

METHOD OF FORMING METAL FILM AND APPARATUS FOR FORMING METAL FILM

TECHNICAL FIELD

[0001] The present disclosure relates to a method of forming a metal film and an apparatus for forming a metal film.

BACKGROUND

[0002] In a process of manufacturing a semiconductor device, a process of forming a metal film, for example, a titanium film, in a recess such as a trench or a via hole formed on a surface of a semiconductor wafer (hereinafter referred to as a "wafer"), which is a substrate, may be performed.

Patent Document 1 proposes a technique of bringing atomic low-pressure hydrogen into contact with a monomolecular layer of titanium tetrachloride in order to form a pure titanium film. It is described that a monomolecular layer of titanium is formed because hydrogen atoms react with chlorides in the monomolecular layer of the titanium tetrachloride to form hydrogen chloride, which is then exhausted.

[0003] Patent Document 2 proposes a technique of forming a titanium nitride film by using a halogenated raw material gas and a reaction gas. It is described that step coverage of the titanium nitride film is improved by performing, a predetermined number of times in a time-divided manner, a process of supplying the halogenated raw material gas, a process of supplying a reaction-inhibiting gas that inhibits a reaction between the halogenated raw material gas and the reaction gas, and a process of supplying the reaction gas.

[Prior Art Documents]

Patent Documents

[0004] Patent Document 1: Japanese Patent Laid-Open Publication No. 2011-184799

Patent Document 2: Japanese Patent Laid-Open Publication No. 2017-69407

SUMMARY

[0005] The present disclosure provides a technique for suppressing a decrease in a film formation rate when forming a metal film using a raw material having a characteristic in which the film formation rate decreases over time.

[0006] The present disclosure is characterized by a method of forming a metal film on a substrate, the method including: forming the metal film on a surface of the substrate by supplying film formation gases containing a metal halide serving as a raw material of the metal film to the substrate and reacting the film formation gases; and in response to the forming the metal film having a characteristic in which a film formation rate decreases over time, vacuum-exhausting, after stopping the supply of the film formation gases, an atmosphere in which the substrate is disposed while supplying a cleaning gas that reacts with byproducts generated by the reaction of the film formation gases, wherein the forming the metal film is performed again after the vacuum-exhausting.

[0007] According to the present disclosure, it is possible to suppress a decrease in a film formation rate when forming a metal film using a raw material having a characteristic in which the film formation rate decreases over time.

BRIEF DESCRIPTION OF DRAWINGS

[0008] FIG. 1 is a vertical cross-sectional view illustrating a configuration example of a film formation apparatus, which is an apparatus for forming a metal film according to the present disclosure.

FIG. 2 is a schematic diagram illustrating a state of forming a titanium film, which is a metal film.

FIG. 3 is a time chart of a method of forming a metal film according to a first embodiment.

FIG. 4A illustrates a first combination example of a film formation process and a vacuum-exhaust process.

FIG. 4B illustrates a second combination example of a film formation process and a vacuum-exhaust process.

FIG. 5 is a time chart of a method of forming a metal film according to a second embodiment.

FIG. 6 is a characteristic diagram illustrating results of Evaluation Experiment 1.

FIG. 7 is a first table illustrating results of Evaluation Experiment 2.

FIG. 8 is a second table illustrating results of Evaluation Experiment 3.

DETAILED DESCRIPTION

[0009] The present disclosure provides a technique that makes it possible to suppress a decrease in film formation rate when forming a metal film by chemical vapor deposition (CVD) using a film formation gas containing a metal halide. Hereinafter, a case is described as an example in which mixed gases of titanium tetrachloride (TiCl_4) gas and hydrogen (H_2) gas are used as film formation gases containing the metal halide, and a titanium (Ti) film, which is a metal film, is formed.

The present disclosers have found that formation of a Ti film by CVD using TiCl_4 gas has a characteristic in which a film formation rate decreases over time, as shown in evaluation experiments described later. The characteristic in which the film formation rate decreases over time means that a relationship between a thickness of the formed metal film and a film formation time is not a linear functional relationship and a slope of the relationship decreases as time elapses.

[0010] To briefly explain the reason for this, it is presumed that, as the formation of the Ti film proceeds, byproducts containing, for example, chlorine (Cl), which are generated by a reaction of the film formation gases, increase and inhibit progress of film formation reaction of the Ti film.

Therefore, in the present disclosure, a decrease in the film formation rate of the Ti film is suppressed by performing a process of vacuum-exhausting an atmosphere in which a wafer is disposed while supplying a cleaning gas that reacts with the byproducts. Hereinafter, a

configuration example of a film formation apparatus 1, which is an apparatus for forming a metal film according to the present disclosure, is described with reference to FIG. 1.

[0011] <Film Formation Apparatus>

Hereinafter, a configuration example of the film formation apparatus 1 according to the present disclosure is described with reference to FIG. 1. FIG. 1 is a vertical cross-sectional view of the film formation apparatus 1 of this example. The film formation apparatus 1 is configured as an apparatus that continuously supplies TiCl_4 gas and H_2 gas, which serve as a film formation gases, and argon (Ar) gas to a surface of a wafer W and forms a Ti film 6 by a plasma CVD method.

[0012] The film formation apparatus 1 includes a substantially cylindrical metal processing container 10 that has corrosion resistance to chlorine and is grounded. An exhaust chamber 11 of, for example, a cylindrical shape that protrudes downward is formed at a center portion of a bottom surface of the processing container 10, and an exhaust path 12 is connected to a side surface of the exhaust chamber 11. An exhauster 13 including a pressure regulating valve constituted by, for example, a butterfly valve is connected to the exhaust path 12 and is configured to vacuum-exhaust an inside of the processing container 10 to a preset vacuum pressure.

[0013] A loading/unloading port 14 is formed on a side surface of the processing container 10 so as to load/unload the wafer W into/from a vacuum transfer chamber which is not shown. The loading/unloading port 14 is configured to be capable of being opened/closed by a gate valve 15. Further, a heater 16 for adjusting temperature inside the processing container 10 is embedded in a wall constituting the processing container 10.

[0014] A stage 2 for holding the wafer W substantially horizontally is provided inside the processing container 10. The stage 2 is supported by a support 21 extending from a bottom portion of the exhaust chamber 11, and the stage 2 and the support 21 are made of conductive materials. A heater 20, which is a heating part, is embedded in the stage 2 and is configured to be capable of heating the wafer W to a set temperature. In this example, a heating temperature

of the wafer W is set to, for example, 450 degrees C, in a range of 350 to 800 degrees C.

[0015] A radio frequency power source 23 that supplies radio frequency power for ion attraction is connected to the stage 2 via a matcher 22. Further, the stage 2 is provided with lifting pins, which are not shown, for holding and then raising or lowering the wafer W placed on the stage 2. The wafer W may be transferred between the stage 2 and an external transferrer, which is not shown, by the raising or lowering of the lifting pins. The stage 2 may be configured such that the radio frequency power for ion attraction is not supplied to the stage 2.

[0016] A flat, disc-shaped shower head 3 that supplies a process gas to the wafer W is installed at a ceiling surface of the processing container 10 via an insulating member 17.

A diffusion chamber 31 for diffusing gases is formed inside the shower head 3, and a plurality of discharge holes 32 for discharging gases toward the wafer W is distributively provided at a bottom surface of the shower head 3. In addition, a heater 36 is, for example, embedded in an upper surface of the shower head 3.

[0017] A radio frequency power source 34 that supplies radio frequency power for plasma generation is connected to the above-mentioned shower head 3 via a matcher 33. This radio frequency power source 34 constitutes a plasma generator. In this way, the film formation apparatus 1 of the present disclosure constitutes a parallel plate type plasma processing apparatus by the shower head 3 serving as an upper electrode and the stage 2 serving as a lower electrode. By placing the wafer W in a space between the shower head 3 and the stage 2 and supplying the TiCl_4 gas, the H_2 gas, and the Ar gas to apply radio frequency power, these gases are ionized to form plasma.

The radio frequency power source 34 may be configured to supply radio frequency power of any frequency of 450 KHz, 2 MHz, 13.56 MHz, 27 MHz, 40 MHz, 60 MHz, 100 MHz, or 2.45 GHz. In addition, the radio frequency power source 34 supplies radio frequency power in a range of frequencies greater than 0 W and equal to or less than 2,000 W.

[0018] Further, a downstream end of a gas supply path 40 is connected to the diffusion chamber 31 of the shower head 3. At an upstream side of the gas supply path 40, a supply flow path 41

for the TiCl_4 gas, which is a raw material gas for film formation, a supply flow path 42 for the H_2 gas, which is a reaction gas, a supply flow path 43 for the Ar gas, which is added for plasma generation, and a supply flow path 44 for NH_3 gas, which is a cleaning gas, merge together.

[0019] To an upstream end of the TiCl_4 gas supply flow path 41, a TiCl_4 gas supply source 410 is connected, and a flow rate controller M41 and a valve V41 are interposed in this order from an upstream side. Further, to an upstream end of the H_2 gas supply flow path 42, a H_2 gas supply source 420 is connected, and a flow rate controller M42 and a valve V42 are interposed in this order from an upstream side. Further, to an upstream end of the Ar gas supply flow path 43, an Ar gas supply source 430 is connected, and a flow rate controller M43 and a valve V43 are interposed in this order from an upstream side. Further, to an upstream end of the NH_3 gas supply flow path 44, an NH_3 gas supply source 440 is connected, and a flow rate controller M44 and a valve V44 are interposed in this order from an upstream side.

[0020] In this example, a film formation gas supply includes the TiCl_4 gas supply flow path 41, the TiCl_4 gas supply source 410, the H_2 gas supply flow path 42, the H_2 gas supply source 420, and the gas supply path 40. Further, a cleaning gas supply includes the NH_3 gas supply flow path 44, the NH_3 gas supply source 440, and the gas supply path 40.

[0021] The film formation apparatus 1 with the above-described configuration includes a controller 100 as shown in FIG. 1. The controller 100 is constituted by a computer including a storage storing a program, a memory, and a central processing unit (CPU). The program includes instructions (steps) incorporated to execute processing for forming the Ti film 6 by outputting a control signal from the controller 100 to each component of the film formation apparatus 1, supplying/cutting off each gas, or supplying radio frequency power. The program is stored in the storage of the computer, for example, a flexible disk, a compact disc, a hard disk, a magneto-optical (MO) disc, or a non-volatile memory, and is read from the storage and installed in the controller 100.

[0022] <First Embodiment of Method of Forming Ti Film>

A first embodiment of a method of forming a Ti film performed in the film formation

apparatus 1 described above is described by taking as an example a case in which the Ti film 6 is formed in a recess 50 formed on a surface of a wafer, as shown in FIG. 2. In this example, the recess 50 is formed at a silicon oxide film (SiO film 52) covering a silicon member 51 constituting the wafer W. Therefore, the silicon member 51 is exposed on a bottom surface of the recess 50, and the SiO film 52 is exposed on a sidewall surface of the recess 50.

Alternatively, instead of the SiO film, the silicon member 51 may be covered with a silicon nitride film (SiN film), and the sidewall surface of the recess 50 may be formed of the SiN film.

[0023] FIG. 3 illustrates an example of a time chart related to formation processing of the Ti film 6 performed using the above-described film formation apparatus 1. This time chart schematically illustrates supply/cutoff timings of the film formation gases (the TiCl_4 gas and the H_2 gas) and the NH_3 gas to the processing container 10, and an application timing of radio frequency power (described as "plasma power source" in FIG. 3) from the radio frequency power source 34.

Control of the supply/cutoff timing of each gas and control of the application timing of the radio frequency power are performed by the controller 100, and the time chart shown in FIG. 3 is executed. That is, the controller 100 performs opening/closing control of the valves V41, V42, V43, and V44, executes supply/cutoff of each gas, and sets flow rates of the respective flow rate controllers M41, M42, M43, and M44.

[0024] The formation processing of the Ti film 6 is described with reference to the time chart of FIG. 3.

In this processing, first, the gate valve 15 is opened, and the wafer W is loaded into the processing container 10 through the loading/unloading port 14 by the transferrer provided in the vacuum transfer chamber (not shown). The loaded wafer W is transferred from the transferrer to the stage 2 via the lifting pins (not shown) and is placed on an upper surface of the stage 2. Thereafter, the transferrer is retracted from the processing container 10, and when the gate valve 15 is closed, the inside of the processing container 10 is vacuum-exhausted by the exhauster 13, and the inside of the processing container 10 is adjusted to a preset pressure. The wafer W is

heated to 450 degrees C by the heater 20 as described above.

[0025] Thereafter, at time T0 shown in FIG. 3, supply of the film formation gases is started, and at the same time, application of the radio frequency power from the radio frequency power sources 34 and 23 to the shower head 3 and the stage 2, respectively, is started. In this way, the supply of the film formation gases and the application of the radio frequency power are performed for a preset period (e.g., 360 seconds) until time T1 shown in FIG. 3. A period from time T0 to time T1 is a process of forming a metal film (Ti film) (hereinafter referred to as a "film formation process").

[0026] In this film formation process, the film formation gases (the TiCl_4 gas and the H_2 gas) and the Ar gas are supplied to the shower head 3 via the respective supply flow paths 41, 42, and 43 and the gas supply path 40. A mixed gas of the film formation gases and the Ar gas flows into the diffusion chamber 31 of the shower head 3 via the gas supply path 40 and is discharged into the processing container 10 through the discharge holes 32. Then, by supplying the radio frequency power from the radio frequency power sources 34 and 23 to the shower head 3 and the stage 2, respectively, these gases are converted into plasma.

[0027] The TiCl_4 gas and the H_2 gas, which are the film formation gases, are supplied into the processing container 10 at preset flow rates during the period from time T0 to time T1. In addition, for example, the Ar gas is continuously supplied from time T0 until completion of a series of processing. The Ar gas functions as an auxiliary gas that assists plasma generation of the film formation gases during a period in which the radio frequency power for plasma generation is applied, and functions as a purge gas during a period in which the application of the radio frequency power is stopped.

[0028] An example of processing conditions of the film formation in this case is as follows: temperature of the wafer W: 450 degrees C, pressure in the processing container: 1.2 kPa (9 Torr), flow rate of the TiCl_4 gas: 25 sccm, flow rate of the H_2 gas: 1,000 sccm, flow rate of the Ar gas: 2,400 sccm, radio frequency power from the radio frequency power source 34: 10 kHz, 100 W, and radio frequency power from the radio frequency power source 23: 10 Hz, 100 W.

[0029] In the above-described film formation process, the TiCl_4 gas, which is a raw material gas, is reduced by plasma-activated H_2 , which is a reaction gas, thereby abundantly forming highly reactive TiCl_2 ions or radicals. These TiCl_2 ions or radicals are adsorbed on the bottom surface of the recess 50 to form the Ti film 6. By the application of the radio frequency power, plasma is formed between parallel plates (the shower head 3 and the stage 2) including an interior of the recess 50, and the radio frequency power for ion attraction is supplied to the stage 2. By this operation, the TiCl_2 ions are supplied even to the bottom surface located at a deep position within the recess 50, so that it may be said that the Ti film 6 can be formed in that region.

[0030] However, the TiCl_4 gas also has a function of etching titanium. In addition, compared with the silicon member 51, the SiO film 52 or the SiN film has a stronger bond between silicon and oxygen or nitrogen, and a bond with the Ti film 6 formed on a surface of the SiO film 52 or the SiN film is relatively weak. Therefore, compared with the bottom surface of the recess 50 where the silicon member 51 is exposed, etching by the TiCl_4 gas tends to proceed more easily on the sidewall surface of the recess 50 where the SiO film (SiN film) 52 is exposed.

Accordingly, although the Ti film is actually formed also on the sidewall surface of the recess 50, a thickness of the Ti film on the sidewall surface is smaller than that of the Ti film on the bottom surface. For this reason, in FIG. 2, illustration of the Ti film 6 on the sidewall surface of the recess 50 is omitted, and only the Ti film 6 formed on the bottom surface is shown.

[0031] In this manner, in the film formation process, TiCl_4 is decomposed into TiCl_2 radicals to proceed with formation of the Ti film. At the start of the process, the TiCl_2 radicals are smoothly generated, leading to rapid formation of the Ti film.

On the other hand, due to decomposition of TiCl_4 , byproducts containing Cl are generated together with the TiCl_2 radicals. When the metal halide is TiCl_4 , since it is Cl that affects a decrease in a reaction rate described later among atoms constituting the byproducts, the byproducts are described herein as "Cl." Since this Cl is not consumed in the formation of the Ti film, a concentration of Cl in the processing container 10 gradually increases. Here, in the above-described film formation processing using CVD, a case is considered in which the film

formation gases are continuously supplied for, for example, 360 seconds. When the film formation is performed for such a long time, even if the inside of the processing container 10 is vacuum-exhausted in parallel, an amount of Cl present in the processing container 10 becomes larger than in a film formation processing using atomic layer deposition (ALD) in which the film formation gases are supplied for a short time and purged.

[0032] As also shown in Evaluation Experiment 1 described later, in the film formation process of the Ti film, the film formation rate of the Ti film gradually decreases over time and eventually reaches a saturation state in which it becomes difficult for the film thickness to increase even if the film formation time increases (Reference Example 1 in FIG. 6 described later). The reason for this is presumed to be as follows. When the concentration of Cl in the processing container 10 increases, a reaction between the TiCl_2 radicals and Cl tends to proceed easily, causing the TiCl_2 ions or radicals to change into TiCl_3 radicals or revert to TiCl_4 . Although the TiCl_3 radicals also function as film formation species, a vapor pressure of the TiCl_3 radicals is higher than that of the TiCl_2 radicals and an adsorption rate of the TiCl_3 radicals on the wafer W is lower than that of the TiCl_2 radicals. That is, even if the TiCl_3 radicals collide with the wafer W, the TiCl_3 radicals are less likely to be adsorbed and are more likely to volatilize and be discharged from the processing container 10. Therefore, contribution of the TiCl_3 radicals to the film formation is considered to be smaller than that of the TiCl_2 radicals. In this way, it is presumed that, when the concentration of Cl in the processing container 10 increases, an unintended reaction occurs even if the TiCl_2 radicals are generated by decomposition of TiCl_4 , resulting in a reduction in an amount of the TiCl_2 radicals that contribute to the film formation. As a result, it is considered that a saturation state is reached in which the film thickness of the Ti film is difficult to increase, and a time required to reach a target film thickness becomes longer.

[0033] From the above description, in the present disclosure, after stopping the supply of the film formation gases, a process of vacuum-exhausting the inside of the processing container 10 (hereinafter referred to as a "vacuum-exhaust process") while supplying the NH_3 gas as the cleaning gas into the processing container 10 is performed during a period from time T2 to time

T3 shown in FIG. 3. The period during which the NH_3 gas is supplied is, for example, 3 seconds. In this vacuum-exhaust process, the radio frequency power is not applied, and the Ar gas and the H_2 gas are also simultaneously supplied together with the NH_3 gas (in FIG. 3, only the supply of the NH_3 gas as the cleaning gas is shown). The reason why the H_2 gas is also supplied in this way is to react the H_2 gas with Cl remaining in the processing container 10 to generate hydrogen chloride (HCl) and to exhaust HCl from the processing container 10. It is presumed that the remaining Cl is more easily purged by converting Cl existing in an unstable state in the processing container 10 into a stable state (HCl). In addition, during a period from time T1 to time T2, supply of the Ar gas and vacuum-exhaust of the processing container 10 are continuously performed, thereby purging the inside of the processing container 10 (purge process). However, during a period in which the application of the radio frequency power for plasma generation is stopped or during a period in which the vacuum-exhaust process is performed, the supply of the Ar gas may be stopped, and nitrogen gas (N_2 gas) may be supplied instead of the Ar gas as the purge gas.

[0034] When the NH_3 gas is supplied into the processing container 10, Cl present in the processing container 10 reacts with NH_3 to generate HCl or NH_4Cl , and these reaction products are discharged to an outside along with exhaust of the processing container 10. In the processing container 10, it is considered that Cl exists in an atmosphere and is also attached to members exposed inside the processing container 10, such as a sidewall surface of the processing container 10 or a surface of the stage 2. In this way, it may be difficult to remove Cl attached to an interior of the processing container 10 simply by performing vacuum-exhaust while supplying an inert gas such as the Ar gas as the purge gas. Therefore, the NH_3 gas is supplied as the cleaning gas that reacts with Cl. As a result, since the reaction products of Cl and NH_3 are discharged to the outside of the processing container 10, it is presumed that it is possible to reduce the concentration of Cl within the processing container 10. Consequently, a decrease in the amount of the TiCl_2 radicals contributing to the film formation is suppressed, and it is possible to suppress a decrease in the film formation rate as compared with a case in which the

vacuum-exhaust process is not performed while supplying the NH_3 gas.

[0035] An example of processing conditions of the above-described vacuum-exhaust process is as follows: temperature of the wafer: 450 degrees C, pressure in the processing container: 0.4 kPa (3 Torr), flow rate of the NH_3 gas: 9,000 sccm, flow rate of the H_2 gas: 4,500 sccm, and flow rate of the Ar gas: 2,000 sccm.

In this way, the supply of the NH_3 gas is stopped at time T3, and a second film formation process is started at time T4. However, during a period from time T3 to time T4, a purge process is performed by supplying the Ar gas and vacuum-exhausting the inside of the processing container 10 similarly to the period from time T1 to time T2. As a result, NH_3 , HCl, NH_4Cl , and the like present in the processing container 10 are discharged to the outside.

[0036] Subsequently, during a period from time T4 to time T5, as the second film formation process, supply of the film formation gases and application of the radio frequency power are performed, and the Ti film is formed in the same manner as in the first film formation process described above. Thereafter, a purge process is performed during a period from time T5 to time T6, a second vacuum-exhaust process is performed during a period from time T6 to time T7, and a purge process is performed during a period from time T7 to time T8, each by the method already described. Subsequently, a third film formation process is started at time T8.

[0037] Although the time chart shown in FIG. 3 illustrates up to time T8, in practice, a processing cycle includes the film formation process, the vacuum-exhaust process, and then the film formation process, and the film formation processing of the Ti film is performed by repeating this processing cycle a preset number of times of one or more. The number of repetitions of the processing cycle is appropriately set depending on the target film thickness of the Ti film, the processing conditions of the film formation process, and the processing conditions of the vacuum-exhaust process.

[0038] In this case, for example, an execution time of each of the film formation process and the vacuum exhaust process may be set such that a total execution time of the film formation process and the vacuum exhaust process until the film thickness of the Ti film reaches a preset target

thickness is minimized. As described earlier, if the film formation process is continued as it is, the saturation state is reached where the film thickness of the Ti film is difficult to increase, and the time required to reach the target film thickness becomes longer. On the other hand, when the vacuum exhaust process is performed, the saturation state is improved, but during a period in which the vacuum-exhaust is being performed, the film formation cannot be performed.

[0039] Therefore, for example, by preliminary experiments, the Ti film is formed while variously changing a film formation time required for the film formation process and a cleaning exhaust time required for the vacuum exhaust process.

For example, FIG. 4A schematically illustrates a change in a film thickness of a Ti film over time during a film formation period in a case in which, in forming the Ti film up to a target thickness D_T , one cycle including a vacuum exhaust process and a subsequent film formation process is performed after an initial film formation process. In the example shown in FIG. 4A, in the initial film formation process, film formation is performed during a period from time T_0 to time T_1 until an increase in the film thickness reaches a saturation state. Thereafter, the vacuum exhaust process is performed while supplying the cleaning gas (time T_2 to time T_3), and then the film formation process is performed again during a period from time T_4 to time T_5 until the film thickness of the Ti film reaches the target thickness D_T . When the first film formation process is performed for a long time, the amount of Cl remaining in the processing container 10 also increases, and in the film formation process performed after the vacuum exhaust process, a film formation rate may not recover to the same level as in the first film formation process. Here, in this example, a period of the vacuum exhaust process during which film formation is not performed occurs only once.

[0040] Compared with the above-described example, FIG. 4B schematically illustrates a change in a film thickness of a Ti film over time in a case in which film formation is performed up to the target thickness D_T by performing two cycles each including a vacuum exhaust process and a subsequent film formation process, after performing an initial film formation process. In the example shown in FIG. 4B, in each film formation process (time T_0 - T_1 , time T_4 - T_5 , and time

T8-T9), film formation is completed in a short time before an increase in the film thickness reaches a saturation state. Therefore, the amount of Cl remaining in the processing container 10 is relatively small, and recovery of the film formation rate in the subsequent film formation process after performing the vacuum exhaust process (time T2-T3 and time T6-T7) is also significant. However, in this example, the period of the vacuum exhaust process during which film formation is not performed occurs twice.

[0041] Comparing FIG. 4A and FIG. 4B and focusing only on the film formation process, it appears that the example of FIG. 4B enables film formation up to the target thickness D_T in a shorter period of time. However, as already described, the period of the vacuum exhaust process during which film formation is not performed occurs once in the example of FIG. 4A, whereas the period occurs twice in the example of FIG. 4B. Therefore, in an evaluation of the preliminary experiments, total times (time T0-T5 in FIG. 4A and time T0-T9 in FIG. 4B) including the periods of the vacuum exhaust process during which film formation is not performed are compared. Then, the execution time of each process or the number of cycles are determined such that the total execution time of the film formation process and the vacuum exhaust process is minimized.

[0042] In this way, a preset number of processing cycles is executed to form the Ti film having the target thickness. Thereafter, along with terminating the application of the radio frequency power from the radio frequency power sources 34 and 23, the supply of the film formation gases and the Ar gas and the heating of the wafer W are stopped. Then, the wafer W is unloaded from the processing container 10 in the reverse order of the loading operation, and loading of the next wafer W is awaited.

Here, in the Ti film 6 formed along an exposed surface (bottom surface) of the silicon member 51, silicon atoms diffuse from the silicon member 51 side over time, and eventually a titanium silicide (TiSi) film is formed.

[0043] As described above, the technique according to the present disclosure aims to improve the film formation rate by identifying the characteristic in which the film formation rate

decreases as a CVD processing time becomes longer in CVD in which the raw material gas (TiCl_4 gas) and the reaction gas (H_2 gas) are simultaneously supplied to cause a reaction. Unlike ALD in which supply and exhaust of the raw material gas and supply and exhaust of the reaction gas are alternately repeated, the raw material gas and the reaction gas are continuously supplied in CVD. For this reason, even when the inside of the processing container 10 is vacuum-exhausted, an amount of byproducts resulting from the reaction between the raw material gas and the reaction gas increases as the processing time becomes longer. However, conventionally, no attention has been paid to the influence of the byproducts remaining in the processing container 10. Further, in the above-described prior art documents 1 and 2, there is no description regarding an effect of substances remaining in the processing container on growth of the Ti film.

[0044] The present disclosure discovers that the byproducts remaining in the processing container 10 inhibit the growth of the Ti film, and improves the saturation state of the film thickness of the Ti film by reducing these byproducts. As a specific method for this improvement, the method is used in which, after the film formation process, the process of vacuum-exhausting the inside of the processing container 10 while supplying the cleaning gas (NH_3 gas) is performed, and Cl-containing byproducts remaining in the processing container 10 react with the cleaning gas to remove the byproducts. As a result, it is considered that it is possible to reduce Cl within the processing container 10 and suppress a reaction between highly reactive TiCl_2 radicals and Cl. Therefore, it is presumed that it is possible to utilize the TiCl_2 radicals for the formation of the Ti film in the processing container 10 and suppress a decrease in the film formation rate over time.

[0045] <Second Embodiment of Method of Forming Ti Film>

Subsequently, a second embodiment of a method of forming a Ti film is described with reference to a time chart of FIG. 5. In this embodiment, during the vacuum exhaust process, plasma-activated H_2 gas is supplied as the cleaning gas instead of the NH_3 gas. A period from time T10 to time T11 shown in FIG. 5 corresponds to a first film formation process, and a period

from time T14 to time T15 corresponds to a second film formation process, each of which is performed in the same manner as in the first embodiment.

[0046] Further, a first vacuum exhaust process is performed during a period from time T12 to time T13, and a second vacuum exhaust process is performed during a period from time T16 to time T17. In these vacuum exhaust processes, the H₂ gas and the Ar gas are supplied to the shower head 3, and the radio frequency power is supplied from the radio frequency power source 34 to the shower head 3, thereby converting these gases into plasma.

[0047] The plasma-activated H₂ gas reacts with Cl present in the processing container 10 to generate HCl, and this HCl is discharged to the outside as the inside of the processing container 10 is exhausted. In this way, in this embodiment as well, the concentration of Cl within the processing container 10 is reduced by performing the vacuum exhaust process.

An example of processing conditions for the vacuum exhaust process of this embodiment is as follows: temperature of the wafer W: 450 degrees C, pressure in the processing container: 0.133 kPa (1 Torr), processing time: 30 seconds, flow rate of the H₂ gas: 4,500 sccm, flow rate of the Ar gas: 1,000 sccm, and radio frequency power from the radio frequency power source 34: 10 kHz, 500 W.

[0048] In this embodiment as well, during the periods T11-T12, T13-T14, T15-T16, and T17-T18 between the film formation process and the vacuum exhaust process, a purge process is performed in the same manner as in the first embodiment. As a result, the inside of the processing container 10 is purged by the Ar gas, and H₂, HCl, and the like present in the processing container 10 are discharged to the outside.

According to this embodiment as well, since the interior of the processing container 10 is vacuum-exhausted while supplying the plasma-activated H₂ gas as the cleaning gas, Cl in the processing container 10 is reduced, making it possible to reduce the reaction between the TiCl₂ radicals and Cl. Therefore, it is possible to suppress a decrease in the film formation rate in the processing container 10.

[0049] As described above, in the present disclosure, although a processing cycle includes the

film formation process, the vacuum exhaust process, and then the subsequent film formation process, the respective processing conditions for the film formation process performed before the vacuum exhaust process and the film formation process performed after the vacuum exhaust process do not necessarily have to be set to the same conditions, and for example, the film formation times may be changed.

[0050] Further, the metal halide is not limited to the example of the TiCl_4 gas, and the present disclosure may also be applied to a method of forming a tungsten (W) film by using a film formation gases containing tungsten pentachloride (WCl_5) or tungsten hexachloride (WCl_6) as the metal halide.

Further, the film formation gases containing the metal halide is not limited to mixed gases of the raw material gas (e.g., the TiCl_4 gas) and the reaction gas (e.g., the H_2 gas). The present disclosure may also be applied to a process of forming a metal film by thermal decomposition CVD using a raw material gas alone as a film formation gas.

[0051] In addition, supplying the NH_3 gas or the plasma-activated H_2 gas as the cleaning gas is not an essential requirement. As the cleaning gas, at least one gas selected from a cleaning gas group of H_2 gas, silane (SiH_4) gas, disilane (Si_2H_6) gas, or nitrogen trifluoride (NF_3) gas may be used. Further, with respect to the NH_3 gas used as the cleaning gas in the first embodiment, it is considered that plasma activation is undesirable because the use of plasma-activated NH_3 gas may cause nitrides to be formed on the surface of the wafer W.

[0052] Further, a target on which the Ti film 6 is formed using the technique of the present disclosure is not limited to the recess 50 shown in FIG. 2. For example, in some cases, a vertical groove is formed on the surface of the wafer W, and a plurality of horizontal grooves are formed on a sidewall surface of the vertical groove so as to be arranged in a thickness direction of the wafer W. These horizontal grooves may be regarded as a recess, and the Ti film 6 may be formed within the recess. Further, a member on which the Ti film 6 is formed is not limited to the silicon member 51 and may be another metal or a metal compound.

[0053] It should be noted that the embodiments disclosed herein are exemplary in all aspects and

are not restrictive. The above-described embodiments may be omitted, replaced, or modified in various forms without departing from the scope and spirit of the appended claims.

Examples

[0054] (Evaluation Experiment 1)

The Ti film 6 was formed in accordance with the first embodiment and the second embodiment, and the state of formation of the Ti film 6 within the recess 50 was confirmed. As an example, a width dimension (W) of the recess 50 is 40 nm and a depth dimension (H) of the recess 50 is 160 nm.

A. Experimental Conditions

For the wafer W in which the recess 50 was formed, the Ti film 6 was formed using the film formation apparatus 1 described with reference to FIG. 1 in each of Reference Example 1 in which only the film formation process was performed, Comparative Example 1 in which the film formation process was performed twice with the purge process with no supply of the cleaning gas interposed therebetween, Example 1-1 performed based on the time chart of FIG. 3, and Example 1-2 performed based on the time chart of FIG. 5. Respective processing conditions were set as follows.

[0055] (Processing Conditions of Reference Example 1)

The film formation processing of the Ti film 6 was performed under the following conditions: temperature of the wafer: 450 degrees C, supply flow rate of the TiCl_4 gas: 25 sccm, supply flow rate of the H_2 gas: 1,000 sccm, supply flow rate of the Ar gas: 2,400 sccm, pressure in the processing container 10: 1.2 kPa (9 Torr), radio frequency power source 34: 10 kHz, 100 W, and no application of the radio frequency power source 23. Under these conditions, the film formation processing was performed for 10 seconds, 30 seconds, 60 seconds, 120 seconds, 360 seconds, and 540 seconds from a start of the processing, and the film thickness of the Ti film formed in each case was measured.

[0056] (Processing Conditions of Comparative Example 1)

The film formation process was performed for 360 seconds from a start of the

processing under the same conditions as in Reference Example 1 and then the supply of the film formation gases and the application of the radio frequency power from the radio frequency power source 34 were stopped. Subsequently, while supplying the Ar gas into the processing container 10 at a flow rate of 2,400 sccm, the purge process of vacuum-exhausting the inside of the processing container 10 was performed for 45 seconds. Thereafter, the film formation process was performed again under the same conditions as in Reference Example 1, and the film thickness of the Ti film obtained at a timing when a total processing time reached 540 seconds was measured. In this way, Comparative Example 1 is an example in which the first film formation process, the purge process, and then the second film formation process are performed. The total processing time refers to time required from a start of the first film formation process to an end of the second film formation process.

[0057] (Processing Conditions of Example 1-1)

The film formation process was performed for 360 seconds from a start of the processing under the same conditions as in Reference Example 1 and then the purge process was performed under the same conditions as in Comparative Example 1. Thereafter, the vacuum exhaust process using the NH₃ gas as described in the first embodiment was performed for 3 seconds and then the second film formation process was performed again under the same conditions as in Reference Example 1. The film thickness of the Ti film obtained at a timing when the total processing time reached 540 seconds was measured.

The processing conditions of the vacuum exhaust process using the NH₃ gas were set as follows: temperature of the wafer: 450 degrees C, supply flow rate of the NH₃ gas: 9,000 sccm, supply flow rate of the H₂ gas: 4,500 sccm, supply flow rate of the Ar gas: 24,000 sccm, and pressure in the processing container 10: 400 Pa (3 Torr).

[0058] (Processing Conditions of Example 1-2)

The film formation process was performed for 360 seconds from a start of the processing under the same conditions as in Reference Example 1 and then the purge process was performed under the same conditions as in Comparative Example 1. Thereafter, the vacuum

exhaust process using the plasma-activated H₂ gas as described in the second embodiment was performed for 30 seconds and then the second film formation process was performed again under the same conditions as in Reference Example 1. The film thickness of the Ti film obtained at a timing when the total processing time reached 540 seconds was measured.

The processing conditions of the vacuum exhaust process using the plasma-activated H₂ gas were set as follows: temperature of the wafer: 450 degrees C, supply flow rate of the H₂ gas: 4,500 sccm, supply flow rate of the Ar gas: 2,400 sccm, pressure in the processing container 10: 133 Pa (1 Torr), and the radio frequency power source 34: 450 kHz, 500 W.

[0059] B. Experimental Results

For each of the wafers W subjected to Reference Example 1, Comparative Example 1, Example 1-1, and Example 1-2, the film thickness of the Ti film 6 formed on the bottom surface of the recess 50 was measured by X-ray fluorescence analysis. Measurement results are shown in FIG. 6. In FIG. 6, the vertical axis represents the film thickness of the Ti film, and the horizontal axis represents the film formation time. The measurement results are plotted as "○" for Reference Example 1, "Δ" for Comparative Example 1, "●" for Example 1-1, and "■" for Example 1-2. In addition, the measurement results of Comparative Example 1, Example 1-1, and Example 1-2 are plotted at the position of 540 seconds, with the total processing time regarded as the film formation time.

[0060] Reference Example 1 is a case in which a conventional film formation process was performed. From the results shown in FIG. 6, it was confirmed that the Ti film was smoothly formed at a relatively high film formation rate of about 0.5 Å/s up to about 30 seconds after a start of the film formation process. However, the film formation rate gradually decreases and eventually reaches a saturation state in which it becomes difficult for the film thickness to increase. Specifically, it is recognized that the film formation rate from 120 seconds to 360 seconds is 0.033 Å/s, the film formation rate from 360 seconds to 540 seconds is 0.022 Å/s, and an amount of film growth decreases when the film formation time exceeds 120 seconds, thus reaching the saturation state.

[0061] Further, comparing the film thickness of the Ti film at a film formation time of 540 seconds, Reference Example 1 was 58 Å, Comparative Example 1 was 59 Å, Example 1-1 was 65 Å, and Example 1-2 was 63 Å. In this way, it was found that there was almost no difference in film thickness between Reference Example 1 and Comparative Example 1 and that even performing the purge process at a film formation time of 360 seconds was not very effective in reducing Cl in the processing container 10.

[0062] In contrast, it was confirmed that the Ti films formed by the methods of Example 1-1 and Example 1-2 increased in thickness by about 5 to 7 Å compared to Reference Example 1. The film formation rate from 360 seconds to 540 seconds was 0.056 Å/s in Example 1-1 and 0.044 Å/s in Example 1-2. Compared with Reference Example 1, it can be said that the saturation state of the increase in the film thickness is improved and the decrease in the film formation rate is suppressed. From the results of Examples 1-1 and 1-2, it can be evaluated that the technique according to the present disclosure is suitable as a method of forming the Ti film 6 while suppressing a decrease in the film formation rate.

[0063] (Evaluation Experiment 2)

In correspondence with the first embodiment, the Ti film 6 was formed under conditions different from those of Evaluation Experiment 1, and a formation state of the Ti film 6 within the recess 50 was confirmed.

A. Experimental Conditions

Similarly to Evaluation Experiment 1, the Ti film 6 was formed in each of Reference Example 2 in which only the film formation process was performed, Comparative Example 2 in which the film formation process was performed twice with the purge process with no supply of the cleaning gas interposed therebetween, and Example 2-1 performed based on the time chart of FIG. 3. A shape of the recess 50 formed in the wafer W was the same as in Evaluation Experiment 1, and respective processing conditions were set as follows.

[0064] (Processing Conditions of Reference Example 2)

The film formation processing of the Ti film 6 was performed under the following

conditions: temperature of the wafer: 450 degrees C, supply flow rate of the TiCl_4 gas: 25 sccm, supply flow rate of the H_2 gas: 1,000 sccm, supply flow rate of the Ar gas: 2,400 sccm, pressure in the processing container 10: 1.2 kPa (9 Torr), radio frequency power source 34: 100 kHz, 100 W, and no application from the radio frequency power source 23. Under these conditions, the film formation processing was performed for 360 seconds, and the film thickness of the formed Ti film was measured.

[0065] (Processing Conditions of Comparative Example 2)

The first film formation process was performed for 360 seconds from a start of the processing under the same conditions as in Reference Example 2 and then the purge process of vacuum-exhausting the inside of the processing container 10 was performed for 45 seconds while supplying the Ar gas into the processing container 10 at a flow rate of 2,400 sccm. Thereafter, the second film formation process was performed under the same conditions as in Reference Example 2, and the film thickness of the Ti film obtained at a timing when the total processing time reached 540 seconds was measured.

[0066] (Processing Conditions of Example 2-1)

The film formation process was performed for 360 seconds from a start of the processing under the same conditions as in Reference Example 2 and then the purge process was performed under the same conditions as in Comparative Example 2. Thereafter, the vacuum exhaust process using the NH_3 gas was performed for 3 seconds and then the second film formation process was performed again under the same conditions as in Reference Example 2. The film thickness of the Ti film obtained at a timing when the total processing time reached 540 seconds was measured.

The processing conditions of the vacuum exhaust process were set as follows: temperature of the wafer: 450 degrees C, supply flow rate of the NH_3 gas: 9,000 sccm, supply flow rate of the H_2 gas: 4,500 sccm, supply flow rate of the Ar gas: 2,000 sccm, and pressure in the processing container 10: 0.4 kPa (3 Torr).

[0067] B. Experimental Results

For each of the wafers W subjected to Reference Example 2, Comparative Example 2, and Example 2-1, a region in which the recess 50 was formed was magnified and photographed using a transmission electron microscope (TEM), and the film thickness of the Ti film formed on the bottom surface of the recess 50 was measured. Results are shown in FIG. 7 as Table 1.

As shown in FIG. 7, even for the Ti film formed under the film formation conditions different from those of Evaluation Experiment 1, it was confirmed that Example 2-1 in which the vacuum exhaust process using the NH_3 gas was performed exhibited a greater film thickness of the Ti film than that of Comparative Example 2 in which only the purge process was performed and that a decrease in the film formation rate of the Ti film can be suppressed.

[0068] (Evaluation Experiment 3)

In correspondence with the second embodiment, the Ti film 6 was formed under conditions different from those of Evaluation Experiment 1, and a formation state of the Ti film 6 within the recess 50 was confirmed.

A. Experimental Conditions

Similarly to Evaluation Experiment 1, the Ti film 6 was formed based on the time chart of FIG. 5. The shape of the recess 50 formed in the wafer W is the same as in Evaluation Experiment 1, and processing conditions were set as follows.

[0069] (Processing Conditions of Example 3-1)

The film formation process was performed for 120 seconds from a start of the processing under the same conditions as in Reference Example 1 of Evaluation Experiment 1 and then the supply of the film formation gases and the application of the radio frequency power from the radio frequency power sources 34 and 23 were stopped. Subsequently, while supplying the Ar gas into the processing container 10 at a flow rate of 2,400 sccm, the purge process of vacuum-exhausting the inside of the processing container 10 was performed for 45 seconds. Thereafter, the vacuum exhaust process of the second embodiment was performed for 30 seconds and then the second film formation process was performed again for 120 seconds under the same conditions as in Reference Example 1. Then the film thickness of the obtained

Ti film was measured. In Example 3-1, the film formation process was repeated twice.

The processing conditions of the vacuum exhaust process were set as follows:
temperature of the wafer: 450 degrees C, supply flow rate of the H₂ gas: 4,500 sccm, supply flow rate of the Ar gas: 1,000 sccm, pressure in the processing container 10: 0.13 kPa (1 Torr), processing time: 30 seconds, and radio frequency power source 34: 450 kHz, 500 W.

[0070] (Processing Conditions of Example 3-2)

Similarly to Example 3-1, the film formation process → purge process → vacuum exhaust process → film formation process was performed. In this processing cycle, the film formation process was repeated four times, and the film thickness of the obtained Ti film was measured. Except that the processing time of each film formation process was set to 60 seconds, the Ti film was formed under the same conditions as in Example 3-1.

[0071] (Processing Conditions of Example 3-3)

As in Example 3-1, the film formation process → purge process → vacuum exhaust process → film formation process was performed. In this processing cycle, the film formation process was repeated eight times, and the film thickness of the obtained Ti film was measured. Except that the processing time of each film formation process was set to 30 seconds, the Ti film was formed under the same conditions as in Example 3-1.

[0072] (Processing Conditions of Example 3-4)

Similarly to Example 3-3, the film formation process was repeated eight times, and the film thickness of the obtained Ti film was measured. The processing conditions in this case were set as follows.

Temperature of wafer: 450 degrees C, supply flow rate of the H₂ gas: 4,500 sccm, supply flow rate of the Ar gas: 2,000 sccm, pressure in the processing container 10: 0.13 kPa (1 Torr), processing time: 30 seconds, and radio frequency power source 34: 450 kHz, 500 W.

[0073] B. Experimental Results

For the wafers W of Examples 3-1, 3-2, 3-3, and 3-4, a region in which the recess 50 is formed was magnified and photographed using a TEM, and the film thickness of the Ti film

formed at the bottom portion of the recess 50 was measured. The results are shown in FIG. 8 as Table 2. The number of cycles refers to the number of film formation processes.

As shown in these results, even for the Ti film formed under the film formation conditions different from those of Evaluation Experiment 1, it was confirmed that the thickness of the Ti film increases by performing the vacuum exhaust process using the plasma-activated H₂ gas and that the amount of film growth increases as the number of film formation processes increases.

[0074] Further, comparing Examples 3-3 and 3-4, it was recognized that even when the number of cycles (the number of film formation processes) is the same, the film thickness of the Ti film increases by increasing the supply flow rate of the Ar gas. Therefore, it is understood that, by optimizing the processing conditions of the vacuum exhaust process, it is possible to suppress a decrease in the film formation rate of the Ti film and to further increase the thickness of the Ti film 6.

[0075] In Example 1-2 of Evaluation Experiment 1, a total film formation time was set to 540 seconds, and the film thickness of the Ti film was 63 Å. On the other hand, in Evaluation Experiment 3, the total film formation time was set to 240 seconds, and it was confirmed that the film thickness of the Ti film was 73 Å or more when the number of cycles was four or more.

[0076] Evaluation Experiment 1 and Evaluation Experiment 3 cannot be directly compared because the processing conditions of the film formation process and the vacuum exhaust process are different. However, from a tendency of the Ti film formation rate shown in FIG. 6, it is recognized that the film formation rate is high up to 60 seconds after the start of the film formation process. Therefore, by stopping the film formation process at a relatively early timing, for example, within 60 seconds from the start of film formation processing, performing the vacuum exhaust process, and increasing the number of film formation processes, the film thickness of the Ti film can be increased even with the same total processing time, and it can be said that this is suitable method for forming the Ti film.

[0077] In other words, these results indicate that, by setting the processing conditions of the film

formation process, it is possible to minimize the total processing time required for the thickness of the Ti film to reach a target thickness. Therefore, for example, in forming a target film thickness, an execution time of the film formation process is specified so that the film formation rate per unit time is maximized, and the cleaning exhaust time is also specified. As a result, it is understood that it is possible to set the total processing time, which is the sum of the film formation time and the cleaning exhaust time, to be minimized, and improve throughput.

[0078] However, appropriate processing conditions for each of the film formation process, the vacuum exhaust process, and the purge process vary depending on a type of a metal film, types of film formation gases, a shape of the recess 50 formed in the wafer W, materials of the film on the bottom surface and sidewall surface of the recess 50, a target film thickness, and the like. Therefore, it is desirable that the execution time and the number of repetitions of the film formation process and the vacuum exhaust process be appropriately set according to each case.

EXPLANATION OF REFERENCE NUMERALS

[0079] W: wafer, 1: film formation apparatus, 10: processing container, 13: exhauster, 2: stage, 410: TiCl₄ gas supply source, 440: NH₃ gas supply source, 6: Ti film, 100: controller

WHAT IS CLAIMED IS:

1. A method of forming a metal film on a substrate, the method comprising:
forming the metal film on a surface of the substrate by supplying film formation gases containing a metal halide serving as a raw material of the metal film to the substrate and reacting the film formation gases; and
in response to the forming the metal film having a characteristic in which a film formation rate decreases over time, vacuum-exhausting, after stopping the supply of the film formation gases, an atmosphere in which the substrate is disposed while supplying a cleaning gas that reacts with byproducts generated by the reaction of the film formation gases,
wherein the forming the metal film is performed again after the vacuum-exhausting.
2. The method of Claim 1, wherein a cycle including the vacuum-exhausting and then the forming the metal film is repeated a plurality of times.
3. The method of Claim 1, wherein the metal halide is TiCl_4 , the film formation gases are mixed gases of TiCl_4 gas and H_2 gas, and in the forming the metal film, the film formation gases are converted into plasma so as to form the metal film.
4. The method of Claim 3, wherein the byproducts include Cl , and the cleaning gas is at least one selected from a cleaning gas group of NH_3 gas, plasma-activated H_2 gas, H_2 gas, SiH_4 gas, Si_2H_6 gas, and NF_3 gas.
5. The method of Claim 1, wherein an execution time of each of the forming the metal film and the vacuum-exhausting is set such that a total execution time of the forming the metal film and the vacuum-exhausting until a film thickness of the metal film reaches a preset target thickness is minimized.

6. An apparatus for forming a metal film on a substrate, comprising:
a processing container including a stage on which the substrate is placed;
a film formation gas supply configured to supply, to the processing container, film formation gases containing a metal halide serving as a raw material of the metal film;
a cleaning gas supply configured to supply, to the processing container, a cleaning gas that reacts with byproducts generated by a reaction of the film formation gases;
an exhauster configured to vacuum-exhaust an inside of the processing container; and
a controller,
wherein the controller is configured to output a control signal to execute:
forming the metal film on a surface of the substrate placed on the stage by supplying the film formation gases to the processing container and reacting the film formation gases; and
in response to the forming the metal film having a characteristic in which a film formation rate decreases over time, vacuum-exhausting, after stopping the supply of the film formation gases, an inside of the processing container while supplying the cleaning gas to the processing container, and
wherein the controller is configured to output a control signal to execute performing the forming the metal film again after the vacuum-exhausting.
7. The apparatus of Claim 6, wherein the controller is configured to output a control signal to execute repeating a cycle, including the vacuum-exhausting and then the forming the metal film, a plurality of times.
8. The apparatus of Claim 6, further comprising a plasma generator configured to convert the film formation gases into plasma,
wherein the metal halide is TiCl_4 , the film formation gases are mixed gases of TiCl_4 gas

and H_2 gas, and in the forming the metal film, the film formation gases are converted into plasma so as to form the metal film.

9. The apparatus of Claim 8, wherein the byproducts include Cl, and the cleaning gas is at least one selected from a cleaning gas group of NH_3 gas, plasma-activated H_2 gas, H_2 gas, SiH_4 gas, Si_2H_6 gas, and NF_3 gas.

10. The apparatus of Claim 6, wherein an execution time of each of the forming the metal film and the vacuum-exhausting is set such that a total execution time of the forming the metal film and the vacuum-exhausting until a film thickness of the metal film reaches a preset target thickness is minimized.