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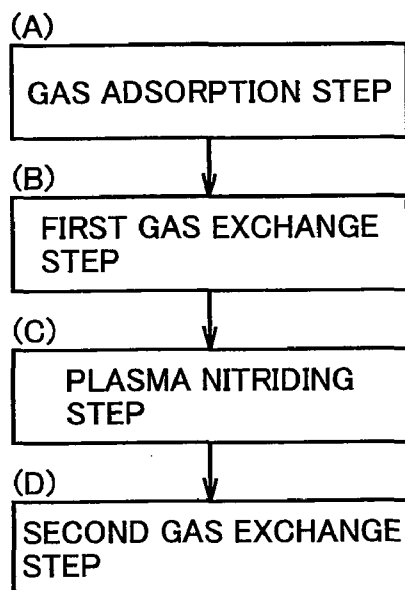
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(54) Title: FILM FORMATION METHOD, SEMICONDUCTOR-DEVICE FABRICATION METHOD, INSULATING FILM AND SEMICONDUCTOR DEVICE

[Fig. 6]



(57) Abstract: In the film formation method, a substrate W, which is a base of a semiconductor device, is firstly held on a holding stage 34. Then, a source gas is adsorbed on the substrate W (FIG. 6(A)). Subsequently, a process chamber 32 is exhausted to remove the excessively adsorbed adsorption gas and exchange the gas (FIG. 6(B)). After the exhaustion, a plasma nitriding process is executed with microwaves (FIG. 6(C)). Upon completion of the plasma nitriding process, the process chamber 32 is exhausted to remove ammonia gas and the like and exchange the gas (FIG. 6(D)). The series of these steps (A) to (D) is repeated until the film reaches a desired thickness.



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DESCRIPTION

Title of Invention

FILM FORMATION METHOD, SEMICONDUCTOR-DEVICE
FABRICATION METHOD, INSULATING FILM AND SEMICONDUCTOR
5 DEVICE

Technical Field

This invention relates to film formation methods, semiconductor-device
fabrication methods, insulating films and semiconductor devices, and more
particular to a film formation method and a semiconductor-device fabrication
10 method using plasma processing and an insulating film and a semiconductor
device formed through plasma processing.

Background Art

Conventionally, silicon oxide films (SiO_2) and silicon nitride films (SiN)
are often used as materials for, in addition to LSI (Large Scale Integrated
15 circuits), CCDs (Charge Coupled Devices) and MOS (Metal Oxide
Semiconductor) devices, gates and isolating trenches (STI: Shallow Trench
Isolation) of semiconductor devices with 3D gates in a Fin structure. In recent
years, the application of metal materials with poor heat resistance to gates has
begun to meet demands associated with improving the performance of the device
20 features. That is a so-called metal-first process in a High-k metal gate
patterning process. However, positive introduction of the poor-heat-resistance
metal materials into the device fabrication process entails the need of a
low-temperature process of the silicon oxide film (SiO_2) and silicon nitride film
(SiN), which are structure members of an LSI device.

25 A problem in deposition of the silicon oxide film (SiO_2) and silicon nitride

film (SiN) at a low temperature of 500°C or lower is quality degradation of the formed insulating film. In the case of silicon oxide films (SiO₂), recently proposed film formation methods using microwave plasma can form high-quality films with excellent electric characteristics and film characteristics even at 400°C or lower, and the methods are being practically used (Japanese Journal of Applied Physics, Vol.48 (2009), p. 126001, by H. Ueda et al. (Non-Patent Literature 1)). However, methods for depositing silicon nitride films (SiN) at a low temperature of approximately 400°C or lower are not yet in actual use as of now, because the resultant SiN film cannot obtain the same quality as SiN films (referred to as “LP-CVD SiN film”) formed through an LP (Low Pressure)-CVD at a high temperature of 700°C or higher.

Citation List

Non Patent Literature

[Non-Patent Literature 1] Japanese Journal of Applied Physics, Vol.48 (2009), p. 126001, by H. Ueda et al.

Summary of Invention

Technical Problem

General plasma-assisted reaction processes are effective in film deposition at low temperatures; however, the use of plasma to an uneven pattern with a large level difference causes considerable quality degradation of films on the side walls of a step in comparison with films on the upper part of the step. This is because, in the case of CVD utilizing general plasma energy, such as parallel plate plasma and ICP (Inductively Coupled Plasma) and ALS film-forming reactions utilizing atomic layer deposition (ALD), the assistant energy to enhance the reaction highly depends on the density of ionized active

species in the plasma. The ionized active species herein denote ionized species among species generated and activated in plasma.

If there is a stepped pattern on a substrate to be processed, many of the ionized species produced in the plasma lose their activity in a recessed portion of, for example, an STI pattern, more specifically, before reaching near the bottom of the trench, and therefore the film on the sidewall and bottom of the step reacts differently from the film on a flat surface of the raised portion of the step. Another technique of depositing SiN films at low temperatures uses sputtering (a reactive sputtering method using plasma). However, if there is an uneven pattern on a substrate to be processed, this sputter deposition method causes poor film characteristics (step coverage) in comparison with plasma film deposition. Even if the sputter deposition method can offer good film quality, it is difficult to apply to devices. Furthermore, the use of typical plasma, such as parallel plate plasma and ICP (Inductively Coupled Plasma), in film forming reaction for depositing films may sometimes cause poor film quality due to plasma damage during plasma film deposition (Non-Patent Literature 1).

In view of these problems, provided is a method for depositing a silicon nitride film (SiN), at low temperatures, with excellent film quality and excellent film characteristics (step coverage) on a step.

This invention provides a method capable of forming a high-quality film.

This invention provides a method capable of fabricating a semiconductor device including the high-quality film.

This invention provides an insulating film with excellent chemical resistance.

This invention provides a semiconductor device including an insulating

film with excellent chemical resistance.

Solution to Problem

The present invention is directed to a film formation method for forming a film on a substrate including the steps of: adsorbing source gas on the substrate to form an adsorption layer of the source gas on the substrate; and performing a plasma nitriding process on the formed adsorption layer with microwave plasma after the gas adsorption step.

According to the method, even if the substrate has a high aspect ratio or microscopic steps, the source-gas adsorption layer formed by adsorbing the source gas on the substrate can completely cover the geometry of the substrate. In addition, the microwave plasma used in the plasma nitriding process can significantly reduce damages caused by plasma. The film formation method therefore can provide a high-quality film.

Preferably, the film formation method is used to form insulating films.

More preferably, the gas adsorption step includes the step of adsorbing source gas containing silicon atoms on the substrate.

The gas adsorption step includes the step of adsorbing source gas containing chlorine atoms on the substrate.

In a preferable embodiment, the gas adsorption step includes the step of supplying source gas containing at least one of either hexachlorodisilane (Si_2Cl_6) or dichlorosilane (SiH_2Cl_2) on the substrate.

The plasma processing step can include the step of nitriding, oxidizing or oxynitriding the adsorption layer formed in the gas adsorption step by plasma processing.

More preferably, the microwave plasma is generated by a radial line slot

antenna (RLSA).

In a more preferable embodiment, the plasma processing step is executed with microwave plasma whose electron temperature is higher than 1.5 eV and whose electron density is higher than $1 \times 10^{11} \text{ cm}^{-3}$ in the vicinity of the surface of the substrate.

Preferably, the plasma processing step is executed at a pressure from 1 Torr to 8 Torr, more preferably at a pressure from 3 Torr to 7 Torr.

As to a process temperature during the plasma nitriding process, the surface temperature of substrate is preferably maintained at approximately 300°C to 450°C. In other words, the plasma processing step includes the step of executing the plasma nitriding process with the surface of the substrate maintained at a temperature from 300°C to 450°C.

Preferably, the gas adsorption step includes the step of changing the volume of a region above the substrate by moving the substrate close to a gas source or other actions.

Preferably, the film formation method includes the step of exhausting the region above the substrate, the exhaustion step being executed between the gas adsorption step and plasma processing step. In addition, the exhaustion step can be executed after the plasma processing step.

In another aspect of the present invention, there is provided a semiconductor device fabrication method including the step of forming a film on a substrate. The film formation step includes the steps of: adsorbing source gas on the substrate to form an adsorption layer of the source gas on the substrate; and performing a plasma nitriding process on the formed adsorption layer with microwave plasma after the gas adsorption step.

In yet another aspect of the present invention, there is provided an insulating film formed on a substrate. The insulation film is formed by adsorbing source gas on the substrate to form an adsorption layer of the source gas on the substrate and performing a plasma nitriding process on the formed
5 adsorption layer with microwave plasma.

In a preferable embodiment, the insulating film is a SiN film.

In yet another aspect of the present invention, there is provided a semiconductor device including an insulating film. The insulating film of the semiconductor device is formed by adsorbing source gas on the substrate to form
10 an adsorption layer of the source gas on the substrate and performing a plasma nitriding process on the formed adsorption layer with microwave plasma.

In yet another aspect of the present invention, there is provided a film formation method for forming a film on a substrate. The film formation method includes the steps of: adsorbing source gas on the substrate to form an
15 adsorption layer of the source gas on the substrate; and performing a plasma nitriding process on the formed adsorption layer with microwave plasma after the gas adsorption step. The plasma nitriding process is executed at a pressure from 1 Torr to 8 Torr.

The film formation method can form a film having excellent chemical
20 resistance (hydrofluoric-acid resistance).

Advantageous Effects of Invention

According to the film formation method, even if the substrate has a high aspect ratio and microscopic steps, the source-gas adsorption layer formed by adsorbing the source gas on the substrate can completely cover the geometry of
25 the substrate. In addition, the microwave plasma used in the plasma nitriding

process can significantly reduce damages caused by plasma. The film formation method therefore can provide a high-quality film.

The semiconductor-device fabrication method according to the invention can provide a semiconductor device with a high-quality film.

5 The insulating film according to the invention has excellent chemical resistance (hydrofluoric-acid resistance).

The semiconductor device according to the invention is provided with an insulating film with excellent chemical resistance (hydrofluoric-acid resistance).

Brief Description of Drawings

10 [FIG. 1] FIG. 1 is a schematic sectional view showing a part of a MOS device.

[FIG. 2] FIG. 2 is a schematic sectional view showing a relevant part of a plasma processing apparatus used in the semiconductor-device fabrication method according to an embodiment of the invention.

15 [FIG. 3] FIG. 3 depicts a slot antenna plate in the plasma processing apparatus shown in FIG. 2 as viewed along the through-thickness direction.

[FIG. 4] FIG. 4 is a graph showing the relationship between the distances from the lower surface of a dielectric window and the electron temperatures of plasma.

20 [FIG. 5] FIG. 5 is a graph showing the relationship between the distances from the lower surface of a dielectric window and the electron densities of plasma.

[FIG. 6] FIG. 6 is a flow chart showing principal process steps to form a film with the plasma processing apparatus in FIG. 2.

25 [FIG. 7] FIG. 7 is a graph showing the relationship between the gas

flow rates in the entire process chamber and the time required to reach a predetermined pressure value.

[FIG. 8] FIG. 8 is a graph showing the relationship between the gas flow rates in a small volume region formed above the holding stage and the time
5 required to reach a predetermined pressure value.

[FIG. 9] FIG. 9 is an enlarged cross-sectional view showing the vicinity of a device isolating region.

[FIG. 10] FIG. 10 is an enlarged picture, taken by a scanning electron microscope (SEM), of a silicon nitride film subjected to PE-ALD with an RLSA
10 and applied as a sidewall protective film in a trench structure, where the aspect ratio is approximately 6.

[FIG. 11] FIG. 11 is an enlarged picture, taken by the scanning electron microscope (SEM), of the silicon nitride film subjected to PE-ALD with the RLSA in FIG. 10 and soaked in a 0.5% HF solution (50%HF:water = 1:100) for 7
15 minutes, where the aspect ratio is approximately 6.

[FIG. 12] FIG. 12 is a graph showing the correlation between the nitriding pressures applied to perform PE-ALD with an RLSA to form a silicon nitride film and the resistance to hydrofluoric acid.

[FIG. 13] FIG. 13 is a graph showing the correlation between the
20 nitriding time consumed to perform PE-ALD with the RLSA to form the silicon nitride film and the resistance to hydrofluoric acid.

[FIG. 14] FIG. 14 is a graph showing the correlation between the stage temperatures and the surface temperatures of the substrate to be processed during PE-ALD with the RLSA to form the silicon nitride film and the resistance
25 to hydrofluoric acid.

[FIG. 15] FIG. 15 is a graph showing the correlation between the nitriding atmosphere states during PE-ALD with the RLSA to form the silicon nitride film, more specifically, the flow rates of ammonia gas in argon-ammonia mixture gas and resistance to hydrofluoric acid.

5 [FIG. 16] FIG. 16 is a graph showing the correlation between the process temperatures when SiN films are formed by various methods and the resistance to hydrofluoric acid.

[FIG. 17] FIG. 17 is a schematic sectional view showing a relevant part of another plasma processing apparatus used in the semiconductor-device
10 fabrication method according to the embodiment of the invention.

[FIG. 18] FIG. 18 is a schematic sectional view showing a part of the plasma processing apparatus including a gas exhaust mechanism with a gas exhaust hole formed in an extending portion of a head.

[FIG. 19] FIG. 19 depicts a substrate W, viewed from above, held on a
15 holding stage in the plasma process chamber shown in FIG. 18 and arrows indicating the directions film-deposition gas flows.

[FIG. 20] FIG. 20 is a schematic sectional view showing a part of the plasma processing apparatus including a gas exhaust mechanism with a gas exhaust hole formed more inside than an extending portion of a head.

20 [FIG. 21] FIG. 21 depicts a substrate W, viewed from above, held on a holding stage in the plasma process chamber in FIG. 20 and arrows indicating the directions film-deposition gas flows.

Description of Embodiments

An embodiment of the present invention will be described below with
25 reference to the drawings. First of all, the configuration of a semiconductor

device according to the embodiment of the invention will be described. FIG. 1 is a schematic sectional view showing a relevant part of a MOS device according to the embodiment of the invention. In the MOS device in FIG. 1, a hatch pattern indicates conductive layers.

5 Referring to FIG. 1, the MOS device 11 includes device isolating regions 13, a p-type well 14a, an n-type well 14b, heavily-doped n-type impurity diffused regions 15a, heavily-doped p-type impurity diffused regions 15b, n-type impurity diffused regions 16a, p-type impurity diffused regions 16b and gate oxide films 17, all of which are formed on a silicon substrate 12. In the
10 heavily-doped n-type impurity diffused regions 15a formed so as to sandwich a gate oxide film 17, one region serves as a drain and the other serves as a source. In the heavily-doped p-type impurity diffused regions 15b formed so as to sandwich a gate oxide films 17, one region serves as a drain and the other serves as a source.

15 On the gate oxide films 17 formed are gate electrodes 18 serving as conductive layers. Gate sidewalls 19, which serve as insulating films, are formed on the sides of the gate electrodes 18. In addition, an insulating film 21 is formed on the silicon substrate 12 with the gate electrodes 18 and other components formed thereon. Formed in the insulating film 21 are contact holes
20 22 in contact with the heavily-doped n-type impurity diffused regions 15a and heavily-doped p-type impurity diffused regions 15b, and the contact holes 22 are filled with plugging electrodes 23. Metal wiring layers 24, which are conductive layers, are formed on those components. Furthermore, an interlayer insulating film (not shown), which is an insulating layer, and a metal
25 wiring layer, which is a conductive layer, are alternatively formed. At last, a

pad (not shown), which is a contact with an external component, is formed. In this manner, the MOS device 11 is fabricated.

The semiconductor device according to the embodiment of the invention, as will be described later, includes a silicon nitride film formed by adsorbing source gas on a substrate W to be processed so that an adsorption layer of the source gas is formed on the substrate W and subjecting the formed adsorption layer to plasma nitriding with microwave plasma. The silicon nitride film is used as, for example, a liner film of the device isolating region 13 or gate sidewalls 19. The liner film of the device isolating region 13 is indicated by numeral number 86 in FIG. 9 to be described later. The insulating film according to the embodiment of the invention is the above-described silicon nitride film making up a transistor device and is formed by adsorbing source gas on a substrate W to be processed so that an adsorption layer of the source gas is formed on the substrate W and subjecting plasma nitriding to the formed adsorption layer with microwave plasma.

Next, the configuration and operation of the plasma processing apparatus used in the semiconductor-device fabrication method according to the embodiment of the invention will be described.

FIG. 2 is a schematic sectional view showing a relevant part of the plasma processing apparatus used in the semiconductor-device fabrication method according to the embodiment of the invention. FIG. 3 depicts a slot antenna plate included in the plasma processing apparatus shown in FIG. 2 as viewed from underneath, specifically speaking, as viewed along the direction of Arrow III in FIG. 2. For the sake of clarity, hatch patterns for some components in FIG. 2 are omitted.

Referring to FIGS. 2 and 3, the plasma processing apparatus 31 includes a process chamber 32 in which a substrate W is subjected to plasma processing, a plasma-processing-gas feeder 33 that feeds reactive gas for plasma processing into the process chamber 32, a disk-like holding stage 34 on which the substrate
5 W is held, a plasma generation mechanism 39 that generates plasma in the process chamber 32, and a controller (not shown) that controls the whole plasma processing apparatus 31. The controller controls the whole plasma processing apparatus 31, including the gas flow rate of the plasma-processing-gas feeder 33, pressure in the process chamber 32 and so on.

10 The process chamber 32 includes a bottom 41 positioned beneath the holding stage 34 and a sidewall 42 extending upwardly from the outer edge of the bottom 41. The sidewall 42 is roughly in the shape of a cylinder. An exhaust hole 43 for discharging gas is formed in the bottom 41 of the process chamber 32 so as to penetrate a part of the bottom 41. An upper part of the
15 process chamber 32 is open, but is designed to be sealed by a cover 44, which is put on the upper side of the process chamber 32, a dielectric window 36, which will be described later, and an O-ring 45, which serves as a sealing member and is interposed between the dielectric window 36 and cover 44.

The plasma-processing-gas feeder 33 includes a first
20 plasma-processing-gas feeder 46 that blows the gas toward the center of the substrate W and a second plasma-processing-gas feeder 47 that blows the gas from the outer side of the substrate W. The first plasma-processing-gas feeder 46 is provided at the radial center of the dielectric window 36 and is recessed further than the bottom surface 48, which faces the holding stage 34, of the
25 dielectric window 36. The first plasma-processing-gas feeder 46 feeds the

plasma-processing gas at a flow rate regulated by a gas feeding system 49 connected to the first plasma-processing-gas feeder 46. The second plasma-processing-gas feeder 47 includes a plurality of plasma-processing-gas feeding holes 50 at a part on the upper side of the sidewall 42 to feed the plasma processing gas into the process chamber 32. The plasma-processing-gas feeding holes 50 are evenly spaced in the circumferential direction. The first and second plasma-processing-gas feeders 46 and 47 are supplied with the same kind of plasma-processing gas from the same reactive gas source. Note that the source gas and plasma-processing gas can be fed in any prescribed manner. One example may suggest that the source gas is fed from only the first plasma-processing-gas feeder 46, while the plasma-processing gas, such as plasma excitation gas, is fed from only the second plasma-processing-gas feeder 47.

The holding stage 34 can hold the substrate W thereon with an electrostatic chuck (not shown). In addition, a temperature control mechanism (not shown) provided inside the holding stage 34 can keep the holding stage 34 at a desired temperature. As will be described later, if not using the electrostatic chuck mechanism for the holding stage 34, the difference between the stage temperature, or the temperature of the upper surface of the holding stage 34, and the actual surface temperature of the substrate W to be processed becomes pronounced. When the stage temperature, or the temperature of the upper surface of the holding stage 34, is 450°C, the surface temperature of the substrate W is approximately 375°C. The correlation between the stage temperature and the surface temperature of the substrate W is indicated on the horizontal axis in FIG. 14 as will be described later. The

holding stage 34 is supported by an insulative cylindrical support portion 51 extending vertically upwardly from beneath the bottom 41. The exhaust hole 43 is formed so as to penetrate through a part of the bottom 41 of the process chamber 32 along the circumference of the cylindrical support portion 51. The lower side of the ring-shaped exhaust hole 43 is connected to an exhaust apparatus (not shown) via an exhaust pipe (not shown). The exhaust apparatus has a vacuum pump, such as a turbo-molecular pump. The exhaust apparatus can reduce the pressure in the process chamber 32 to a predetermined pressure.

The plasma generation mechanism 39 includes a microwave generator 35 that is disposed outside the process chamber 32 and generates microwaves to excite plasma, a dielectric window 36 that is disposed so as to face the holding stage 34 and introduces the microwaves generated by the microwave generator 35 into the process chamber 32, a slot antenna plate 37 that is provided with a plurality of slots 40, is disposed on the upper side of the dielectric window 36 and radiates the microwaves to the dielectric window 36, and a dielectric member 38 that is disposed on the upper side of the slot antenna plate 37 and radially propagates the microwaves introduced by a coaxial waveguide 56, which will be described later.

The microwave generator 35 including a matching mechanism 53 is connected to an upper part of the microwave-introducing coaxial waveguide 56 through a mode converter 54 and a waveguide 55. For example, a microwave in TE mode generated by the microwave generator 35 passes through the waveguide 55, is converted into TEM mode by the mode converter 54, and propagates to the coaxial waveguide 56. A selected frequency of microwaves

generated by the microwave generator 35 is, for example, 2.45 GHz.

The dielectric window 36 is roughly in the shape of a disk and is made of a dielectric material. At a part of the bottom surface 48 of the dielectric window 36, provided is a ring-shaped recessed portion 57 that is recessed and tapered to facilitate the introduced microwaves to form standing waves. This recessed portion 57 enables efficient generation of plasma under the dielectric window 36 with the microwaves. As specific materials of the dielectric window 36, quartz and alumina can be cited.

The slot antenna plate 37 is a thin disk plate. The plurality of elongated slots 40 are divided into pairs, as shown in FIG. 3, spaced at a predetermined interval along the circumferential direction, the slots in each pair being orthogonal to each other like a folding fan.

A microwave generated by the microwave generator 35 passes through the coaxial waveguide 56, is propagated to the dielectric member 38, and radiates from the slots 40 formed in the slot antenna plate 37 to the dielectric window 36. The microwave having passed through the dielectric window 36 creates an electric field immediately under the dielectric window 36 and generates plasma in the process chamber 32. In short, the microwave plasma to be used in the plasma processing apparatus 31 is generated by a radial line slot antenna (RLSA) including the slot antenna plate 37 and dielectric member 38 configured as mentioned above.

FIG. 4 is a graph showing the relationship between the distances from the bottom surface 48 of the dielectric window 36 in the process chamber 32 and the electron temperatures of the plasma generated in the plasma processing apparatus 31. FIG. 5 is a graph showing the relationship between the

distances from the bottom surface 48 of the dielectric window 36 in the process chamber 32 and the electron densities of the plasma generated in the plasma processing apparatus 31.

Referring to FIGS. 4 and 5, the area immediately under the dielectric window 36, more specifically, the area 26, enclosed by a dashed dotted line, of approximately 10 mm from the dielectric window 36 is a so-called plasma generation area. In the area 26, the electron temperature is relatively high and the electron density is higher than $1 \times 10^{12} \text{ cm}^{-3}$. On the other hand, the area 27 beyond 10 mm enclosed by a dashed double-dotted line is referred to as a plasma diffusion area. In the vicinity of the stage in this area 27, the electron temperature is approximately 1.0 to 1.3 eV or lower than at least 1.5 eV and the electron density is approximately $1 \times 10^{12} \text{ cm}^{-3}$ or higher than at least $1 \times 10^{11} \text{ cm}^{-3}$. The plasma processing to a substrate W, which will be described later, takes place in the plasma diffusion area. Specifically, the plasma processing step is a plasma nitriding step using microwave plasma whose electron temperature is lower than 1.5 eV and whose electron density is higher than $1 \times 10^{11} \text{ cm}^{-3}$ in the vicinity of the surface of the substrate W.

Next, a method for fabricating a semiconductor device with an insulating film using the above-described plasma processing apparatus 31 will be described by referring to FIGS. 1 to 6 and Table 1. FIG. 6 is a flow chart showing principal process steps to form a film on a substrate W with the plasma processing apparatus shown in FIG. 2 and other drawings. Table 1 shows the process flow and process conditions. The temperature of the holding stage 34 during the aftermentioned plasma processing can be any temperature, but is selected from the range between, for example, 300°C and 450°C. The absence of

the electrostatic chuck causes a gap between the temperature of the holding stage 34 and the actual surface temperature of the substrate W, which should receive careful attention. Furthermore, the substrate used herein is a silicon wafer with a thickness of 300 mm.

5 [Table 1]

STEP	(A)	(B)	(C)	(D)
STEP	GAS ADSORPTION STEP	FIRST GAS EXCHANGE STEP	PLASMA NITRIDING STEP	SECOND GAS EXCHANGE STEP
PRESSURE (Torr)	5	5 >	5	5 >
Ar GAS FLOW RATE (sccm)	2000	2000	2000	2000
NH ₃ GAS FLOW RATE (sccm)	0	0	500	0
PRECURSOR FLOW RATE (sccm)	50	0	0	0
MICROWAVE OUTPUT (kW)	0	0	4	0

Referring to Table 1 and FIGS. 1 to 6, firstly, the substrate W is held on the holding stage 34 with the electrostatic chuck.

Then, adsorption gas is adsorbed on the substrate W (FIG. 6(A)). In this step, for example, the adsorption gas is supplied to the substrate W while the process chamber 32 is maintained at a pressure shown in Table 1. The adsorption gas is supplied through the plasma-processing-gas feeder 33. For the adsorption gas containing silicon atoms and chlorine atoms, an adsorption gas containing HCD (hexachlorodisilane), shown in Table 1, is used as a precursor.

Subsequently, the process goes to the first gas exchange step (B) in Table

1 to exhaust the process chamber 32 to remove excessively adsorbed adsorption gas (FIG. 6(B)). The exhaustion of the process chamber 32 is carried out through the exhaust hole 43, exhaust apparatus and some other components. Specifically, only Ar gas is supplied and the excess precursor is removed from
5 the process chamber 32.

After the exhaustion, the process goes to step (C) in Table 1 to perform plasma processing with microwaves (FIG. 6(C)). In this step, supplying microwaves through the plasma generation mechanism 39 and feeding ammonia gas and Ar gas into the process chamber 32 generate plasma that is
10 used to perform plasma nitriding on the adsorption layer on the substrate W. The temperature of the holding stage 34 in this step is set to 400°C.

After plasma processing is completed, the process goes to the second gas exchange step (D) in Table 1 to exhaust the process chamber 32 of residual ammonia gas and so on (FIG. 6(D)). Specifically, only the Ar gas is supplied
15 and the ammonia gas and the like are removed from the process chamber 32.

The series of steps (A) to (D) is repeated until the film obtains a desired thickness. Actual thickness is selected from, for example, 1 nm to 500 nm. Thus, the silicon nitride film for the substrate W is formed. After that, etching and other processes are repeatedly performed on a desired part of the substrate
20 W to fabricate a semiconductor device as shown in FIG. 1. The above-described process is referred to as PE-ALD process using an RLSA. In a PE-ALD cycle, that is, the series of steps (A) to (D), a SiN film subjected to the PE-ALD process using the RLSA grows from approximately 0.5 angstrom (Å) to 1.0 angstrom. The resultant SiN film has film uniformity of ±3% or less. The PE-ALD process
25 using the RLSA offers good coverage.

In the gas adsorption step, as shown in FIG. 17, a small volume region can be formed above a holding stage 134, more specifically, on a substrate W held on the holding stage 134 to perform the gas adsorption step in the small volume region. Prepared to form the small volume region is a gas feeding
5 mechanism 161 including a head 162 that is, for example, large enough to cover the substrate W, can be placed above the holding stage 134, and can supply adsorption gas onto the substrate W. In a gas feeding step, the head 162 is moved above the holding stage 134 with a substrate W mounted thereon to form a region smaller in volume than the entire process chamber 132. Then,
10 adsorption gas is fed to the region formed between the holding stage 134 and head 162 at a pressure shown in step (A) in Table 1.

For reference sake, the configuration of the plasma processing apparatus shown in FIG. 17 will be briefly described as follows. The plasma processing apparatus 131 includes a process chamber 132 in which a substrate W is
15 subjected to plasma processing, a plasma-processing-gas feeder 133 that feeds reactive gas for plasma processing into the process chamber 132, a disk-like holding stage 134 on which the substrate W is held, a plasma generation mechanism 139 that generates plasma in the process chamber 132, and a controller (not shown) that controls the whole plasma processing apparatus 131.
20 The controller controls the whole plasma processing apparatus 131, including the gas flow rate of the plasma-processing-gas feeder 133, pressure in the process chamber 132 and so on.

The process chamber 132 includes a bottom 141 positioned beneath the holding stage 134 and a sidewall 142 extending upwardly from the outer edge of
25 the bottom 141. The sidewall 142 is roughly in the shape of a cylinder except

for one part. An exhaust hole 143 for discharging gas is formed in the bottom 141 of the process chamber 132 so as to penetrate a part of the bottom 141. An upper part of the process chamber 132 is open, but is designed to be sealed by a cover 144, which is disposed on the upper side of the process chamber 132, a dielectric window 136, which will be described later, and an O-ring 145, which serves as a sealing member and is interposed between the dielectric window 136 and cover 144.

The plasma-processing-gas feeder 133 includes a plurality of plasma-processing-gas feeding holes 146 at a part on the upper side of the sidewall 142 to feed the plasma-processing gas into the process chamber 132. The plasma-processing-gas feeding holes 146 are evenly spaced in the circumferential direction. The plasma-processing-gas feeder 133 is supplied with plasma-processing gas from a reactive gas source (not shown).

The holding stage 134 can hold the substrate W thereon with an electrostatic chuck (not shown). In addition, a temperature control mechanism (not shown) provided inside the holding stage 134 can keep the holding stage 134 at a desired temperature. The holding stage 134 is supported by an insulative cylindrical support portion 149 extending vertically upwardly from beneath the bottom 141. The exhaust hole 143 is formed so as to penetrate through a part of the bottom 141 of the process chamber 132 along the circumference of the cylindrical support portion 149. The lower side of the ring-shaped exhaust hole 143 is connected to an exhaust apparatus (not shown) via an exhaust pipe (not shown). The exhaust apparatus has a vacuum pump, such as a turbo-molecular pump. The exhaust apparatus can reduce the pressure in the process chamber 132 to a predetermined pressure.

The plasma generation mechanism 139 includes a microwave generator 135 that is disposed outside the process chamber 132 and generates microwaves to excite plasma, a dielectric window 136 that is disposed so as to face the holding stage 134 and introduces the microwaves generated by the microwave generator 135 into the process chamber 132, a slot antenna plate 137 that is provided with a plurality of slots 140, is disposed on the upper side of the dielectric window 136 and radiates the microwaves to the dielectric window 136, and a dielectric member 138 that is disposed on the upper side of the slot antenna plate 137 and radially propagates the microwaves introduced by a coaxial waveguide 154, which will be described later.

The microwave generator 135 including a matching mechanism 151 is connected to an upper part of the microwave-introducing coaxial waveguide 154 through a mode converter 152 and a waveguide 153. For example, a microwave in TE mode generated by the microwave generator 135 passes through the waveguide 153, is converted into TEM mode by the mode converter 152, and propagates to the coaxial waveguide 154. A selected frequency of microwaves generated by the microwave generator 135 is, for example, 2.45 GHz.

The dielectric window 136 is roughly in the shape of a disk and is made of a dielectric material. As specific materials of the dielectric window 136, quartz and alumina can be cited. In addition, the lower surface 148 of the dielectric window 136 is flat.

The slot antenna plate 137 is a thin disk plate. The plurality of elongated slots 140 are configured in the same manner as those of the slot antenna plate 37 in FIG. 3.

A microwave generated by the microwave generator 135 passes through

the coaxial waveguide 154, is propagated to the dielectric member 138, and radiates from the slots 140 formed in the slot antenna plate 137 to the dielectric window 136. The microwave having passed through the dielectric window 136 creates an electric field immediately under the dielectric window 136 and generates plasma in the process chamber 132. In short, the microwave plasma to be used in the plasma processing apparatus 131 is generated by a radial line slot antenna (RLSA) including the slot antenna plate 137 and dielectric member 138 configured as mentioned above.

The plasma processing apparatus 131 includes a gas feeding mechanism 161. The gas feeding mechanism 161 includes a head 162 that can move between a first position above the holding stage 134 and a second position different in position from the first position and can feed adsorption gas, a support portion 163 that extends from a side of the sidewall 142 of the process chamber 132 and supports the head 162 with an inner end 164, which is an inner portion of the support portion 163, coupled with the head 162. When the head 162 is in the first position, the gas feeding mechanism 161 feeds adsorption gas to a small volume region defined by the head 162 and holding stage 134 to adsorb the adsorption gas on the substrate W. The first and second positions will be described later. The small volume region denotes a region defined by the head 162 and holding stage 134 and being smaller in volume as compared with the process chamber 132, which has a large volume.

Next, the configuration of the head 162 in the gas feeding mechanism 161 will be described in detail. The head 162 includes a thin disk portion 166 and a ring-shaped extending portion 167 extending in the through-thickness direction from the outer rim of the disk portion 166. Specifically, the extending

portion 167 is roughly in the shape of a cylinder and extends downwardly. The disk portion 166 is larger than the substrate W. The above-mentioned first position denotes a position in which the disk portion 166 covers the upper side of the holding stage 134. At the first position, the upper surface 147 of the outer rim of the holding stage 134 faces the lower surface 170 of the extending portion 167.

The head 162 includes gas feeding holes 168 that supply adsorption gas. When the head 162 is in the first position, more specifically, is positioned above the holding stage 134, the gas feeding holes 168 are positioned to face the substrate W held on the holding stage 34. The plurality of gas feeding holes 168 are provided to partially open a surface on the lower side of the disk portion 166 of the head 162. The gas feeding holes 168 are approximately evenly spaced in rows and columns at a predetermined interval as viewed from the through-thickness direction.

In the interior of the head 162 and support portion 163 provided is a gas feeding path 169 having one end connecting to the gas feeding holes 168 and the other end connecting to a gas feeding unit (not shown) that is provided outside the process chamber 132 and feeds the adsorption gas. Through the gas feeding path 169 and gas feeding holes 168, adsorption gas can be supplied from the outside of the process chamber 132 to the substrate W.

The process chamber 132 in the plasma processing apparatus 131 is provided with a storage portion 171 that is formed as if a part of the sidewall 142 is stretched outwardly and stores the head 162. The storage portion 171 is formed so as to straightly extend outwardly from a part of the sidewall 142. The inner area of the storage portion 171 is the second position, in the plasma

processing apparatus 131, to which the head 162 can move.

As described above, the head 162 can move between the first position above the holding stage 134 and the second position inside the storage portion 171. In other words, the head 162 can move in the direction of Arrow A₁ in FIG. 17 and opposite to the direction.

In addition, the plasma processing apparatus 131 is provided with a shielding plate 172 that serves as a blockage mechanism blocking the area inside the storage portion 171 from the area outside the storage portion 171, or the area in the process chamber 132. The shielding plate 172 can move along the inner sidewall 173 of the sidewall 142 in the direction of Arrow A₂ in FIG. 17 and opposite to that direction.

Now, pressure adjustment for the thus configured plasma processing apparatus 131 will be described. FIG. 7 is a graph showing the relationship between the gas flow rates in the entire process chamber and time required to reach a predetermined pressure value. FIG. 8 is a graph showing the relationship between the gas flow rates in the small volume region defined by the holding stage 134 and head 162 and time required to reach a predetermined pressure value. In FIGS. 7 and 8, the vertical axis represents time (seconds), while the horizontal axis represents the gas flow rates (sccm). The gas flow rate is expressed in terms of Ar (argon) gas. The graphs shown in FIGS. 7 and 8 are obtained when pressure rises from 1 Torr to 3 Torr. In the case of FIG. 7, the volume of the entire process chamber 132 is approximately 54 liters. In the case of FIG. 8, the volume of the small volume region defined by the holding stage 134 and head 162 is approximately 0.75 liters.

Referring to FIGS. 7 and 8, it is found that the pressure in the small

volume region in FIG. 8 reaches 3 Torr quite quicker at any gas flow rate. Such a mechanism, therefore, can significantly enhance the throughput. In addition, because the inner wall of the process chamber is not exposed to the adsorption gas, a cleaning step for the inner wall can be omitted or reduced in number or in
5 time, and furthermore, particle problems caused by reaction products of the adsorption gas adhered to the inner wall of the process chamber can be alleviated. During plasma processing, it is preferable for the head 162 to retract to a position other than the position above the holding stage 134 for efficient plasma processing.

10 In addition, it is preferable to set the pressure in the process chamber during the plasma nitriding step to 1 Torr or more. Specifically, the pressure in the process chamber is set to, for example, approximately 5 Torr. This enables high-quality film formation.

The film formation method has effective applicability to form a liner film
15 in a device isolating region (STI: Shallow Trench Isolation) formed in semiconductor devices. FIG. 9 is an enlarged cross-sectional view showing the vicinity of a device isolating region.

Referring to FIG. 9, the device isolating region 81 is a trench filled with an insulative material. The trench is recessed downwardly from a main
20 surface of the silicon substrate 82.

The process for forming the device isolating region 81 includes forming a trench 84 recessed downwardly from a predetermined position of a main surface 83 of the silicon substrate 82 and filling the trench 84 with a material having insulation properties. The device isolating region 81 is formed in that manner.

25 For the purpose of enhancing the insulating performance at the interface,

more specifically, at the boundary surface between the silicon substrate 82 and the insulator filled in the trench 84, an insulative silicon nitride layer, called a liner film 86, is formed on the surface 85 of the trench 84. An insulative buried layer 87 is then formed so as to fill the trench 84. The present invention is effective for formation of such a liner film 86 that is required to have high insulating performance and excellent step coverage.

FIG. 10 is an enlarged picture, taken by a scanning electron microscope (SEM), of a cross section of a silicon nitride film (process temperature: surface temperature of the substrate W is approximately 350°C) subjected to PE-ALD with an RLSA and applied as a sidewall protective film in a trench structure, where the trench width is approximately 100 nm and the aspect ratio is approximately 6. FIG. 11 is an enlarged picture, taken by the scanning electron microscope (SEM), of a cross section of the silicon nitride film subjected to PE-ALD with the RLSA in FIG. 10 and soaked in a 0.5% HF (hydrofluoric acid) solution (50%HF:water = 1:100) for 7 minutes, where the aspect ratio is approximately 6 times.

FIG. 10 shows that when the aspect ratio is approximately 6, the silicon nitride film with excellent step coverage is formed in the trench up to the deepest part thereof as a liner film. FIG. 11 shows that even the silicon nitride film deposited on the sidewall inside the trench is not inferior in resistance to the HF solution in comparison with the silicon nitride film deposited on the upper part of the trench.

FIG. 12 shows the nitriding pressures applied to perform PE-ALD with the RLSA to form a silicon nitride film and the resistance to hydrofluoric acid (HF) of the SiN film subjected to nitriding under various conditions. The

hydrofluoric-acid resistance is presented on the vertical axis by values of the etch rates of the SiN film in the hydrofluoric-acid solution normalized to the etch rates of a thermal oxide film in the hydrofluoric-acid solution, namely with an index indicating how many times the etch rate of the SiN film is higher or lower than the etch rate of the thermal oxide film. The horizontal axis indicates nitriding pressures (Torr), more specifically, pressures in the process chamber during plasma nitriding. FIG. 13 also shows the correlation between the nitriding time per 1 ALD cycle consumed for PE-ALD with the RLSA to form a silicon nitride film and the resistance to hydrofluoric-acid at the nitriding time.

The vertical axis indicates hydrofluoric-acid resistance by values of the etch rates of the SiN film in the hydrofluoric-acid solution normalized to the etch rates of a thermal oxide film in the hydrofluoric-acid solution, namely with an index indicating how many times the etch rate of the silicon nitride film is higher or lower than the etch rate of the thermal oxide film, while the horizontal axis indicates the nitriding time (seconds). FIG. 13 shows the results when the films are subjected to nitriding process at a fixed process pressure of 5 Torr. FIG. 14 is a graph showing the resistance to hydrofluoric-acid (etch rate) of the silicon nitride film formed (nitrided) by PE-ALD with the RLSA with stage temperatures (and the corresponding actual surface temperatures of the substrate) varied. The vertical axis indicates hydrofluoric-acid resistance by values of the etch rates of the SiN film in the hydrofluoric-acid solution normalized to the etch rates of a thermal oxide film in the hydrofluoric-acid solution, namely with an index indicating how many times the etch rate of the silicon nitride film is higher or lower than the etch rate of the thermal oxide film, while the horizontal axis indicates the stage temperatures (Stage Temp), namely

the temperatures (°C) of the upper surface of the holding stage 34. The horizontal axis also indicates the surface temperatures of the substrate ("Actual wafer Temp" shown in FIG. 14) in correspondence with the stage temperatures. The samples shown in FIG. 14 are subjected to the process at a pressure of 5 Torr, with microwave power of 4 kW and at various stage temperatures.

The legend "3 kW (315°C) 30 sec" in FIG. 12 denotes process conditions for the samples, i.e., "microwave power: 3 kW, surface temperature of substrate: 315°C, nitriding time: 30 seconds". The black diamonds in FIG. 12 indicate samples obtained under the process conditions "microwave power: 3 kW, surface temperature of substrate: 315°C, nitriding time: 30 seconds", the black square in FIG. 12 indicates a sample obtained under the process conditions "microwave power: 3 kW, surface temperature of substrate: 315°C, nitriding time: 60 seconds", and the black circles in FIG. 12 indicate samples obtained under the process conditions "microwave power: 4 kW, surface temperature of substrate: 350°C, nitriding time: 60 seconds". The white triangle in FIG. 13 indicates a sample obtained under the process conditions "microwave power: 3 kW, surface temperature of substrate: 200°C", the black triangles in FIG. 13 indicate samples obtained under the process conditions "microwave power: 3 kW, surface temperature of substrate: 315°C", the black diamonds in FIG. 13 indicate samples obtained under the process conditions "microwave power: 4 kW, surface temperature of substrate: 350°C", and the black squares in FIG. 13 indicate samples obtained under the process conditions "microwave power: 4 kW, surface temperature of substrate: 375°C". The black squares in FIG. 14 indicate samples obtained under the process conditions "nitriding time: 20 seconds (Nitridation 20 sec)", and the black circles in FIG. 14 indicate samples obtained

under the process conditions “nitriding time: 60 seconds (Nitriding 60 sec)”.

In FIG. 12 and the other drawings, as an index to measure the quality of the SiN film, the etch rate of the SiN film in the hydrofluoric-acid solution is used since the etch rate is highly correlated to the film density. To represent
5 how low the etch rates of the SiN films in the hydrofluoric-acid solution are, the values are normalized to an etch rate of a thermal oxide film in the hydrofluoric-acid solution. The index used herein indicates how many times the etch rate of the silicon nitride film is higher or lower than the etch rate of the thermal oxide film. For purpose of reference, the etch rate of the SiN film
10 formed by LP-CVD at a high temperature of 700°C or higher is approximately 0.2 times that of the thermal silicon oxide film (Thermal-SiO₂) in the hydrofluoric-acid solution.

In this description, the quality of the SiN film formed by LP-CVD at a high temperature of 700°C or higher is set as a standard of the film quality of
15 SiN films, and the etch rate, exhibiting a strong correlation with film density, of the SiN film in the hydrofluoric-acid solution is used as an evaluation criterion of the film quality. In addition to those, the quality of the SiN film can be determined based on the residual stress of the film and the microscopic planarity of the surface. There are also indices to determine the merits of dry
20 etching characteristics and electric characteristics of the SiN film. The reason why the etch rate of the SiN film in the hydrofluoric-acid solution is chosen as the film evaluation criterion is that the etch rate of the SiN film in the hydrofluoric-acid solution is the most closely connected to a measure of the density of the SiN film. Also, the past studies prove that the SiN film with
25 excellent chemical resistance is in general good at the above-mentioned

properties, i.e., the residual stress, microscopic surface planarity and electrical insulation. In this description, the focus falls on only the low etch rate of the SiN film in the hydrofluoric-acid solution, but not on approaches to improve etch resistance to the hydrofluoric-acid solution, for example, by intentionally adding
5 carbon or other ingredients in the SiN film. This is because, even if the hydrofluoric-acid resistance is improved by intentionally adding carbon or other ingredients in the film, this approach is considered to degrade electrical insulation performance.

FIG. 12 shows that the pressure applied during nitriding process is
10 correlated with the quality of the silicon nitride film to be formed. For example, the samples formed under the process conditions "microwave power: 4 kW, surface temperature of substrate: 350°C, nitriding time: 60 seconds" exhibit etch rates, in the form of normalized values, of 1.5 at 1 Torr, 0.7 at 2 Torr, and 0.21 at 3 Torr. It is found that the samples formed at a pressure up to approximately 8
15 Torr have etch rates as low as the sample formed at 3 Torr. This shows that a good range of nitriding pressure is from 1 Torr to 8 Torr, and more preferably, from 3 Torr to 7 Torr. It looks like there is no problematic significant changes in quality of the nitride film formed at 8 Torr or higher in FIG. 12; however, the lower the pressure during nitriding is, the more advantageously the source gas
20 filled in the process chamber can be exchanged, from the viewpoint of the purge efficiency in the ALD sequence. In addition, nitriding at a pressure of 8 Torr or higher tends to cause degradation of the quality of the nitride film even to some degree.

It is considered that the amount of radical formation on the substrate W
25 varies depending on the difference in pressure in the plasma nitriding step. As

shown in Table 1, in the case where NH_3/Ar mixture gas is used in the plasma nitriding process, the film formed at 1 Torr is different in quality from the film formed at 5 Torr. Specifically, the wet etch rate of the film formed at 1 Torr is 0.57; while the wet etch rate of the film formed at 5 Torr is 0.48. This difference
5 is possibly caused by the following factors.

When pressure is low, plasma is generated in an area away from the dielectric window, but close to the substrate W in the process chamber. Accordingly, the irradiation energy of ion to the substrate W increases in the plasma nitriding process. As a result, more damage may occur during the film
10 forming process. On the contrary, when pressure is high, plasma is generated in an area closed to the dielectric window, but away from the substrate W in the process chamber. This decreases the irradiation energy of ion to the substrate W in the plasma nitriding process.

As seen from FIG. 13, the normalized values of the etch rates tend to be
15 lower (better) with increase in length of nitriding time for the silicon nitride film. The etch rate is also strongly correlated with the microwave power supplied during the nitriding process and the surface temperature of the substrate W. The greater the microwave input power (microwave power) is (see FIG. 13) or the higher the surface temperature of the substrate W is (see FIG. 14), the lower
20 (better) the etch rate tends to be. With the combination of them, the nitriding process time can be reduced. At the least, a 20-second or 40-second nitriding time per 1 ALD cycle is not necessary.

FIG. 15 is a graph showing the correlation between the nitriding atmosphere states in which a silicon nitride film is subjected to PE-ALD with an
25 RLSA, more specifically, the flow rates of ammonia gas in argon-ammonia

mixture gas and hydrofluoric-acid characteristics. The vertical axis indicates hydrofluoric-acid resistance by values of the etch rates of the SiN film in the hydrofluoric-acid solution normalized to the etch rates of a thermal oxide film in the hydrofluoric-acid solution, namely with an index indicating how many times the etch rate of the silicon nitride film is higher or lower than the etch rate of the thermal oxide film, while the horizontal axis indicates the flow rates of the ammonia gas (sccm). Note that the flow rate of Ar gas is 2000 (sccm). That is, ammonia gas flows at a predetermined rate with 2000 sccm of Ar gas flow. FIG. 15 shows that, as to ammonia gas atmosphere during nitriding process, it is preferable to flow approximately 10% or more ammonia gas with respect to Argon (Ar) gas, which is a diluent gas, and it is more preferable to flow 20% or more ammonia gas with respect to Ar gas.

In summary, it is demonstrated that the silicon nitride film subjected to PE-ALD with an RLSA on the substrate W with a surface temperature of 400°C or lower exhibits the same level of hydrofluoric-acid resistance as the SiN film subjected to LP-CVD at 700°C or higher. FIG. 16 is a graph showing the correlation between the process temperatures at which the SiN films are formed by the various methods, or nitriding temperatures, and the resistance to hydrofluoric-acid. The vertical axis indicates the SiN film characteristics against the hydrofluoric-acid (normalized etch rate values), or values of the etch rates of the SiN film in the hydrofluoric-acid solution normalized to the etch rates of a thermal oxide film in the hydrofluoric-acid solution, namely the hydrofluoric-acid resistance with an index indicating how many times the etch rate of the silicon nitride film is higher or lower than the etch rate of the thermal oxide film, while the horizontal axis indicates the nitriding temperatures (°C),

which are the surface temperatures of the substrate. The various methods shown in FIG. 16 will be described: black triangles indicate SiN films formed by RLSA-ALD of the present invention; a white triangle indicates a SiN film formed by RLSA-CVD; black squares indicate SiN films formed by conventional ALD (Conventional ALD-SiN); and a black diamond indicates a SiN film formed by LP-CVD. FIG. 16 shows that desirably higher-quality films obtained in the semiconductor device fabrication, in other words, films formed at a lower temperature and a lower etch rate are plotted at a lower and a more left side of the graph. It is apparent that the silicon nitride film according to the present invention is plotted at a lower and more left side than the other films formed through the other methods. Noble gases other than Ar are also suitable as the diluent gas.

In the embodiment, the holding stage can be configured to move in at least one of either the vertical or horizontal direction. The movement allows executing the gas adsorption step in a more efficient way. For example, the holding stage is controlled to move upwardly in the gas adsorption step to make the volume of the upper area of the holding stage small, thereby reducing the amount of the adsorption gas to be supplied and shorten the time required for pressure adjustment. In this manner, the gas adsorption step can be executed efficiently. In the plasma processing step, the holding stage is controlled to move downwardly to the plasma diffusion area where the plasma processing is performed.

Suppose a plasma processing apparatus includes a gas feeding mechanism with the above-described head, it is possible to keep generating microwave plasma all the time. In this case, in the gas adsorption step, the

head is located in the area on the upper side of the holding stage to perform gas adsorption. In the plasma processing step, the head can be retracted from the area on the upper side of the holding stage to perform plasma processing on the substrate W located in the plasma diffusion area. As a result, further
5 improvement of throughput can be achieved.

In the embodiment, the exhaustion step between the gas adsorption step and plasma processing step and the exhaustion step following the plasma processing step can be omitted if necessary.

The plasma processing apparatus including a gas feeding mechanism
10 with the above-described head can also be configured to include a gas exhaust mechanism that discharges the adsorption gas supplied by the gas feeding mechanism. In this case, the head may include a part of the gas exhaust mechanism. The gas exhaust hole included in the gas exhaust mechanism is formed preferably in an area on the radially inner side relative to the extending
15 portion rather than on the lower side of the extending portion.

This configuration will be described with drawings. FIG. 18 is a schematic sectional view showing a part of the plasma processing apparatus including a gas exhaust mechanism with a gas exhaust hole formed in the extending portion of a head. FIG. 19 depicts a substrate W, viewed from above,
20 held on the holding stage in the plasma process chamber shown in FIG. 18 and arrows indicating the directions film-forming gas flows. The plasma processing apparatus in FIG. 18 and aftermentioned FIG. 20 is the same in configuration as the plasma processing apparatus in FIG. 17 except for the structure of the head and gas exhaust mechanism, and the same configuration will not be
25 reiterated. The cross sections shown in FIGS. 18 and 20 correspond to a part of

the cross section shown in FIG. 17.

Referring to FIGS. 18 and 19, the plasma processing apparatus 181 includes a gas feeding mechanism and a gas exhaust mechanism. The gas feeding mechanism includes a head 182 that can move between a first position
5 above the holding stage 183 and a second position different in position from the first position and can feed adsorption gas and a support portion 184 that extends from a side of the sidewall of the process chamber and supports the head 182 with an inner end, which is an inner portion of the support portion 184, coupled with the head 182. When the head 182 is moved to the first position, the gas
10 feeding mechanism feeds adsorption gas to a small volume region defined by the head 182 and holding stage 183 to adsorb the adsorption gas on the substrate W. The gas exhaust mechanism discharges the adsorption gas and so on supplied from the gas feeding mechanism.

The head 182 includes a thin disk portion 185 and a ring-shaped
15 extending portion 186 extending in the through-thickness direction from the outer rim of the disk portion 185. The head 182 includes gas feeding holes 187 that are formed so as to face the substrate W held on the holding stage 183 when the head 182 is in the first position and supplies adsorption gas. The plurality of gas feeding holes 187 are provided to partially open a surface on the lower
20 side of the head 182. The gas feeding holes 187 are approximately evenly spaced in rows and columns at a predetermined interval as viewed from the through-thickness direction.

In the interior of the head 182 and support portion 184 provided is a gas feeding path 188 having one end connecting to the gas feeding hole 187 and the
25 other end connecting to a gas feeding unit (not shown) that is placed outside the

process chamber and supplies adsorption gas. Through the gas feeding path 188 and gas feeding holes 187, adsorption gas can be supplied to the substrate W from the outside of the process chamber.

5 The gas exhaust mechanism has a gas exhaust hole that discharges excess adsorption gas from the adsorption gas fed from the gas feeding mechanism. The gas exhaust hole 189 is formed so as to open a part of a lower surface of the extending portion 186, in other words, a surface facing the holding stage 183. The gas exhaust hole 189 may be a ring-shaped hole or a group of holes spaced at predetermined intervals. In the interior of the head 182 and support portion 184 provided is a gas exhaust path 190 having one end 10 connecting to the gas exhaust hole 189 and the other end connecting to a gas exhaust unit (not shown) that is provided outside the process chamber 183 and discharges excess adsorption gas and so on. Through the gas exhaust path 190 and gas exhaust hole 189, the adsorption gas can be discharged from the small 15 volume region defined by the head 182.

However, this configuration may permit excess gas in the adsorption gas supplied from the gas feeding hole 187, in other words, adsorption gas that is not chemisorbed on the surface of the substrate W to flow toward the circumference of the substrate W. The flows go toward the circumference in the immediately 20 lateral direction in an area immediately under the extending portion 186, more specifically, in an area between the extending portion 186 and holding stage 183. As shown in FIG. 19, the adsorption gas flows in the direction indicated by arrows as viewed from above the substrate W. If the adsorption gas flowing in an area immediately under the extending portion 186 in the immediately lateral 25 direction is not discharged through the gas exhaust hole 189 formed in the lower

surface of the extending portion 186 and spreads outside the head 182 or spreads out in the process chamber, the adsorption gas may react with plasma generated in the process chamber, causing generation of particles and adhesion of reaction products to the sidewall of the process chamber.

5 To solve the problem, the gas exhaust mechanism provided in the head 192 can have its gas exhaust hole 193 more inside than the extending portion 194 as shown in the plasma processing apparatus 191 in FIG. 20,. FIG. 20 is a schematic sectional view showing a part of the plasma processing apparatus 191 including a gas exhaust mechanism with a gas exhaust hole 193 formed more
10 inside than the extending portion 194 of the head 192. FIG. 21 depicts a substrate W, viewed from above, held on a holding stage 195 in the plasma process chamber 191 shown in FIG. 20 and arrows indicating the directions film-forming gas flows. Referring to FIG. 20, the plasma processing apparatus 191 includes a gas feeding mechanism provided with a head 192 and support
15 portion 196 and a gas exhaust mechanism. The gas exhaust mechanism has a gas exhaust hole 193 that discharges excess adsorption gas supplied from the gas feeding mechanism. The gas exhaust hole 193 is formed to open a part of a lower side of a disk portion 197 of the head 192 at a position more inside than the extending portion 194. In the interior of the head 192 and support portion
20 196 provided is a gas exhaust path 198 having one end connecting to the gas exhaust hole 193 and the other end connecting to a gas exhaust unit (not shown) that is provided outside the process chamber and discharges excess adsorption gas and so on. Through the gas exhaust path 198 and gas exhaust hole 193, the adsorption gas is exhausted from a small volume region defined by the head 192.

25 This configuration allows excess gas in the adsorption gas supplied from

the gas feeding holes 199, in other words, adsorption gas that is not chemisorbed on the surface of the substrate W to flow toward the inner radius of the substrate W. Accordingly, the excess gas flows toward the inner radius in the immediately lateral direction even in an area immediately under the extending
5 portion 194 as indicated by the arrows in FIG. 21. This can reduce the possibility for the adsorption gas to spread outside the head 192 and spreads out in the process chamber, thereby reducing generation of particles caused by the excess adsorption gas in the process chamber and adhesion of reaction products onto the sidewall of the process chamber.

10 In the above embodiment, a silicon nitride film is formed by feeding HCD (hexachlorodisilane) as adsorption gas and performing plasma processing on an adsorption layer; however, the present invention is not limited thereto and can be applied to the formation of metal nitride film with materials other than silicon, for example, titanium, tantalum, ruthenium and aluminum.
15 Specifically, the present invention can be applied to nitride film formation by which a gas containing a nitride, for example, N₂ gas and hydrogen is fed into the process chamber to perform plasma processing subsequent to the above-described gas adsorption step.

In addition, a gas containing hexachlorodisilane (Si₂Cl₆) is used as
20 adsorption gas in the above-described embodiment; however, there is of course no problem to use other gases containing dichlorosilane (SiH₂Cl₂) or other kinds of silicon halide. It is also possible to use gases other than ammonia gas in the plasma processing. It is known that nitriding reaction suggested by the present invention can be made effectively with NH radicals or N radicals and
25 the RLSA plasma using microwaves can effectively generate the great number of

NH radicals and N radicals. To obtain radical species contributing to nitriding, pressure ranging from 1 Torr to 8 Torr is effective (see FIG. 12).

The above embodiment presented a liner film formed on the surface of a trench, which is formed in a device isolating region, before filling the trench with an insulative buried film; however, the present invention is not limited thereto and can be applied to the formation of, for example, a gate oxide film and other insulating layers, such as an interlayer insulating film and gate sidewall, in a MOS transistor. The present invention is also suitable for various nitride film structures used to fabricate semiconductor devices with Fin-structure 3D gates and of course has advantageous applicability to CCDs, LSIs and so on. In summary, the present invention can be applied to all film formation processes including the combination of a gas adsorption step in which adsorption gas is fed on a substrate to form an adsorption layer and a plasma processing step using microwave plasma.

The substrate to be processed can be in any forms, for example, a rectangle substrate and flexible film, in addition to the disk wafer, and can be made of any materials including silicon carbide (SiC), glass and resin in addition to silicon.

In a modification of the embodiment, an oxynitride film can be formed by adding oxidized gas during the plasma processing step. For example, HCD (hexachlorodisilane) is used as an adsorption gas and oxygen gas is added in addition to ammonia gas during the plasma processing, resulting in a SiON film. In this case, setting the flow rate of the oxygen gas to 1% or less relative to the total gas can suppress the formation of the oxide film and consequently form an excellent oxynitride film.

In addition, the plasma processing step can be divided into two steps: a step of subjecting the adsorption gas adsorbed on the substrate to plasma oxidization to form an oxide film; and a step of introducing nitrogen to the formed oxide film by a plasma nitriding method, thereby forming an oxynitride
5 film.

Specific films will be listed below: insulating films containing N (nitrogen) atoms, such as SiN, AlN, HfN, ZrN, TaN and LaN; mixture films thereof; and oxynitride films thereof. There are a wide variety of devices and processes to which the present invention can be applied, for example, an
10 insulating film material of a trench capacitor in DRAM (Dynamic Random Access Memory), an nitride liner film heavily used to fabricate 3D device structures such as Fin FET (Field Effect Transistor), a nano laminate in MEMS (Micro Electro Mechanical Systems), a UV block layer, an alumina insulating film in organic EL (Electro Luminescence) device, an optical device, a solar cell,
15 a metal nitride film for a piezo-electric element and so on.

Although the silicon nitride film is formed and subjected to plasma processing in the same process chamber in the above embodiment, the present invention is not limited thereto and the step of forming the silicon nitride film and the plasma processing step can be executed in different process chambers.

20 In the plasma processing step, the plasma processing can be executed plural times (for example, twice).

Although the plasma processing in the above embodiment uses microwaves generated by RLSA with a slot antenna plate, the present invention is not limited thereto and can employ a microwave plasma processing apparatus
25 with a comb-shaped antenna and a microwave plasma processing apparatus

emitting microwaves from a slot to generate surface-wave plasma. In addition to the plasma processing apparatus utilizing microwaves, any plasma processing apparatuses capable of generating plasma of high densities and at low electron temperatures can be used in the present invention.

5 The plasma processing in the embodiment is executed with microwave plasma whose electron temperature is lower than 1.5 eV and whose electron density is higher than $1 \times 10^{11} \text{ cm}^{-3}$; however, the present invention is not limited thereto and can be utilized in the case where the plasma electron density is in a range lower than $1 \times 10^{11} \text{ cm}^{-3}$.

10 Although the substrate is processed on a one-by-one basis in the process apparatus in the present invention, it is possible to process a plurality of substrates at once.

 The above embodiment describes formation of an insulating film, such as a silicon nitride film; however, the present invention is not limited thereto and
15 can be applied to formation of conductive films. In addition, the process herein can be used to form nitride films used as sealing films.

 The foregoing has described the embodiment of the present invention by referring to the drawings. However, the invention should not be limited to the illustrated embodiment. It should be appreciated that various modifications
20 and changes can be made to the illustrated embodiment within the scope of the appended claims and their equivalents.

Industrial Applicability

 The film formation method, semiconductor-device fabrication method, insulating film and semiconductor device according to the present invention can
25 be advantageously used to meet demands for high chemical resistance

(hydrofluoric-acid resistance) and excellent step coverage.

Reference Signs List

11: MOS device; 12, 79, 82: silicon substrate; 13, 81: device isolating region; 14a: p-type well, 14b: n-type well; 15a: heavily-doped n-type impurity
5 diffused region; 15b: heavily-doped p-type impurity diffused region; 16a: n-type impurity diffused region; 16b: p-type impurity diffused region; 17, 78: gate oxide film; 18: gate electrode; 19: gate sidewall; 21: insulating film; 22: contact hole; 23: plugging electrode; 24: metal wiring layer; 26, 27: area; 31, 131, 181, 191: plasma processing apparatus; 32, 132: process chamber; 33, 46, 47, 133: gas
10 feeder; 34, 134, 183, 195: holding stage; 35, 135: microwave generator; 36, 136: dielectric window; 37, 137: slot antenna plate; 38, 138: dielectric member; 39, 139: plasma generation mechanism; 40, 140: slot; 41, 141: bottom; 42, 142: sidewall; 43, 143: exhaust hole; 44, 144: cover; 45, 145: O-ring; 48, 148, 170: bottom surface; 49: gas feeding system; 50, 146, 168, 187, 199: gas feeding hole;
15 51, 149: cylindrical support portion; 53, 151: matching mechanism; 54, 152: mode converter; 55, 153: waveguide; 56, 154: coaxial waveguide; 57: recessed portion; 83: main surface; 84: trench; 85: surface; 86: liner film; 87: buried layer; 147: upper surface; 161: gas feeding mechanism; 162, 182, 192: head; 163, 184, 196: support portion; 164: end; 166, 185, 197: disk portion; 167, 186, 194:
20 extending portion; 169, 188: gas feeding path; 171: storage portion; 172: shielding plate; 173: inner sidewall; 189, 193: gas exhaust hole; 190, 198: gas exhaust path.

CLAIMS

- [1] A film formation method for forming a film on a substrate comprising the steps of:
- adsorbing source gas on the substrate to form an adsorption layer of the source gas on the substrate; and
- performing a plasma nitriding process on the formed adsorption layer with microwave plasma after the gas adsorption step.
- [2] The film formation method according to claim 1 being a method for forming an insulating film.
- [3] The film formation method according to claim 1, wherein the gas adsorption step includes the step of adsorbing source gas containing chlorine atoms on the substrate.
- [4] The film formation method according to claim 3, wherein the gas adsorption step includes the step of supplying source gas containing at least one of either hexachlorodisilane (Si_2Cl_6) or dichlorosilane (SiH_2Cl_2) onto the substrate.
- [5] The film formation method according to claim 1, wherein the plasma processing step is executed at a pressure from 1 Torr to 8 Torr.
- [6] The film formation method according to claim 1, wherein the plasma processing step includes the step of performing a plasma nitriding process with a surface of the substrate maintained at a temperature from 300°C to 450°C.
- [7] The film formation method according to claim 1, wherein the plasma processing step is executed in an atmosphere supplied with a

mixture gas containing 10% or more ammonia (NH₃) gas in noble gas.

[8] The film formation method according to claim 7, wherein
the plasma processing step is executed in an atmosphere supplied with a
mixture gas further containing 5% or more hydrogen gas in the total
mixture gas.

[9] The film formation method according to claim 1, wherein
the microwave plasma is generated by a radial line slot antenna (RLSA).

[10] The film formation method according to claim 1, wherein
the plasma processing step is executed with microwave plasma having a
plasma electron temperature lower than 1.5 eV and a plasma electron
density higher than $1 \times 10^{11} \text{ cm}^{-3}$ in the vicinity of a surface of the
substrate.

[11] The film formation method according to claim 1, wherein
the gas adsorption step includes the step of changing the volume of a
region above the substrate to form the adsorption layer.

[12] The film formation method according to claim 1 comprising the step of
exhausting a region above the substrate between the gas adsorption step
and the plasma processing step.

[13] The film formation method according to claim 1 comprising the step of
exhausting a region above the substrate after the plasma processing
step.

[14] A semiconductor-device fabrication method comprising the step of
forming a film on a substrate, wherein
the film formation step includes the steps of:

adsorbing source gas on the substrate to form an adsorption layer of the

source gas on the substrate; and

performing a plasma nitriding process on the formed adsorption layer with microwave plasma after the gas adsorption step.

[15] An insulating film formed on a substrate, wherein

5 the insulating film is formed by adsorbing source gas on the substrate to form an adsorption layer of the source gas on the substrate and performing a plasma nitriding process on the formed adsorption layer with microwave plasma.

[16] The insulating film according to claim 15, wherein

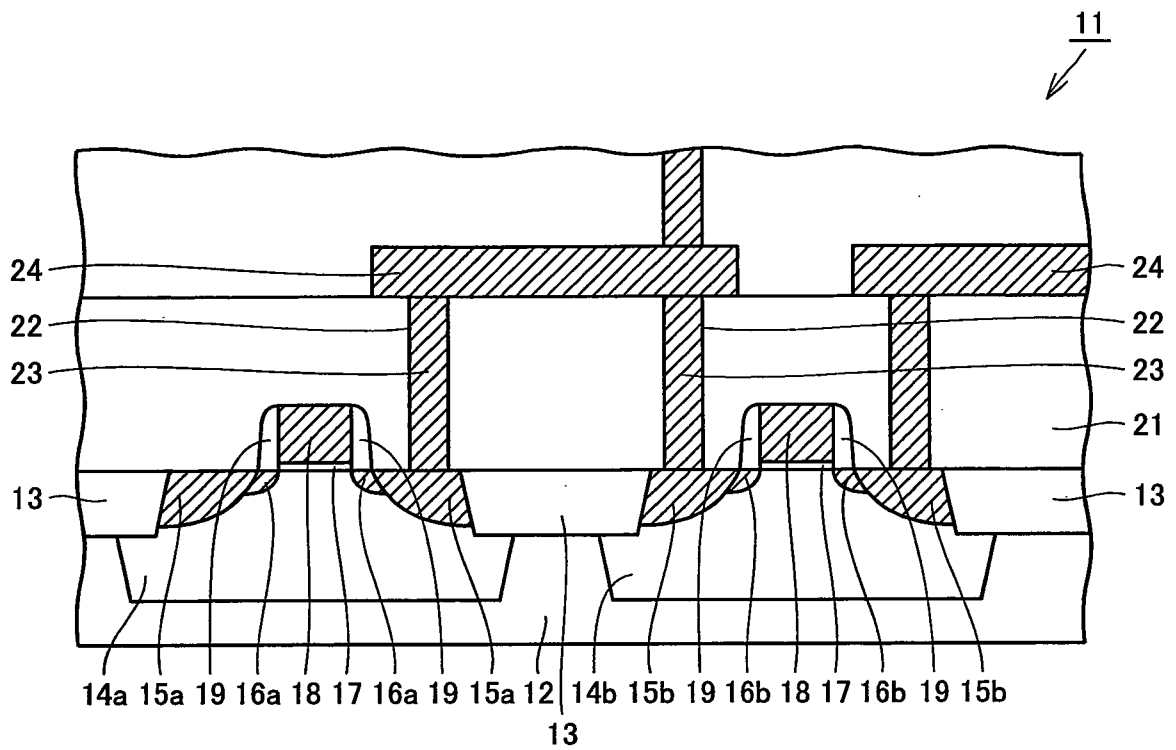
10 the insulating film is a SiN film.

[17] A semiconductor device comprising an insulating film, wherein

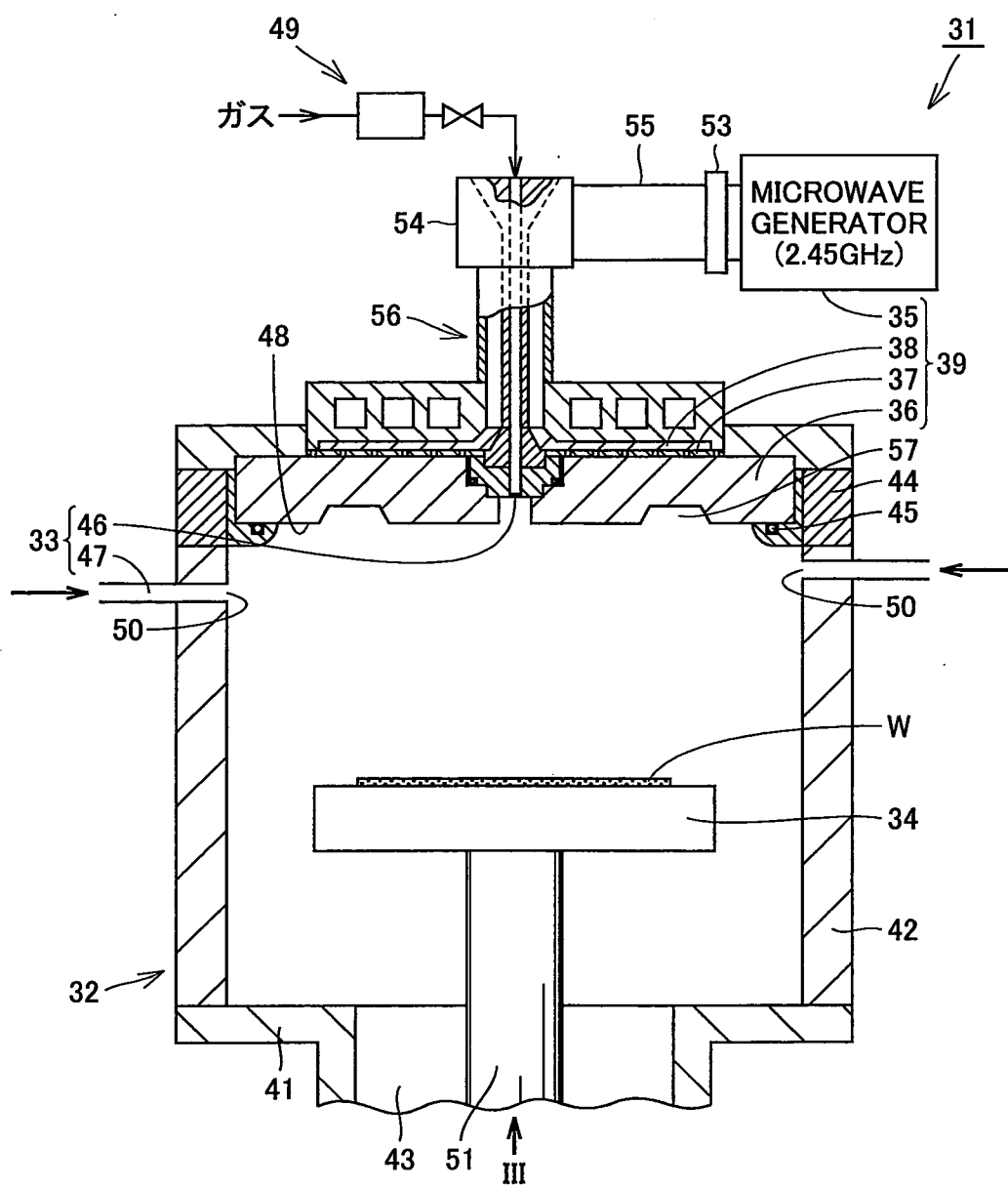
the insulating film is formed by adsorbing source gas on a substrate to form an adsorption layer of the source gas on the substrate and performing a plasma nitriding process on the formed adsorption layer with microwave plasma.

15

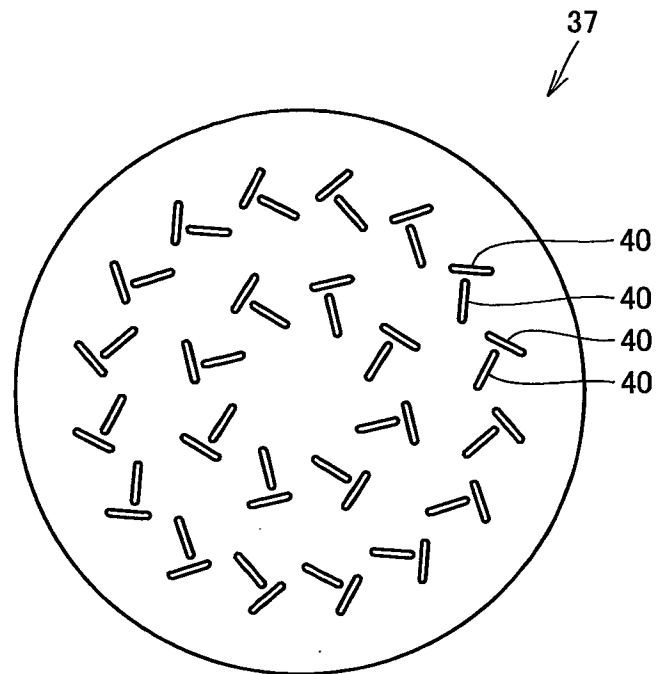
[Fig. 1]



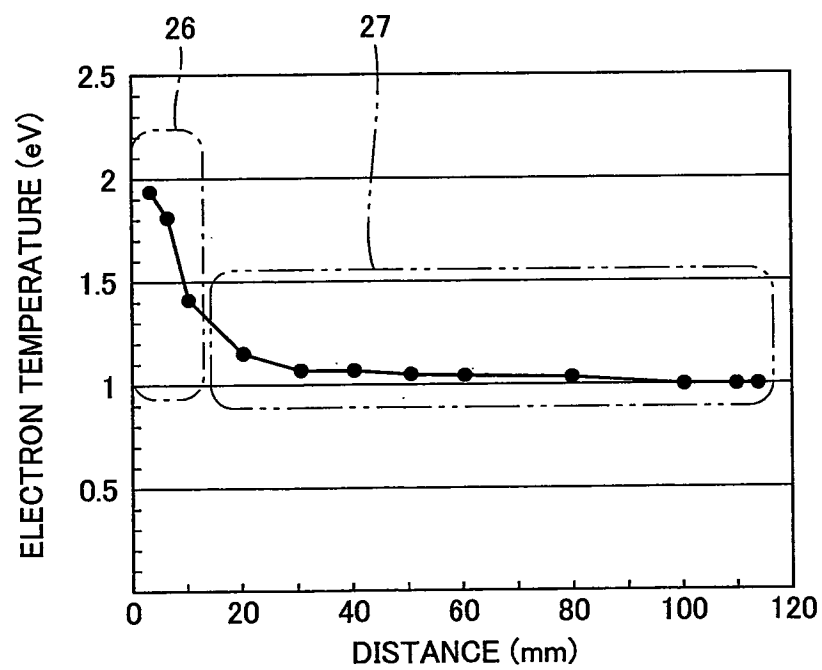
[Fig. 2]



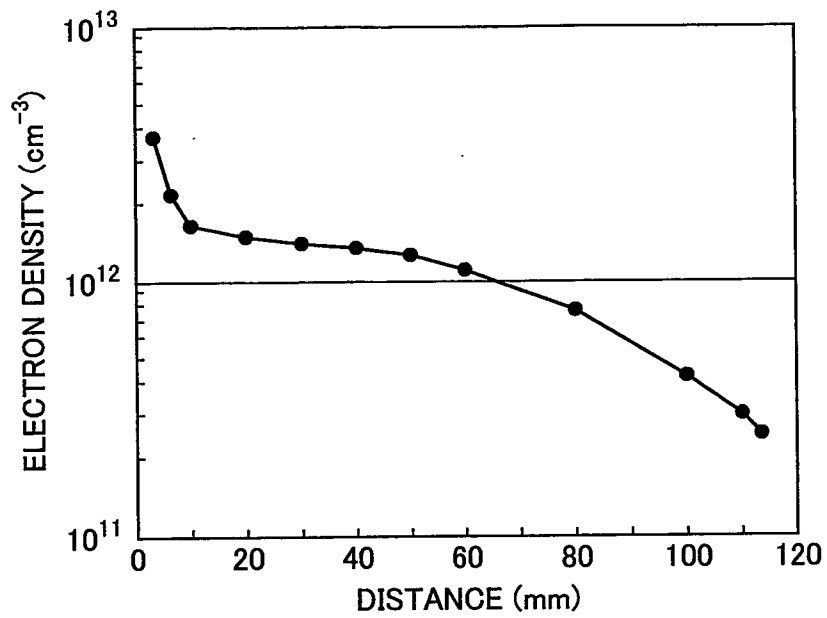
[Fig. 3]



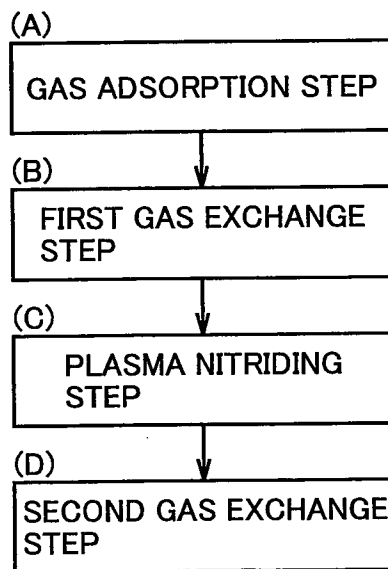
[Fig. 4]



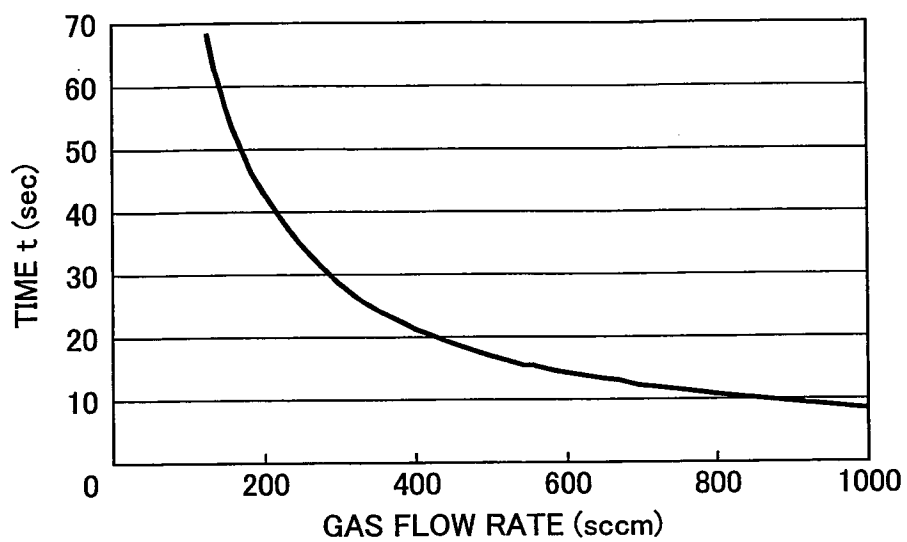
[Fig. 5]



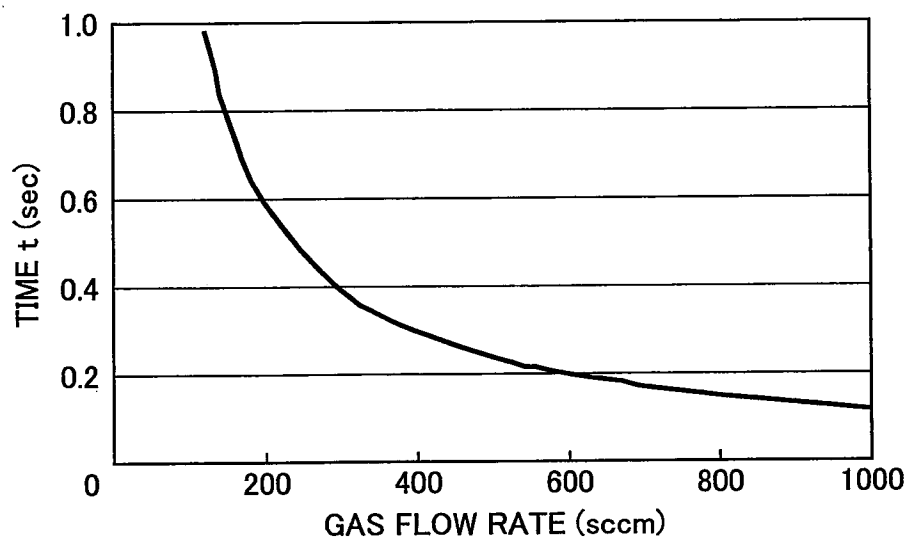
[Fig. 6]



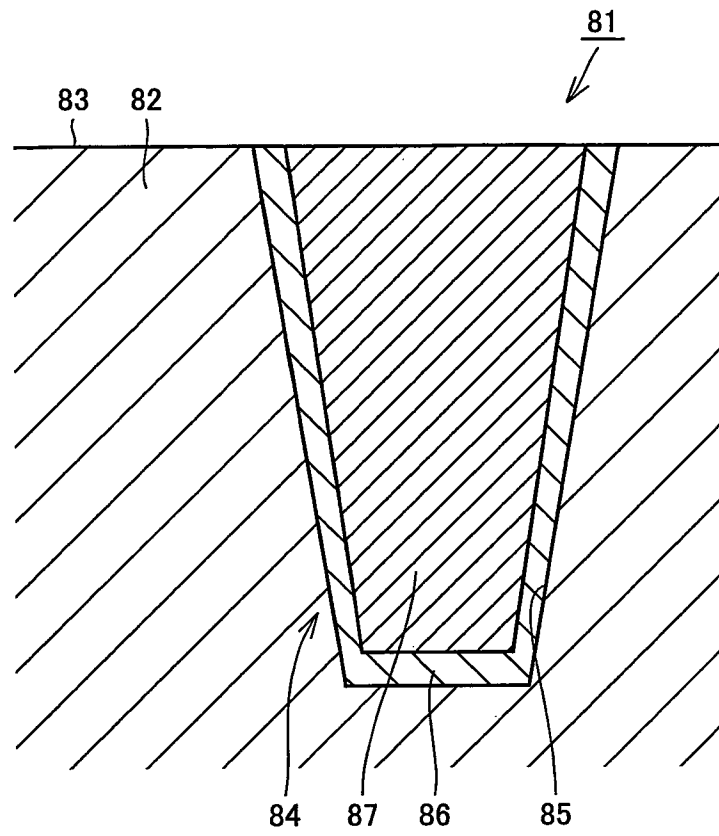
[Fig. 7]



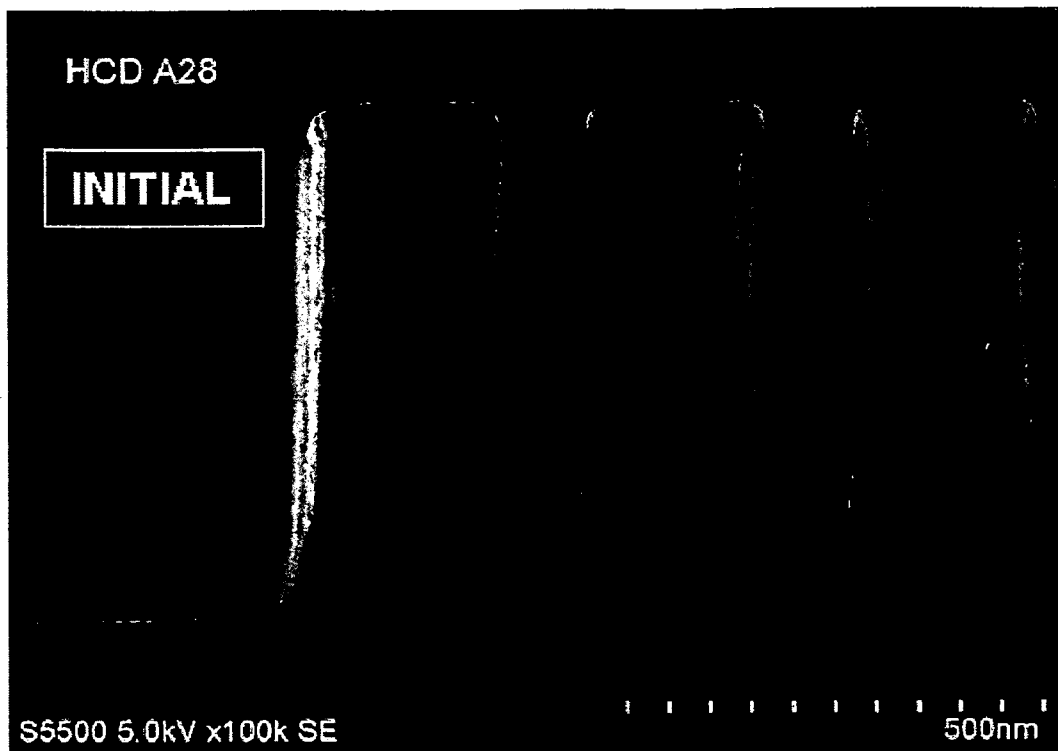
[Fig. 8]



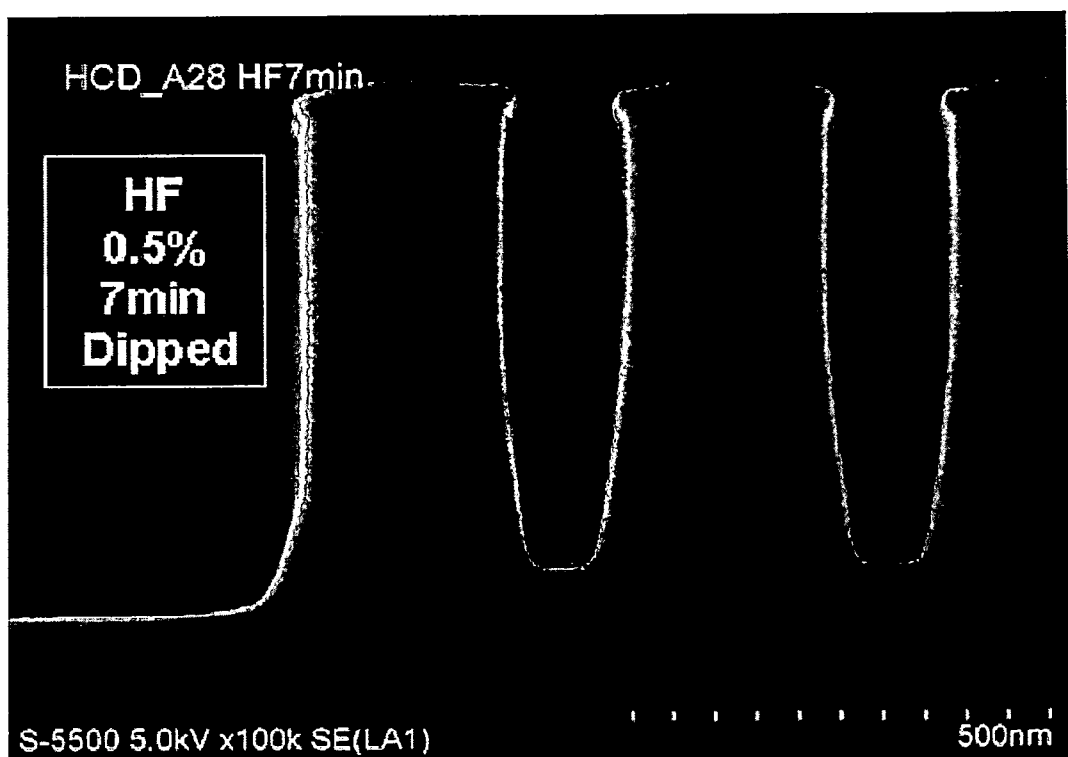
[Fig. 9]



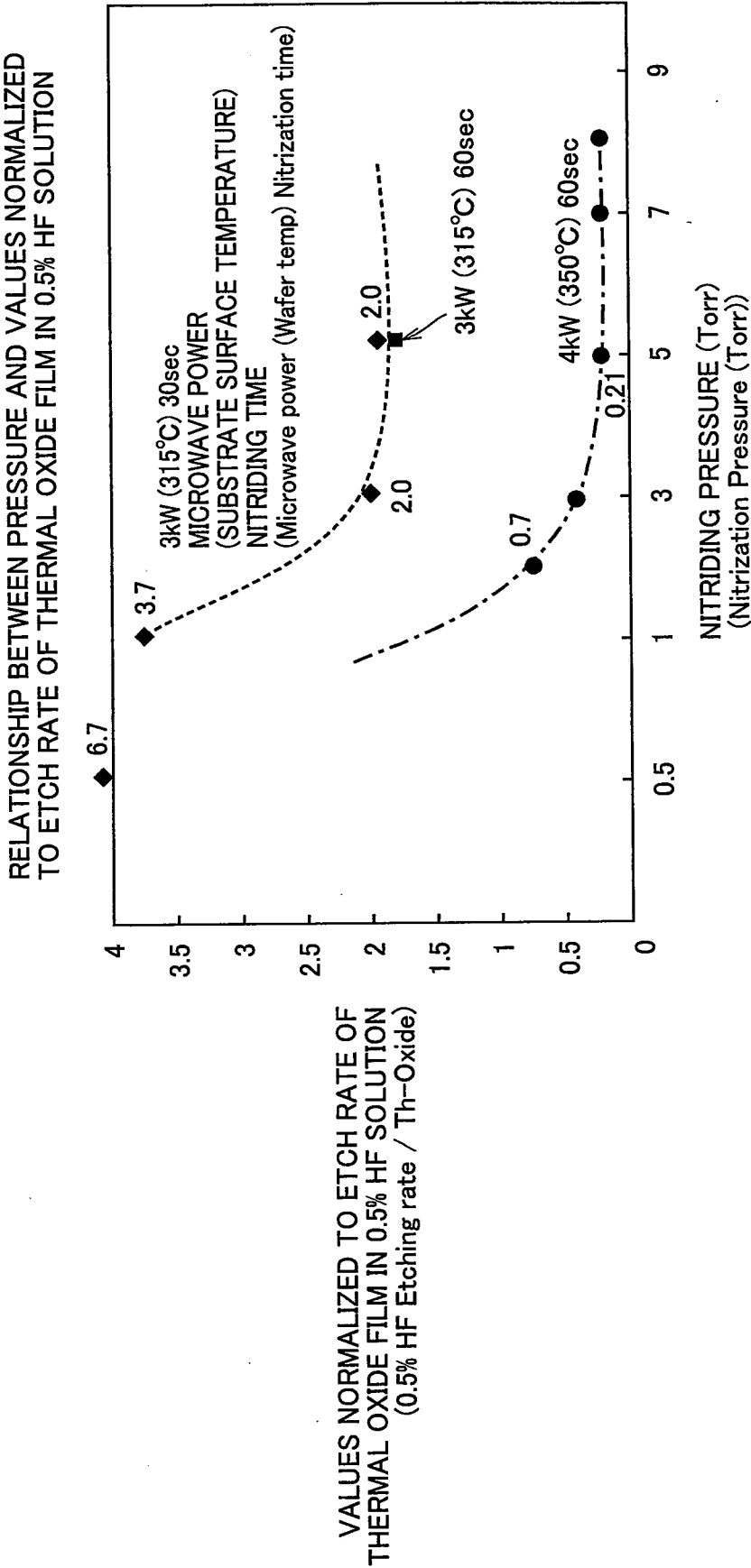
[Fig. 10]



[Fig. 11]

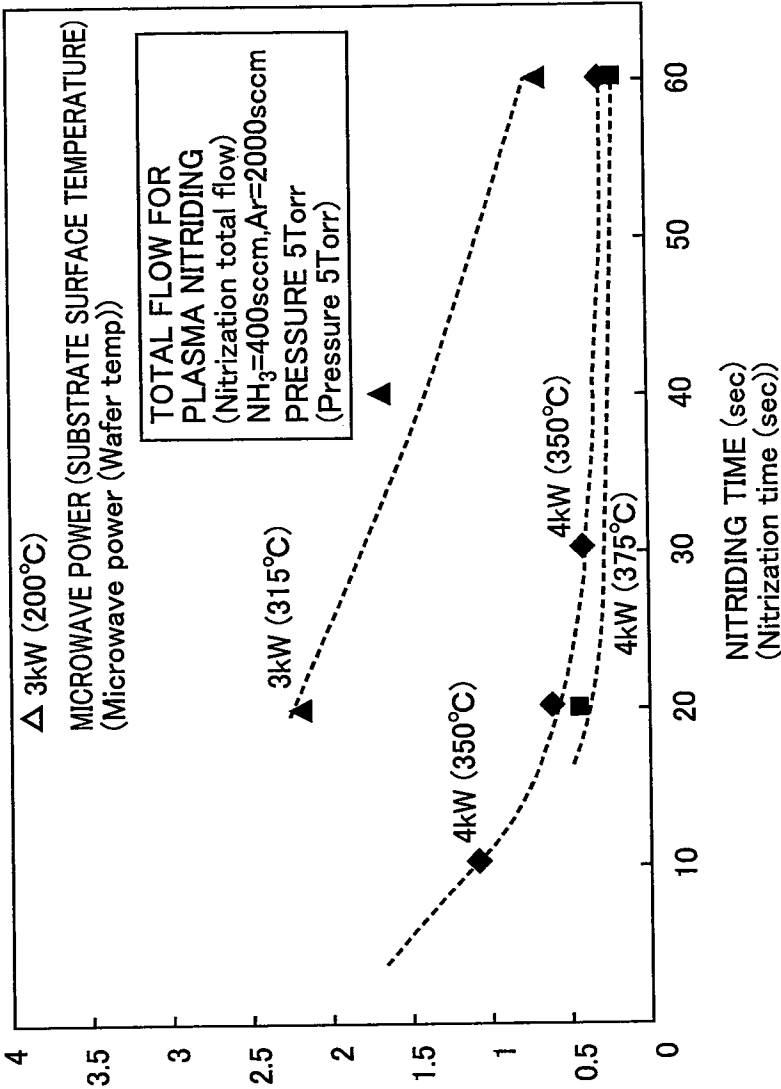


[Fig. 12]



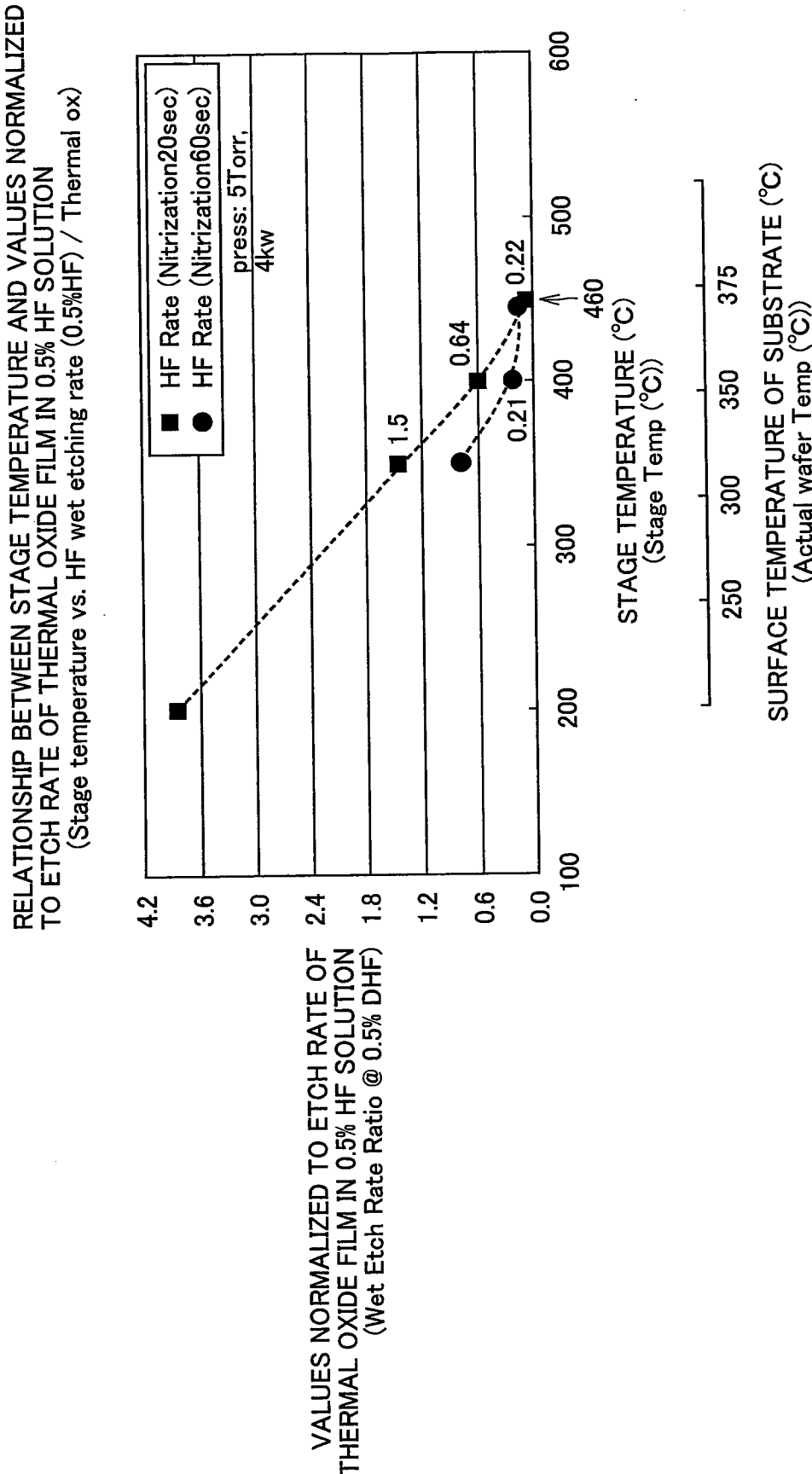
[Fig. 13]

RELATIONSHIP BETWEEN NITRIDING TIME AND VALUES NORMALIZED
TO ETCH RATE OF THERMAL OXIDE FILM IN 0.5% HF SOLUTION
(Nitriding Time vs. 0.5% HF Etching rate / WVG Oxide)

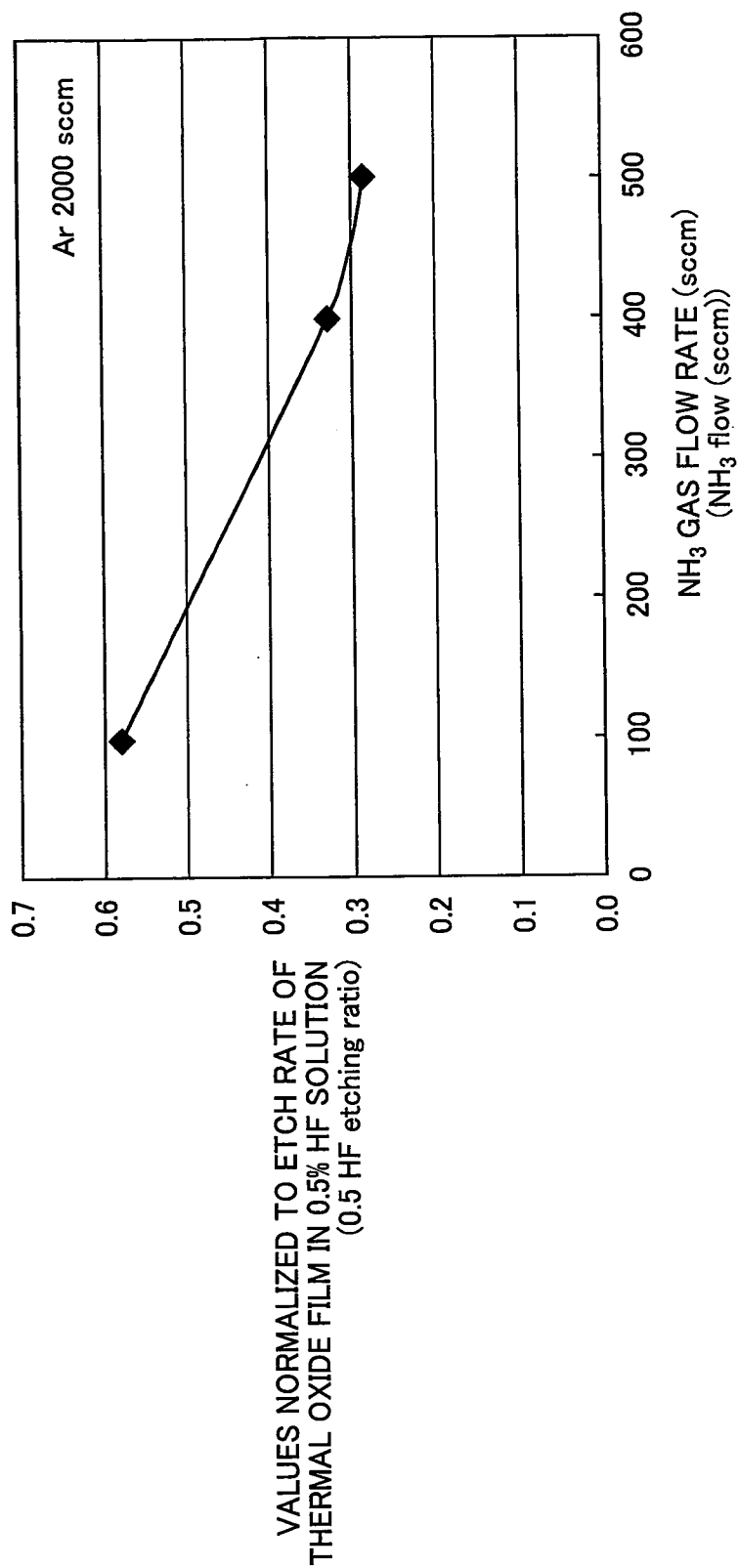


VALUES NORMALIZED TO ETCH RATE OF
THERMAL OXIDE FILM IN 0.5% HF SOLUTION
(0.5% HF Etching rate / Th-Oxide)

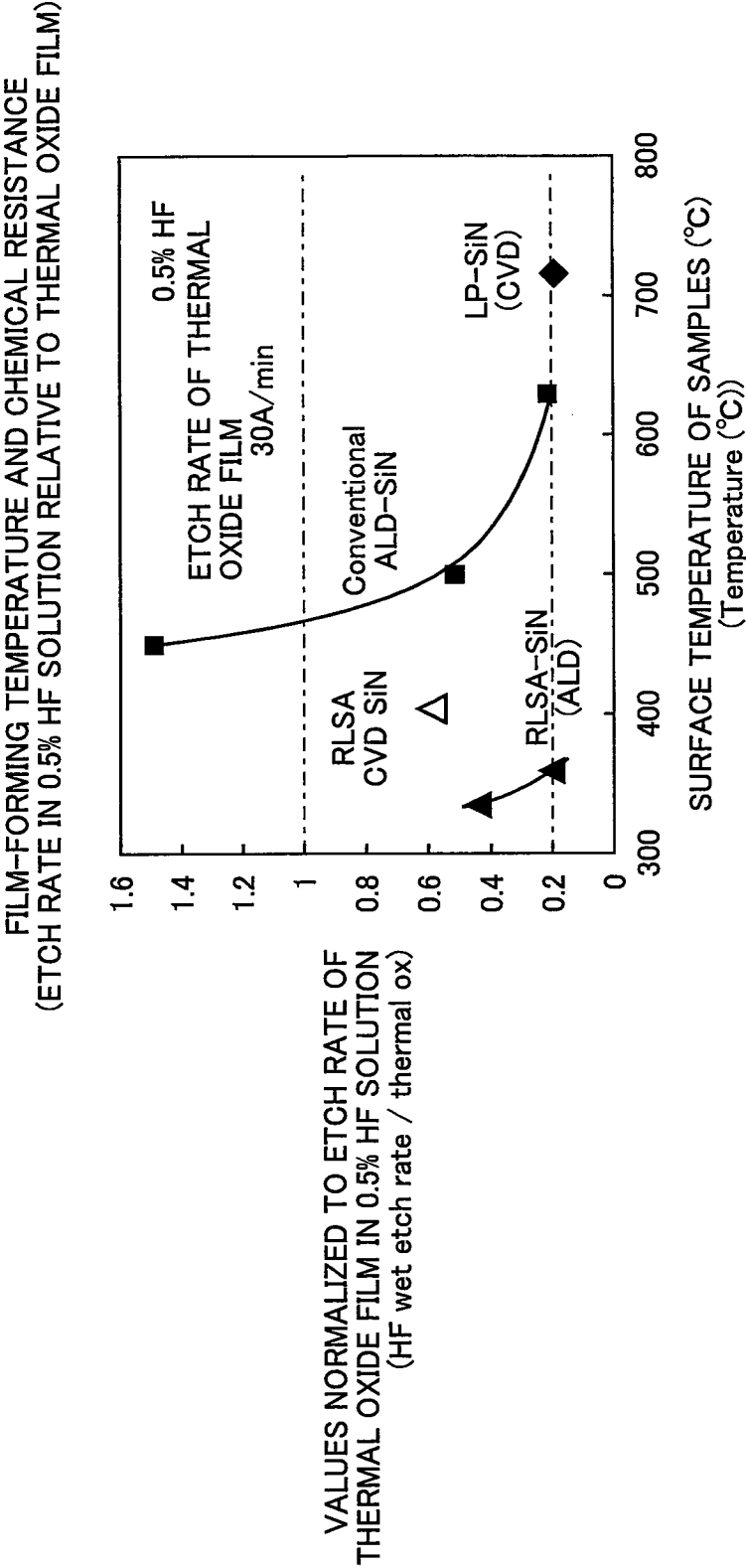
[Fig. 14]



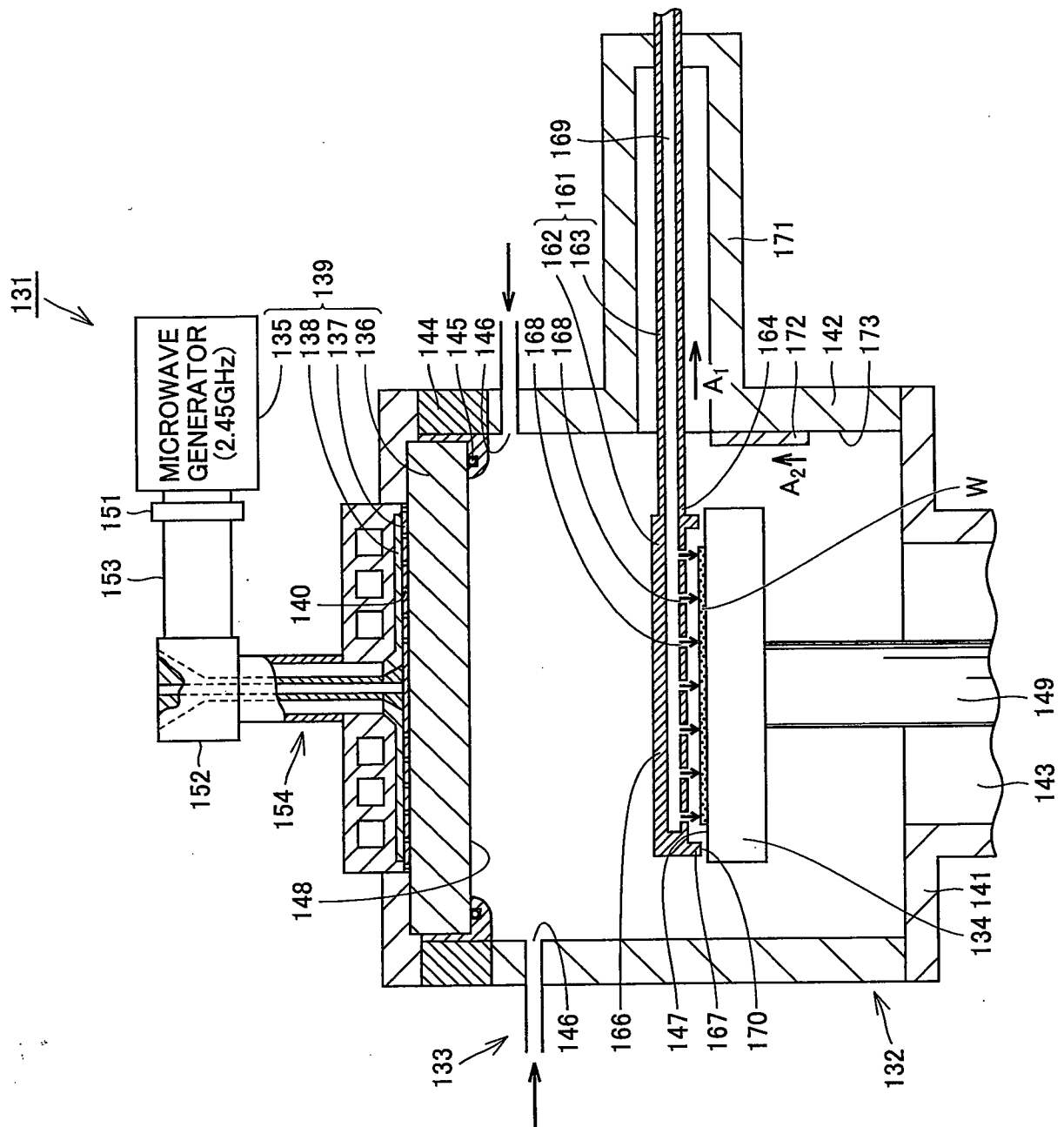
[Fig. 15]



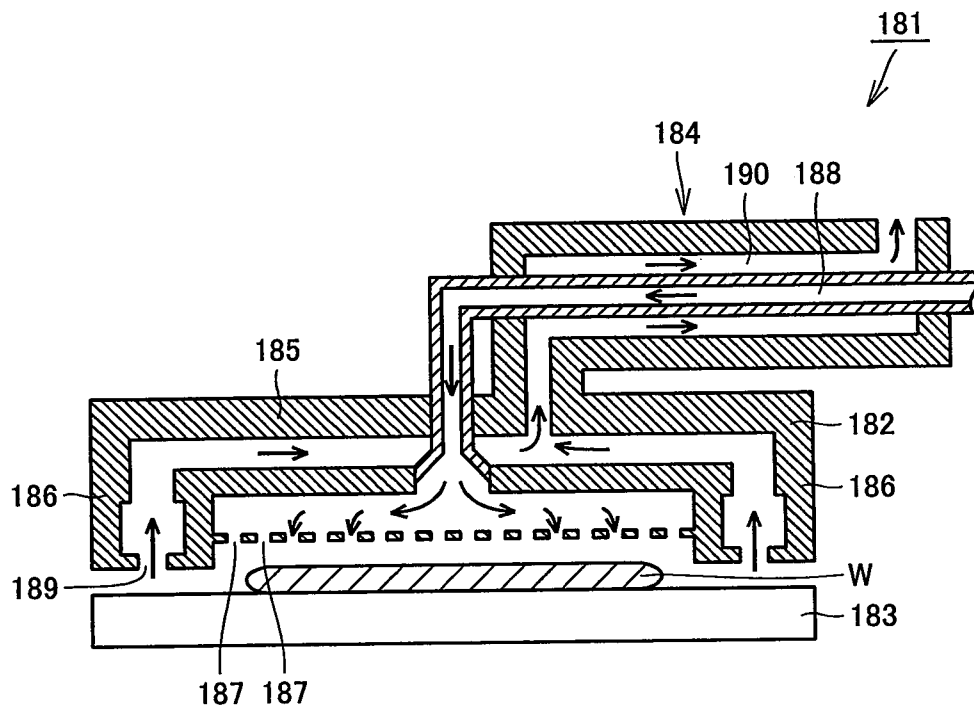
[Fig. 16]



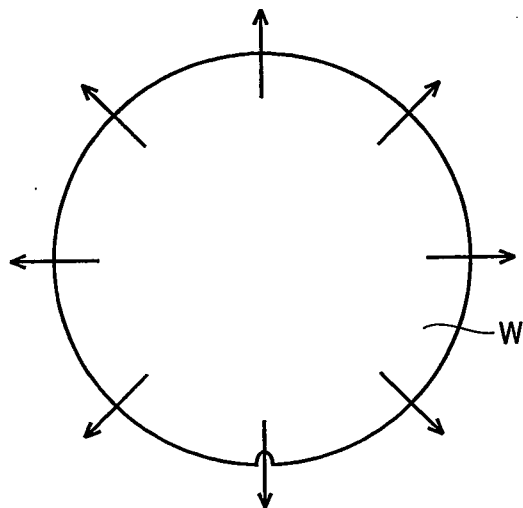
[Fig. 17]



[Fig. 18]



[Fig. 19]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/063629

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. H01L21/318, H01L21/76, H01L21/8234, H01L21/8242, H01L27/088, H01L27/108, H01L29/78

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2011
 Registered utility model specifications of Japan 1996-2011
 Published registered utility model applications of Japan 1994-2011

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/076338 A1 (INFINEON TECHNOLOGIES AG) 2005.08.18, Page 23-24 & JP 2007-527621 A & US 2007/0031599 A1 & DE 102004005385 A	1, 2, 5, 6, 14, 15, 17
X	WO 2006/101857 A2 (TOKYO ELECTRON LIMITED) 2006.09.28, [0037], [0039], [0065], [00106], Fig.3 & JP 2008-537979 A & US 2006/0211246 A1 & KR 10-2008-0000593 A & CN 101147247 A	1-4, 9, 12-17



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

22.08.2011

Date of mailing of the international search report

30.08.2011

Name and mailing address of the ISA/JP

Japan Patent Office

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4R

3949

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/063629

CLASSIFICATION OF SUBJECT MATTER

H01L21/318(2006.01) i, H01L21/76(2006.01) i, H01L21/8234(2006.01) i,
H01L21/8242(2006.01) i, H01L27/088(2006.01) i, H01L27/108(2006.01) i,
H01L29/78(2006.01) i

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/063629

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

As stated on the extra sheet, the claims of this international application include four inventions.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-6, 9, 12-17

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

D1) WO 2005/076338 A1 (INFINEON TECHNOLOGIES AG) 2005.08.18, Page 23-24 & JP 2007-527621 A & US 2007/0031599 A1 & DE 102004005385 A

D2) WO 2006/101857 A2 (TOKYO ELECTRON LIMITED) 2006.09.28, [0037], [0039], [0065], [00106], Fig.3 & JP 2008-537979 A & US 2006/0211246 A1 & KR 10-2008-0000593 A & CN 101147247 A

D1 discloses a method for forming a Hafnium Oxynitride film by the microwave assisted RPE-ALD method. D2 discloses a method for forming a silicon nitride film by the microwave assisted PEALD method. Therefore, claims 1-6, 9, 12-17 lack novelty over D1 and D2, and involve no special technical features. Thus, there are 4 inventions in the claims of this application.

Note that claims 1-6, 9, 12-17 which involves no special technical features, is grouped into Invention 1.

(Invention 1) claims 1-6, 9, 12-17

(Invention 2) claims 7-8

"A film formation method" having the technical feature of the invention of claim 7 is considered to be "a special technical feature".

(Invention 3) claim 10

"A film formation method" having the technical feature of the invention of claim 10 is considered to be "a special technical feature".

(Invention 4) claim 11

"A film formation method" having the technical feature of the invention of claim 11 is considered to be "a special technical feature".