] The stage 3 is disposed below the processing space U. The stage 3 has a stage surface 31 on which the wafer W is placed. A heater 32 is embedded in the stage 3. A surface temperature of the stage surface 31 during the film formation process may be adjusted by the heater 32 to, for example, 300 degrees C or higher and 500 degrees C or lower, and more specifically 420 degrees C or higher and 480 degrees C or lower. With this configuration, it is possible to heat the wafer W during the film formation process, for example, without excess or deficiency, and thereby reliably forming a Zr film on the wafer W. Further, the stage 3 may be configured to be movable in a vertical direction by a driving mechanism (not illustrated). The

shower head 4, which is made of, for example, a metallic material such as aluminum, is disposed on a ceiling of the Zr film formation chamber 2. In the processing space U between the stage 3 and the shower head 4, as will be described later, zirconium chloride (ZrCl_x) plasma is generated from zirconium chloride (IV) (ZrCl_4) gas serving as a processing gas.

[0014] In addition, surfaces of components such as the stage 3 and the shower head 4, at least a part of which is exposed to the processing space U, may be covered with an underlying layer formed of, for example, a material without containing oxygen such as an aluminum nitride (AlN). With this configuration, it is possible to prevent oxidation of the components and to prevent corrosion caused by chlorine (Cl_2) gas and the like, which will be described later. Further, since the underlying layer and the aluminum-made portion 23 do not contain oxygen, even when the underlying layer or the aluminum-made portion 23 is etched by plasma, for example, oxygen is not released and it is possible to prevent oxidation of the Zr film.

[0015] A loading/unloading port 21 for loading and unloading the wafer W with respect to the processing space U and a gate valve 22 for opening and closing the loading/unloading port 21 are provided in a sidewall of the Zr film formation chamber 2. An exhaust system 7 is disposed at a bottom of the Zr film formation chamber 2. The exhaust system 7 includes a pump (not illustrated) such as a turbo-molecular pump or a dry pump for exhausting the processing space U, and an exhaust valve (not illustrated) such as an auto pressure controller (APC) valve for controlling a pressure of the processing space U.

[0016] The shower head 4 is disposed to face the wafer W placed on the stage 3. The shower head 4 includes a gas diffusion chamber 41 formed in an interior of the shower head 4, and a plurality of gas holes 42 that allow the gas diffusion chamber 41 to communicate with the processing space U. Further, the processing gas supply 5 is connected to the shower head 4 via a pipe 51. The processing gas supply 5 supplies a ZrCl_4 gas as a processing gas to the gas diffusion chamber 41. The ZrCl_4 gas supplied to the gas diffusion chamber 41 is introduced into the processing space U via the respective gas holes 42. The processing gas only needs to include the ZrCl_4 gas, and may also include a dilution gas, for example. Examples of the dilution gas may include Ar gas.

[0017] The shower head 4 is connected to the radio frequency power supply 6. The radio frequency power supply 6 is capable of supplying radio frequency power for plasma generation, having a frequency of, for example, 450 kHz to the shower head 4. Thus, the shower head 4 functions as an upper electrode, and an electric field is generated in the processing space U. The electric field generated in the processing space U excites and decomposes the ZrCl_4 gas introduced into the processing space U, thereby generating ZrCl_4 plasma. The ZrCl_4 plasma adheres to the wafer W, and by simultaneously supplying H_2 gas as a reducing gas to the adhered ZrCl_4 , H radicals generated by excitation cause a reduction reaction, whereby chlorine (Cl) is removed from ZrCl_4 and a Zr film is formed on the wafer W. In addition to the H_2 gas, a hydrogen halide such as HCl or SiH_4 may also be used as the reducing gas.

[0018] FIG. 2 is a block diagram illustrating an example of a hardware configuration of the substrate processing apparatus illustrated in FIG. 1. As illustrated in FIG. 2, the substrate processing apparatus 1 includes a controller 10 communicably connected to the processing gas supply 5 and the like. The controller 10 is constituted by a computer including at least a CPU 11 and a memory 12, and various recipes (programs) for executing the film formation process, a post-film formation process to be described later, and the like are stored in advance in the memory 12.

[0019] As described above, the substrate processing apparatus 1 is an apparatus that forms a Zr film on the wafer W in the Zr film formation chamber 2. Further, the Zr film formation chamber 2 has the aluminum-made portion 23, which is formed of aluminum, at least in a portion thereof exposed to the processing space U. When ZrCl_4 gas is used as a processing gas in the film formation process in the substrate processing apparatus 1, Cl_2 gas may remain in the interior of the Zr film formation chamber 2 as the formation of the Zr film on the wafer W is repeated. The Cl_2 gas reacts with the aluminum-made portion 23 of the Zr film formation chamber 2 to produce AlCl_x (aluminum chloride). The AlCl_x may cause metal contamination in which AlCl_x adhere to the Zr film on the wafer W as metallic foreign substances. Further, when the formation of the Zr film on the wafer W is repeated, a Zr film or a ZrCl_x (zirconium chloride) film may be formed on an inner wall of the Zr film formation chamber 2. These films

may be finely fragmented and peeled off from the inner wall of the Zr film formation chamber 2 over time. Further, the peeled-off substances may adhere to the Zr film on the wafer W as particles.

[0020] Therefore, the substrate processing apparatus 1 is configured to be capable of suppressing occurrence of metal contamination and adhesion of particles with respect to the Zr film on the wafer W, by means of a post-film-formation processing method of performing processing on the Zr film formation chamber 2 after film formation. Configurations and operations thereof will be described below.

[0021] As illustrated in FIG. 1, the substrate processing apparatus 1 includes an NH₃ gas supply (hydrogen nitride-based gas supply) 8 and an N₂ gas supply 9. In the substrate processing apparatus 1, when performing the post-film-formation processing method, an NH₃ gas supply process (hydrogen nitride-based gas supply process) and an N₂ gas supply process (nitrogen gas supply process) are performed individually. The NH₃ gas supply process is a process of supplying ammonia (NH₃) gas into the processing space U from the NH₃ gas supply 8. The N₂ gas supply process is a process of supplying nitrogen (N₂) gas into the processing space U from the N₂ gas supply 9.

[0022] Further, in the substrate processing apparatus 1, prior to the NH₃ gas supply process, a wafer loading process, a film formation process, a ZrCl₄ gas discharge process (processing gas discharge process), and an unloading process are performed sequentially in this order. The wafer loading process is a process of loading the wafer W before film formation into the processing space U. The film formation process is a process of supplying ZrCl₄ gas, which is a processing gas, into the processing space U to form a Zr film on the wafer W. The ZrCl₄ gas discharge process is a process of discharging the ZrCl₄ gas as a processing gas from the processing space U. The unloading process is a process of unloading the wafer W after film formation from the processing space U.

[0023] In the wafer loading process, first, the gate valve 22 is opened. Subsequently, the wafer W is loaded into the processing space U by an arm that loads and unloads the wafer W, and is placed on the stage 3. Subsequently, the arm retracts from the processing space U, and the gate

valve 22 is closed. Thus, it becomes possible to perform film formation in the subsequent film formation process.

[0024] In the film formation process, as described above, ZrCl_4 gas is supplied into the processing space U, plasma is generated from the ZrCl_4 gas, and a Zr film is formed on the wafer W. As described above, as a film formation condition at this time, the surface temperature of the stage surface 31 may be adjusted to, for example, 400 degrees C or higher and 450 degrees C or lower. Further, the pressure of the processing space U may be adjusted to, for example, several tens of mTorr. Furthermore, the power supplied to the shower head 4 may be set to radio frequency power for plasma generation of, for example, 450 kHz. Further, after continuing the film formation process for a predetermined period of time, the supply of the ZrCl_4 gas is stopped, and the supply of the radio frequency power, that is, generation of the plasma, is also stopped. This stopped state is maintained in the ZrCl_4 gas discharge process and the N_2 gas supply process.

[0025] In the ZrCl_4 gas discharge process, gases such as the ZrCl_4 gas remaining in the processing space U are discharged from the processing space U by operating the exhaust system 7. Thus, in the present embodiment, the exhaust system 7 functions not only as a pressure adjuster for adjusting the pressure of the processing space U during plasma generation, but also as a processing gas discharger for discharging the ZrCl_4 gas from the processing space U. In the ZrCl_4 gas discharge process, the pressure of the processing space U may be made substantially equal to a pressure outside the gate valve 22 by discharging the ZrCl_4 gas. Thus, it is possible to suppress or prevent, when the gate valve 22 is open in the subsequent unloading process, generation of airflow between the processing space U and the outside of the gate valve 22 and scattering of, for example, dust or debris in the processing space U.

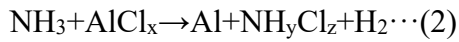
[0026] In the unloading process, first, the gate valve 22 is opened. Subsequently, the wafer W on the stage 3 is unloaded from the processing space U by the arm. Subsequently, the gate valve 22 is closed.

[0027] In the NH_3 gas supply process, NH_3 gas is supplied into the processing space U by the NH_3 gas supply 8. The NH_3 gas supply 8 is connected to the Zr film formation chamber 2 via a

pipe 80. Further, a switching valve 81 for opening and closing the pipe 80 is disposed in the pipe 80. By setting the switching valve 81 to an open state and setting a switching valve 91 to be described later to a closed state, NH_3 gas can be supplied from the NH_3 gas supply 8 to the Zr film formation chamber 2 (processing space U) via the pipe 80. By switching the switching valve 81 to a closed state, the supply of the NH_3 gas from the NH_3 gas supply 8 to the Zr film formation chamber 2 can be stopped.

[0028] In the N_2 gas supply process, N_2 gas is supplied into the processing space U by the N_2 gas supply 9. The N_2 gas supply 9 is connected via a pipe 90 to a portion of the pipe 80 on a downstream side of the switching valve 81. The switching valve 91 for opening and closing the pipe 90 is disposed in the pipe 90. By setting the aforementioned switching valve 81 to the closed state and the switching valve 91 to an open state, N_2 gas can be supplied from the N_2 gas supply 9 to the Zr film formation chamber 2 via the pipe 90 and the pipe 80 in sequence. The supplied N_2 gas traps decomposition products, which will be described later, generated in the NH_3 gas supply process, and is discharged together with the decomposition products from the interior of the Zr film formation chamber 2 by the exhaust system 7. Thus, in the present embodiment, the N_2 gas or Ar gas functions as a purge gas, and prevents the decomposition products generated in the NH_3 gas supply process from adhering to the wafer W and structures of the Zr film formation chamber 2. In addition, the supply of the N_2 gas from the N_2 gas supply 9 to the Zr film formation chamber 2 can be stopped by switching the switching valve 81 to the closed state.

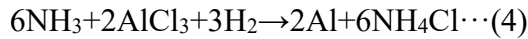
[0029] However, as described above, when the formation of the Zr film on the wafer W is repeated, Cl_2 gas may remain in the interior of the Zr film formation chamber 2, that is, in the processing space U. The residual Cl_2 gas reacts with the aluminum-made portion 23 of the Zr film formation chamber 2 to produce AlCl_x , which causes metal contamination, for example, on a surface of the aluminum-made portion 23. In this regard, in the NH_3 gas supply process, NH_3 gas is supplied into the processing space U. At this time, at least one of a reaction of the following chemical reaction formula (1) or a reaction of the following chemical reaction formula (2) occurs in the processing space U.



[0030] As a specific example of the chemical reaction formula (1), the following chemical reaction formula (3) may be given.



[0031] As a specific example of the chemical reaction formula (2), the following chemical reaction formula (4) may be given.



[0032] As illustrated in the chemical reaction formulas (1) to (4), even when AlCl_x is generated on the surface of the aluminum-made portion 23, the AlCl_x is decomposed into aluminum (Al), aluminum nitride (AlN), ammonium chloride (NH_4Cl), and hydrogen (H_2) gas by supplying NH_3 gas. In other words, since AlCl_x no longer exists in the interior of the Zr film formation chamber 2, it is possible to suppress occurrence of metal contamination in which AlCl_x is peeled off from the surface of the aluminum-made portion 23 and adheres to the Zr film on the wafer W as metallic foreign substances. In addition, although the right side of the chemical reaction formula (3) lacks " H_2 ," which corresponds to " H_2 " on the right side of the chemical reaction formula (1), this does not pose a particular problem. Similarly, although the right side of the chemical reaction formula (4) lacks " H_2 ," which corresponds to " H_2 " on the right side of the chemical reaction formula (2), this also does not pose a particular problem.

[0033] Al and AlN generated by the reaction between AlCl_x and NH_3 are chemically stable, and therefore, remain on the surface of the aluminum-made portion 23 without being peeled off. Further, NH_4Cl generated by the above reaction has a high vapor pressure and easily vaporizes, and like H_2 gas, is discharged from the interior of the Zr film formation chamber 2 by the exhaust system 7. Accordingly, since decomposition products generated by the reaction between AlCl_x and NH_3 do not adhere to the Zr film on the wafer W, it is also possible to suppress occurrence of contamination caused by the decomposition products.

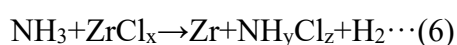
[0034] FIG. 3 is a graph illustrating an example of a comparison of occurrence of metal contamination between the substrate processing apparatus illustrated in FIG. 1 and a

conventional substrate processing apparatus. In this graph, an "aluminum atom distribution," which is the number of Al atoms (aluminum atoms) adhering to the wafer W per unit area, is used as an index of occurrence of metal contamination caused by AlCl_x . Further, the aluminum atom distribution in the substrate processing apparatus 1 in which the NH_3 gas supply process is performed is indicated as "with NH_3 post-processing," and the aluminum atom distribution in the conventional substrate processing apparatus in which the NH_3 gas supply process is not performed is indicated as "conventional."

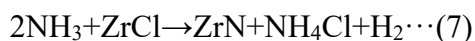
[0035] As illustrated in the graph of FIG. 3, in both cases of "with NH_3 post-processing" and "conventional," the distribution density of Al atoms (aluminum atoms) tends to decrease as the number of processed wafers W increases. However, the aluminum atom distribution in the case of "with NH_3 post-processing" is significantly lower than that in the case of "conventional." Thus, it can be said that the NH_3 gas supply process exhibits an effect of suppressing occurrence of metal contamination of Al in the substrate processing apparatus 1.

[0036] Further, although Cl_2 gas that has not completely reacted with the aluminum-made portion 23 may exist in the interior of the Zr film formation chamber 2, the Cl_2 gas reacts with NH_3 gas and is converted into NH_4Cl gas and H_2 gas in the NH_3 gas supply process. Since the NH_4Cl gas and the H_2 gas are discharged from the interior of the Zr film formation chamber 2 by the exhaust system 7, the Cl_2 gas may also be removed by supplying the NH_3 gas.

[0037] As described above, when the formation of the Zr film on the wafer W is repeated, a Zr film or a ZrCl_x film, which may become particles, may be formed on the inner wall of the Zr film formation chamber 2. In this regard, NH_3 gas is supplied into the processing space U in the NH_3 gas supply process. At this time, at least one of a reaction of the following chemical reaction formula (5) or a reaction of the following chemical reaction formula (6) occurs in the processing space U.



[0038] As a specific example of the chemical reaction formula (5), the following chemical reaction formulas (7) to (9) may be given.



[0039] As illustrated in the chemical reaction formulas (5) to (9), even when a Zr film or a ZrCl_x film is formed on the inner wall of the Zr film formation chamber 2, the AlCl_x is decomposed into zirconium (Zr), zirconium nitride (ZrN), NH_4Cl gas, and H_2 gas by supplying NH_3 gas. In other words, since the formed Zr film or the ZrCl_x film does not remain, it is possible to suppress the formed film from being finely fragmented and peeled off, and adhering, as particles, to the Zr film on the wafer W.

[0040] Further, Zr and ZrN generated by the reaction between Zr, ZrCl_x , and NH_3 are chemically stable, and therefore remain on the inner wall of the Zr film formation chamber 2 without being peeled off. Further, as described above, NH_4Cl generated by the above reactions easily vaporizes, and like H_2 gas, is discharged from the interior of the Zr film formation chamber 2 by the exhaust system 7. Accordingly, since decomposition products generated by the reactions between Zr, ZrCl_x , and NH_3 are not peeled off from the inner wall of the Zr film formation chamber 2 and do not adhere to the Zr film on the wafer W, it is also possible to suppress adhesion of particles caused by the decomposition products. In addition, ZrN is a stable inorganic compound and may also function as a protective film for protecting the aluminum-made portion 23.

[0041] FIG. 4 is a graph illustrating an example of a comparison of the number of particles adhering to a wafer between the substrate processing apparatus illustrated in FIG. 1 and the conventional substrate processing apparatus. In this graph, the number of particles per a single wafer W in the substrate processing apparatus 1 in which the NH_3 gas supply process is performed is indicated as "with NH_3 post-processing," and the number of particles per a single wafer W in the conventional substrate processing apparatus in which the NH_3 gas supply process is not performed is indicated as "conventional."

[0042] As illustrated in the graph of FIG. 4, the number of particles per a single wafer W in the case of "with NH_4 post-processing" is significantly lower than that in the case of "conventional."

Specifically, the number of particles per a single wafer W in the case of "with NH_4 post-processing" is suppressed to 5 or less. Thus, it can be said that the NH_3 gas supply process exhibits an effect of suppressing adhesion of particles in the substrate processing apparatus 1.

[0043] In the NH_3 gas supply process, a partial pressure of NH_3 gas and a supply time of NH_3 gas may be adjusted. FIG. 5 is a graph illustrating an example of a relationship between a product of a partial pressure of a hydrogen nitride-based gas and a supply time of the hydrogen nitride-based gas, and the aluminum atom distribution, which is an index of occurrence of metal contamination, in the substrate processing apparatus illustrated in FIG. 1. As illustrated in the graph of FIG. 5, the aluminum atom distribution decreases as the product of the partial pressure of NH_3 gas and the supply time of NH_3 gas increases. However, when the product of the partial pressure of NH_3 gas and the supply time of NH_3 gas reaches 25 Torr·sec or more, the decrease in the aluminum atom distribution saturates. Accordingly, from the viewpoint of suppressing occurrence of metal contamination of Al, the product of the partial pressure of NH_3 gas and the supply time of NH_3 gas may be set to 25 Torr·sec or more. With this configuration, it is possible to suppress occurrence of metal contamination of Al. However, from the viewpoint of reducing NH_3 gas consumption and improving throughput, the product of the partial pressure of NH_3 gas and the supply time of NH_3 gas may be smaller. Accordingly, the product may be set to 25 Torr·sec or more and 40 Torr·sec or less. With this configuration, it is possible to achieve both reduction in NH_3 gas consumption or improvement in throughput, and suppression of occurrence of metal contamination of Al.

[0044] When obtaining the relationship illustrated in FIG. 5, in the NH_3 gas supply process, a flow rate of NH_3 gas was set to 800 sccm or more and 10,000 sccm or less, the supply time of NH_3 gas was set to 10 seconds or more and 60 seconds or less, and the pressure of the processing space U was set to 1 Torr or more and 9 Torr or less. However, from the viewpoint of reducing NH_3 gas consumption, the flow rate of NH_3 gas may be set to 800 sccm or more and 4,000 sccm or less. Further, from the viewpoint of improving throughput, the supply time of NH_3 gas may be set to 10 seconds or more and 40 seconds or less. Furthermore, from the viewpoint of promoting vaporization of NH_4Cl , the pressure of the processing space U may be set to 1 Torr or

more and 9 Torr or less.

[0045] In addition, in the NH_3 gas supply process, the temperature of the aluminum-made portion 23 of the Zr film formation chamber 2 may be set to be equal to or higher than the temperature of the aluminum-made portion 23 during the film formation process. With this configuration, it is possible to thermally shrink dust or debris adhering to the aluminum-made portion 23 and peel it off from the aluminum-made portion 23, and to promptly remove it from the interior of the Zr film formation chamber 2 together with the NH_4Cl gas and the H_2 gas. In addition, in this case as well, the temperature of the aluminum-made portion 23 may be set to 200 degrees C or lower in order to prevent softening of the aluminum-made portion 23.

[0046] The NH_3 gas supply process is performed in a state where plasma generation is stopped in the present embodiment, but the present disclosure is not limited thereto. The NH_3 gas supply process may be performed in a state where plasma is generated. Since a density of plasma is high in the shower head 4 and in a vicinity thereof and NH_3 plasma generated from NH_3 gas promotes the reactions of the aforementioned chemical reaction formulas (5) to (9), the Zr film and the ZrCl_x film adhering to the shower head 4 and the vicinity thereof may be removed in a concentrated manner.

[0047] In addition, the gas supplied in the NH_3 gas supply process is NH_3 gas in the present embodiment, but the present disclosure is not limited thereto. Any hydrogen nitride-based gas may be used. As the hydrogen nitride-based gas other than the NH_3 gas, N_2H_4 (hydrazine) gas, for example, may be used.

[0048] Next, modifications of a sequence of processes executed in the substrate processing apparatus 1 will be described with reference to FIGS. 6A to 6D. FIGS. 6A to 6D are flowcharts illustrating examples of processes performed in the substrate processing apparatus illustrated in FIG. 1. In the modification illustrated in FIG. 6A, the wafer loading process, the film formation process, the ZrCl_4 gas discharge process, the unloading process, the NH_3 gas supply process, and the N_2 gas supply process are executed sequentially in this order, while the NH_3 gas supply process and the N_2 gas supply process are repeated. In addition, Ar gas may be used instead of the N_2 gas. Here, since the product of the partial pressure of NH_3 gas and the supply time of

NH₃ gas may be set to 25 Torr·sec or more as described above, when the NH₃ gas supply process is repeated, an accumulation of a product of the partial pressure of NH₃ gas and a total supply time of supplying the NH₃ gas may also be set to 25 Torr·sec or more.

[0049] In the modification illustrated in FIG. 6B, the wafer loading process, the film formation process, the ZrCl₄ gas discharge process, the unloading process, and the NH₃ gas supply process are executed sequentially in this order, while the N₂ gas supply process (Ar gas supply process) is omitted. By omitting the N₂ gas supply process, it is possible to further improve throughput.

[0050] The modification illustrated in FIG. 6C corresponds to a case in which a plurality of film formation processes are repeated, but in this modification, the NH₃ gas supply process and the N₂ gas supply process are not executed each time the unloading process is executed. In other words, while the wafer loading process, the film formation process, the ZrCl₄ gas discharge process, and the unloading process are repeated, the NH₃ gas supply process and the N₂ gas supply process are repeatedly executed first after the Zr film is formed on a predetermined number of wafers W. With this configuration, it is possible to reduce the number of executions of the NH₃ gas supply process and the N₂ gas supply process as a whole and to further improve throughput.

[0051] Compared to the modification illustrated in FIG. 6C, the modification illustrated in FIG. 6D corresponds to a case in which the NH₃ gas supply process and the N₂ gas supply process are not repeatedly executed and the N₂ gas supply process is omitted. With this configuration, it is possible to further reduce the number of executions of the NH₃ gas supply process and the N₂ gas supply process as a whole and to significantly improve throughput.

[0052] While the embodiments of the present disclosure have been described above, the present disclosure is not limited to the above-described embodiments, and various modifications and changes can be made within the scope and spirit of the present disclosure.

[0053] This application claims priority to Japanese Patent Application No. 2024-006671 filed on January 19, 2024, which is incorporated herein by reference in its entirety.

EXPLANATION OF REFERENCE NUMERALS

[0054] 1: substrate processing apparatus, 2: Zr film formation chamber, 7: exhaust system, 8:
NH₃ gas supply, 23: aluminum-made portion, U: processing space, W: wafer

WHAT IS CLAIMED IS:

1. A post-film-formation processing method of performing processing on a chamber having a processing space into which a processing gas containing zirconium chloride is supplied in a state where a substrate is accommodated in the processing space and in which a film formation process of forming a film formed of zirconium on the substrate is performed, at least a portion of the chamber exposed to the processing space being formed of a material containing aluminum, the method comprising:

a processing gas discharge process of stopping supply of the processing gas after the film formation process and discharging the processing gas from the processing space; and

a hydrogen nitride-based gas supply process of supplying a hydrogen nitride-based gas into the processing space after the processing gas discharge process.

2. The post-film-formation processing method of Claim 1, wherein in the hydrogen nitride-based gas supply process, a partial pressure of the hydrogen nitride-based gas and a supply time of the hydrogen nitride-based gas are adjusted.

3. The post-film-formation processing method of Claim 2, wherein a product of the partial pressure of the hydrogen nitride-based gas and the supply time of the hydrogen nitride-based gas is 25 Torr·sec or more.

4. The post-film-formation processing method of Claim 1, wherein in the hydrogen nitride-based gas supply process, a flow rate of the hydrogen nitride-based gas is set to 800 sccm or more and 10,000 sccm or less.

5. The post-film-formation processing method of Claim 1, wherein in the hydrogen nitride-based gas supply process, the film formed of zirconium is formed on the portion of the chamber formed of the material containing aluminum and covers the portion.

6. The post-film-formation processing method of Claim 1, wherein a stage having a stage surface on which the substrate is placed is provided in the processing space, and
wherein a surface temperature of the stage surface during the film formation process is 400 degrees C or higher and 450 degrees C or lower.
7. The post-film-formation processing method of Claim 1, wherein a temperature of the portion of the chamber formed of the material containing aluminum during the film formation process is 200 degrees C or lower.
8. The post-film-formation processing method of Claim 1, wherein the hydrogen nitride-based gas is ammonia gas or hydrazine gas.
9. The post-film-formation processing method of Claim 1, further comprising a nitrogen gas supply process of supplying nitrogen gas into the processing space after the hydrogen nitride-based gas supply process.
10. The post-film-formation processing method of Claim 9, wherein the hydrogen nitride-based gas supply process and the nitrogen gas supply process are repeated.
11. The post-film-formation processing method of Claim 10, wherein in the hydrogen nitride-based gas supply process, a partial pressure of the hydrogen nitride-based gas and a supply time of the hydrogen nitride-based gas are adjusted, and
wherein when the hydrogen nitride-based gas supply process is repeated, an accumulation of a product of the partial pressure of the hydrogen nitride-based gas and a total supply time of supplying the hydrogen nitride-based gas is 25 Torr·sec or more.

12. The post-film-formation processing method of Claim 1, further comprising an unloading process of unloading the substrate from the processing space after the processing gas discharge process.

13. The post-film-formation processing method of Claim 1, wherein the film formation process is a process performed by generating plasma from the processing gas in the processing space, and

wherein in the processing gas discharge process and the hydrogen nitride-based gas supply process, generation of the plasma is stopped.

14. The post-film-formation processing method of Claim 1, wherein a volume of the processing space in the chamber is 15 L or more and 30 L or less.

15. A substrate processing apparatus comprising a chamber having a processing space into which a processing gas containing zirconium chloride is supplied in a state where a substrate is accommodated in the processing space and in which a film formation process of forming a film formed of zirconium on the substrate is performed, at least a portion of the chamber exposed to the processing space being formed of a material containing aluminum, the apparatus comprising:

a processing gas discharger configured to stop supply of the processing gas after the film formation process and to discharge the processing gas from the processing space; and

a hydrogen nitride-based gas supply configured to supply a hydrogen nitride-based gas into the processing space after the processing gas has been discharged from the processing space by the processing gas discharger.