METHOD OF MANUFACTURING SEMICONDUCTOR DEVICE, SUBSTRATE PROCESSING APPARATUS, AND PROGRAM

TECHNICAL FIELD

[0001] The present disclosure relates to a method of manufacturing a semiconductor device, a substrate processing apparatus, and a program.

BACKGROUND

[0002] As a process of manufacturing a semiconductor device, there is a process to be performed for forming a film on a substrate (for example, *see* Patent Document 1).

[Prior Art Documents]

[0003] Patent Documents

Patent Document 1: Japanese laid-open publication No. 2008-109093

[0004] The present disclosure provides some embodiments of a technique capable of improving a step coverage of a film formed on a substrate.

SUMMARY

[0005] According to one embodiment of the present disclosure, there is provided a technique that includes forming a film on a substrate by performing, a predetermined number of times, forming a first layer by supplying a halogen-free precursor, which includes Si-N bonds and Si-H bonds and contains an amino group, to the substrate under a condition in which the precursor is pyrolyzed when the precursor exists alone, wherein in the act of forming the first layer, a deactivating agent for deactivating intermediates generated by pyrolyzing the precursor is supplied to the substrate together with the precursor.

[0006] According to the present disclosure, it is possible to improve a step coverage of a film formed on a substrate.

BRIEF DESCRIPTION OF DRAWINGS

[0007] FIG. 1 is a schematic configuration diagram of a vertical type process furnace of a substrate processing apparatus suitably used in an embodiment of the present disclosure, in which a portion of the process furnace is shown in a vertical cross sectional view.

[0008] FIG. 2 is a schematic configuration diagram of a vertical type process furnace of the substrate processing apparatus suitably used in an embodiment of the present disclosure, in which a portion of the process furnace is shown in a cross sectional view taken along line A-A in FIG. 1.

[0009] FIG. 3 is a schematic configuration diagram of a controller of the substrate processing apparatus according to one embodiment of the present disclosure, in which a control system of a controller is shown in a block diagram.

[0010] FIG. 4 is a diagram illustrating a film-forming sequence according to an embodiment of the present disclosure.

[0011] FIG. 5 is a diagram illustrating a chemical structural formula of BDEAS used as a precursor.

[0012] FIGS. 6A and 6B are diagrams illustrating example chemical structures of active intermediates generated by pyrolyzing BDEAS.

[0013] FIGS. 7A and 7B are diagrams illustrating example chemical structures of deactivated intermediates.

DETAILED DESCRIPTION

<One Embodiment of the Present Disclosure>

[0014] An embodiment of the present disclosure will now be described in detail mainly with reference to FIGS. 1 to 4.

(1) Configuration of the Substrate Processing Apparatus

[0015] As illustrated in FIG. 1, a process furnace 202 includes a heater 207 as a heating mechanism (temperature adjustment part). The heater 207 has a cylindrical shape and is supported by a holding plate so as to be vertically installed. The heater 207 functions as an

activation mechanism (an excitation part) configured to thermally activate (excite) a gas.

[0016] A reaction tube 203 is disposed inside the heater 207 to be concentric with the heater 207. The reaction tube 203 is made of a heat resistant material, for example, quartz (SiO_2), silicon carbide (SiC) or the like, and has a cylindrical shape with its upper end closed and its lower end opened. A process chamber 201 is formed in a hollow cylindrical portion of the reaction tube 203. The process chamber 201 is configured to accommodate a wafer 200 as a substrate. The processing of the wafers 200 is performed in the process chamber 201.

[0017] Nozzles 249a and 249b are installed in the process chamber 201 so as to penetrate a lower sidewall of the reaction tube 203. Gas supply pipes 232a and 232b are respectively connected to the nozzles 249a and 249b.

[0018] Mass flow controllers (MFCs) 241a and 241b, which are flow rate controllers (flow rate control parts), and valves 243a and 243b, which are opening/closing valves, are installed in the gas supply pipes 232a and 232b sequentially from the corresponding upstream sides of gas flow, respectively. Gas supply pipes 232c and 232d are respectively connected to the gas supply pipes 232a and 232b at the downstream side of the valves 243a and 243b. MFCs 241c and 241d and valves 243c and 243d are respectively installed in the gas supply pipes 232c and 232d sequentially from the corresponding upstream sides of gas flow.

[0019] As illustrated in FIG. 2, the nozzles 249a and 249b are disposed in a space with an annular plan-view shape between the inner wall of the reaction tube 203 and the wafers 200 such that the nozzles 249a and 249b extend upward along an arrangement direction of the wafers 200 from a lower portion of the inner wall of the reaction tube 203 to an upper portion of the inner wall of the reaction tube 203. That is, the nozzles 249a and 249b are installed at a lateral side of a wafer arrangement region in which the wafers 200 are arranged, namely at a region which horizontally surrounds the wafer arrangement region, so as to extend along the wafer arrangement region. Gas supply holes 250a and 250b for supplying a gas are installed on the side surfaces of the nozzles 249a and 249b, respectively. The gas supply holes 250a and 250b are opened toward the center of the reaction tube 203 so as to allow a gas to be supplied toward the wafers 200. The gas supply holes 250a and 250b may be formed in a plural number

between the lower portion of the reaction tube 203 and the upper portion of the reaction tube 203.

[0020] As a precursor (precursor gas), for example, a halogen-free aminosilane-based gas, which includes chemical bonds (Si-N bonds) of silicon (Si) as a main element constituting a film formed on the wafer 200 and nitrogen (N) and chemical bonds (Si-H bonds) of Si and hydrogen (H), and contains an amino group, is supplied from the gas supply pipe 232a into the process chamber 201 via the MFC 241a, the valve 243a, and the nozzle 249a. The precursor gas refers to a gaseous precursor, for example, a gas obtained by vaporizing a precursor which remains in a liquid state under a room temperature and an atmospheric pressure, or a precursor which remains in a gas state at room temperature and atmospheric pressure. The amino group refers to a monovalent functional group expressed by a structural formula of $-NR_2$ in which an alkyl group (R) such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group or the like is bonded to an N atom. The aminosilane-based gas acts not only as a Si source but also as an N source and a C source. As the aminosilane-based gas, it may be possible to use, for example, a bis (diethylamino) silane ($SiH_2[N(C_2H_5)_2]_2$, abbreviation: BDEAS) gas. As illustrated in the chemical structural formula in FIG. 5, BDEAS includes two Si-N bonds and two Si-H bonds in one molecule.

[0021] As a deactivating agent, for example, an N-containing gas expressed by a general formula NR_3 (where R is a hydrogen atom or various kinds of alkyl groups described above), is supplied from the gas supply pipe 232b into the process chamber 201 via the MFC 241b, the valve 243b, and the nozzle 249b. The N-containing gas acts to deactivate a portion of a plurality of active intermediates, which is generated by pyrolyzing the aforementioned precursor at step 1 to be described later, to lower a probability of adsorption of the intermediates to the wafer 200, thereby reducing an adsorption efficiency of the intermediates. As the N-containing gas, it may be possible to use, for example, an ammonia (NH_3) gas.

[0022] As a reactant (reaction gas), for example, an oxygen (O)-containing gas, is supplied from the gas supply pipes 232b into the process chamber 201 via the MFC 241b, the valve 243b, and

the nozzle 249b. The O-containing gas acts as an oxidizing agent (oxidizing gas), that is, an O source. As the O-containing gas, it may be possible to use, for example, an oxygen (O_2) gas.

[0023] A nitrogen (N_2) gas as an inert gas is supplied from the gas supply pipes 232c and 232d into the process chamber 201 via the MFCs 241c and 241d, the valves 243c and 243d, the gas supply pipes 232a and 232b, and the nozzles 249a and 249b. The N_2 gas acts as a purge gas, a carrier gas, a dilution gas, or the like.

[0024] A precursor supply system is mainly configured by the gas supply pipe 232a, the MFC 241a, and the valve 243a. A deactivating agent supply system and a reactant supply system are each mainly configured by the gas supply pipe 232b, the MFC 241b, and the valve 243b. An inert gas supply system is mainly configured by the gas supply pipes 232c and 232d, the MFCs 241c and 241d, and the valves 243c and 243d.

[0025] One or all of various supply systems described above may be configured as an integrated supply system 248 in which the valves 243a to 243d, the MFCs 241a to 241d, and the like are integrated. The integrated supply system 248 is connected to each of the gas supply pipes 232a to 232d so that a supply operation of various kinds of gases into the gas supply pipes 232a to 232d, that is, an opening/closing operation of the valves 243a to 243d, a flow rate adjusting operation by the MFCs 241a to 241d or the like, is controlled by a controller 121 to be described later. The integrated supply system 248 is configured as an integral type or division type integrated unit, and is also configured so that it is detachable from the gas supply pipes 232a to 232d or the like, so as to perform maintenance, replacement, expansion or the like of the integrated supply system 248, on an integrated unit basis.

[0026] An exhaust pipe 231 configured to exhaust an internal atmosphere of the process chamber 201 is installed at a lower side of the sidewall of the reaction tube 203. A vacuum pump 246 as a vacuum exhaust device is connected to the exhaust pipe 231 via a pressure sensor 245 as a pressure detector (pressure detection part) which detects the internal pressure of the process chamber 201 and an auto pressure controller (APC) valve 244 as a pressure regulator (pressure regulation part). The APC valve 244 is configured so that a vacuum exhaust of the interior of the process chamber 201 and a vacuum exhaust stop can be performed by opening and

closing the APC valve 244 while operating the vacuum pump 246, and the internal pressure of the process chamber 201 can be adjusted by adjusting an opening degree of the APC valve 244 based on pressure information detected by the pressure sensor 245 while operating the vacuum pump 246. An exhaust system is mainly configured by the exhaust pipe 231, the pressure sensor 245 and the APC valve 244. The vacuum pump 246 may be regarded as being included in the exhaust system.

[0027] A seal cap 219, which serves as a furnace opening cover configured to hermetically seal a lower end opening of the reaction tube 203, is installed under the reaction tube 203. The seal cap 219 is made of a metal material such as, e.g., stainless steel (SUS) or the like, and is formed in a disc shape. An O-ring 220, which is a seal member making contact with the lower end portion of the reaction tube 203, is installed on an upper surface of the seal cap 219. A rotation mechanism 267 configured to rotate a boat 217, which will be described later, is installed under the seal cap 219. A rotary shaft 255 of the rotation mechanism 267, which penetrates the seal cap 219, is connected to the boat 217. The rotation mechanism 267 is configured to rotate the wafer 200 by rotating the boat 217. The seal cap 219 is configured to be vertically moved up and down by a boat elevator 115 which is an elevator mechanism installed outside the reaction tube 203. The boat elevator 215 is configured as a transfer device (transfer mechanism) which loads and unloads (transfers) the wafer 200 into and from (out of) the process chamber 201 by moving the seal cap 219 up and down.

[0028] The boat 217 serving as a substrate support is configured to support a plurality of wafers 200, for example, 25 to 200 wafers, in such a state that the wafers 200 are arranged in a horizontal posture and in multiple stages along a vertical direction with the centers of the wafers 200 aligned with one another. That is, the boat 217 is configured to arrange the wafers 200 in a spaced-apart relationship. The boat 217 is made of a heat resistant material such as quartz or SiC. Heat insulating plates 218 made of a heat resistant material such as quartz or SiC are installed below the boat 217 in a horizontal posture and in multiple stages.

[0029] A temperature sensor 263 serving as a temperature detector is installed in the reaction tube 203. Based on temperature information detected by the temperature sensor 263, a state of

supplying electric power to the heater 207 is adjusted such that the interior of the process chamber 201 has a desired temperature distribution. The temperature sensor 263 is installed along the inner wall of the reaction tube 203.

[0030] As illustrated in FIG. 3, the controller 121, which is a control part (control means), may be configured as a computer including a central processing unit (CPU) 121a, a random access memory (RAM) 121b, a memory device 121c, and an I/O port 121d. The RAM 121b, the memory device 121c and the I/O port 121d are configured to exchange data with the CPU 121a via an internal bus 121e. An input/output device 122 formed of, e.g., a touch panel or the like, is connected to the controller 121.

[0031] The memory device 121c is configured by, for example, a flash memory, a hard disk drive (HDD), or the like. A control program for controlling operations of a substrate processing apparatus, a process recipe for specifying sequences and conditions of a film-forming process as described hereinbelow, or the like is readably stored in the memory device 121c. The process recipe functions as a program for causing the controller 121 to execute each sequence in the film-forming process, as described hereinbelow, to obtain a predetermined result. Hereinafter, the process recipe and the control program will be generally and simply referred to as a "program." Furthermore, the process recipe will be simply referred to as a "recipe." When the term "program" is used herein, it may indicate a case of including only the recipe, a case of including only the control program, or a case of including both the recipe and the control program. The RAM 121b is configured as a memory area (work area) in which a program, data and the like read by the CPU 121a is temporarily stored.

[0032] The I/O port 121d is connected to the MFCs 241a to 241d, the valves 243a to 243d, the pressure sensor 245, the APC valve 244, the vacuum pump 246, the temperature sensor 263, the heater 207, the rotation mechanism 267, the boat elevator 115, and the like, as described above.

[0033] The CPU 121a is configured to read the control program from the memory device 121c and execute the same, and also reads the recipe from the memory device 121c according to an input of an operation command from the input/output device 122. The CPU 121a is configured to control, according to the contents of the recipe thus read, the flow rate adjusting operation of

various kinds of gases by the MFCs 241a to 241d, the opening/closing operation of the valves 243a to 243d, the opening/closing operation of the APC valve 244, the pressure regulating operation performed by the APC valve 244 based on the pressure sensor 245, the driving and the stopping of the vacuum pump 246, the temperature adjusting operation performed by the heater 207 based on the temperature sensor 263, the operation of rotating the boat 217 with the rotation mechanism 267 and adjusting the rotation speed of the boat 217, the operation of moving the boat 217 up and down with the boat elevator 115, and the like.

[0034] The controller 121 may be configured by installing, on the computer, the aforementioned program stored in an external memory device 123. The external memory device 123 may include, for example, a magnetic disc such as an HDD, an optical disc such as a CD, a magneto-optical disc such as an MO, and a semiconductor memory such as a USB memory. The memory device 121c or the external memory device 123 is configured as a computer-readable recording medium. Hereinafter, the memory device 121c and the external memory device 123 will be collectively and simply referred to as a "recording medium." When the term "recording medium" is used herein, it may indicate a case of including only the memory device 121c, a case of including only the external memory device 123, or a case of including both the memory device 121c and the external memory device 123. Furthermore, the program may be supplied to the computer using a communication means such as the Internet or a dedicated line, instead of using the external memory device 123.

(2) Substrate Processing

[0035] A substrate processing sequence example of forming a film on a wafer 200 as a substrate using the aforementioned substrate processing apparatus, that is, a film-forming sequence example, as a process for manufacturing a semiconductor device, will be described with reference to FIG. 4. In the following descriptions, the operations of the respective parts constituting the substrate processing apparatus are controlled by the controller 121.

[0036] In the film-forming sequence illustrated in FIG. 4, step 1 of forming a first layer by supplying a BDEAS gas as a halogen-free precursor, which includes Si-N bonds and Si-H bonds

and contains an amino group, to a wafer 200 under a condition in which the BDEAS gas is pyrolyzed when the BDEAS gas exists alone, is performed a predetermined number of times. At step 1, an NH_3 gas as a deactivating agent for deactivating intermediates generated by pyrolyzing the BDEAS gas is supplied to the wafer 200 together with the BDEAS gas.

[0037] In the film-forming sequence illustrated in FIG. 4, step 2 of forming a second layer by supplying an O_2 gas as a reactant to the wafer 200 to modify the first layer is further performed. Specifically, a cycle which non-simultaneously performs steps 1 and 2 is performed a predetermined number of times. Thus, a silicon oxycarbonitride film (SiOCN film), which is a film containing Si, O, C, and N, is formed as a film on the wafer 200.

[0038] In the present disclosure, for the sake of convenience, the film-forming sequence illustrated in FIG. 4 may sometimes be denoted as follows.

$$(\mathrm{BDEAS}+\mathrm{NH_3} \rightarrow \mathrm{O_2})\times n \Rightarrow \mathrm{SiOCN}$$

[0039] When the term "wafer" is used herein, it may refer to a wafer itself or a laminated body of a wafer and a predetermined layer or film formed on the surface of the wafer. In addition, when the phrase "a surface of a wafer" is used herein, it may refer to a surface of a wafer itself or a surface of a predetermined layer or the like formed on a wafer. Furthermore, in the present disclosure, the expression "a predetermined layer is formed on a wafer" may mean that a predetermined layer is directly formed on a surface of a wafer itself or that a predetermined layer is formed on a layer or the like formed on a wafer. In addition, when the term "substrate" is used herein, it may be synonymous with the term "wafer."

(Wafer Charging and Boat Loading)

[0040] A plurality of wafers 200 is charged on the boat 217 (wafer charging). Thereafter, as illustrated in FIG. 1, the boat 217 supporting the plurality of wafers 200 is lifted up by the boat elevator 115 and is loaded into the process chamber 201 (boat loading). In this state, the seal cap 219 seals the lower end of the reaction tube 203 through the O-ring 220.

(Pressure Regulation and Temperature Adjustment)

[0041] The interior of the process chamber 201, namely the space in which the wafer 200 is located, is vacuum-exhausted (depressurization-exhausted) by the vacuum pump 246 so as to reach a desired pressure (degree of vacuum). In this operation, the internal pressure of the process chamber 201 is measured by the pressure sensor 245. The APC valve 244 is feedback-controlled based on the measured pressure information. Furthermore, the wafer 200 in the process chamber 201 are heated by the heater 207 to a desired processing temperature. In this operation, the state of supplying electric power to the heater 207 is feedback-controlled based on the temperature information detected by the temperature sensor 263 such that the interior of the process chamber 201 has a desired temperature distribution. In addition, the rotation of the wafer 200 by the rotation mechanism 267 begins. The driving of the vacuum pump 246 and the heating and the rotation of the wafers 200 may be continuously performed until all or at least the processing of the wafers 200 is completed.

(Film-Forming Step)

[0042] Next, the following steps 1 and 2 are sequentially performed.

[Step 1]

[0043] At this step, a BDEAS gas and an NH_3 gas are simultaneously supplied to the wafer 200 in the process chamber 201. Specifically, the valves 243a and 243b are opened to allow a BDEAS gas and an NH_3 gas to flow through the gas supply pipes 232a and 232b, respectively. The flow rates of the BDEAS gas and the NH_3 gas are adjusted by the MFCs 241a and 241b. The BDEAS gas and the NH_3 gas are supplied into the process chamber 201 via the nozzles 249a and 249b, mixed in the process chamber 201, and are exhausted from the exhaust pipe 231. At this time, the BDEAS gas and the NH_3 gas are simultaneously (together) supplied to the wafer 200. Simultaneously, the valves 243c and 243d may be opened to allow an N_2 gas to flow through the gas supply pipes 232c and 232d.

[0044] The processing conditions at this step may be exemplified as follows:

Processing temperature: 500 to 650 degrees C, specifically 550 to 650 degrees C

Processing pressure: 26.6 to 2,666 Pa, specifically 66.5 to 266 Pa

BDEAS gas supply flow rate: 1 to 1,000 sccm, specifically 50 to 100 sccm

NH_3 gas supply flow rate: 4 to 30,000 sccm, specifically 200 to 3,000 sccm

N_2 gas supply flow rate (per gas supply pipe): 0 to 10,000 sccm

Supply time of each gas: 1 to 120 seconds, specifically 5 to 60 seconds.

[0045] Furthermore, in the present disclosure, the expression of the numerical range such as "500 to 650 degrees C" may mean that a lower limit value and an upper limit value are included in that range. Therefore, for example, "500 to 650 degrees C" may mean "500 degrees C or higher and 650 degrees C or lower". The same applies to other numerical ranges.

[0046] By supplying the BDEAS gas to the wafer 200 under the aforementioned conditions, a silicon carbonitride layer (SiCN layer), which is a layer containing Si, C, and N, is formed as a first layer (initial layer) on the outermost surface of the wafer 200.

[0047] The aforementioned processing conditions (particularly, the processing temperature) are conditions in which intermediates as illustrated in FIGS. 6A and 6B can be generated by pyrolyzing the BDEAS gas when the BDEAS gas exists alone in the process chamber 201. Among various chemical bonds of the BDEAS gas, particularly Si-H bonds have a characteristic that is more easily broken than other chemical bonds (Si-N bonds or the like) under the aforementioned processing conditions. The intermediates generated under the aforementioned processing conditions contain dangling bonds generated by breaking the Si-H bonds, so that the intermediates have an active characteristic that is easily adsorbed on the surface of the wafer 200. By performing the supply of the BDEAS gas under the aforementioned processing conditions to generate the active intermediates as illustrated in FIGS. 6A and 6B, it is possible to efficiently perform the formation of the first layer on the wafer 200. At this time, the formation of the first layer may be performed under a situation in which the supply rate controlling of the intermediates becomes more dominant than the surface reaction rate controlling of the intermediates, and furthermore, under a situation of the supply rate controlling of the intermediates rather than the surface reaction rate controlling of the intermediates.

[0048] At this step, if the processing temperature is lower than 500 degrees C, there may be a

case where it is difficult for the BDEAS gas to be pyrolyzed so that the aforementioned active intermediates are not generated. As a result, the formation of the first layer on the wafer 200 may be difficult. By setting the processing temperature at a temperature of 500 degrees C or higher, the BDEAS gas can be pyrolyzed to generate the active intermediates. This makes it possible to allow the formation of the SiOCN film on the wafer 200 to go ahead at a practical deposition rate. By setting the processing temperature at a temperature of 550 degrees C or higher, it is possible to more reliably achieve the aforementioned effects.

[0049] At this step, if the processing temperature exceeds 650 degrees C, an excessive gas phase reaction may occur. Thus, the wafer in-plane film thickness uniformity and step coverage of the SiOCN film formed on the wafer 200 are likely to deteriorate, so that the control thereof may become difficult. By setting the processing temperature at a temperature of 650 degrees C or lower, it becomes possible to solve these problems.

[0050] Accordingly, it is desirable that the processing conditions (particularly, the processing temperature) at step 1 be set to predetermined conditions which fall within the aforementioned range. The aforementioned processing conditions are conditions capable of resolving the aforementioned problems, such as an excessive gas phase reaction occurring when the first layer is formed. Furthermore, the aforementioned processing conditions include a condition in which the supply rate controlling of the intermediates is more dominant than the surface reaction rate controlling of the intermediates.

[0051] In addition, when the formation of the first layer is performed under the condition in which the supply rate controlling of the intermediates is more dominant than the surface reaction rate controlling of the intermediates, there may be a case where it is difficult to improve the step coverage of the SiOCN film formed on the wafer 200, to improve the in-plane film thickness uniformity of the wafer, and to improve the controllability of the film thickness. That is, if a degree of the supply rate controlling of the intermediates is too strong, the step coverage of the SiOCN film formed on the wafer 200 may deteriorate, the in-plane film thickness uniformity of the wafer may deteriorate, and the controllability of the film thickness may deteriorate. Therefore, in the present embodiment, in order to appropriately reduce the degree of the supply

rate controlling of the intermediates, the NH_3 gas is supplied to the wafer 200 as a deactivating agent together with the BDEAS gas.

[0052] By supplying the NH_3 gas together with the BDEAS gas to the wafer 200 under the aforementioned processing conditions, the NH_3 gas can be caused to collide with a portion of the plurality of intermediates generated by the pyrolysis of the BDEAS gas so as to deactivate such a portion of the intermediates. That is, N of the NH_3 gas can be bonded to an element constituting such a portion of the intermediates, for example, Si having dangling bonds. As illustrated in FIGS. 7A and 7B, intermediates which have reacted by colliding with the NH_3 gas are modified into substances which have no dangling bond and are difficult to be adsorbed on the surface of the wafer 200. In the present disclosure, the intermediates, which are reduced in activity due to the loss of dangling bonds by the reaction with the NH_3 gas, will be referred to as deactivators. The deactivators become in a state that is more difficult to be adsorbed on the surface of the wafer 200 than the intermediates before the activity is reduced, that is, a state that the contribution to the formation of the first layer is reduced, and are thus discharged (removed) from the exhaust pipe 231. In addition, at this time, another portion other than the portion of the intermediates, that is, the intermediates which do not collide with the NH_3 gas and are not been deactivated, can be adsorbed on the surface of the wafer 200.

[0053] As described above, by supplying the NH_3 gas together with the BDEAS gas under the aforementioned processing conditions, it is possible to change (deactivate) the state of the portion of the active intermediates generated by the pyrolysis of the BDEAS gas to a state that is difficult to be adsorbed on the surface of the wafer 200, which is reduced in the activity. That is, it is possible to lower the probability of adsorption of the intermediates (precursor) on the wafer 200. This makes it possible to appropriately reduce the amount of the intermediates (precursor) which can contribute to the formation of the first layer, and to appropriately reduce the degree of the supply rate controlling of the intermediates (precursor). As a result, it is possible to discharge (remove) a portion of the BDEAS gas supplied to the wafer 200 from the exhaust pipe 231 without contribution to the formation of the first layer. Consequently, it is possible to improve the step coverage of the SiOCN film formed on the wafer 200, to improve

the in-plane film thickness uniformity of the wafer, and to improve the controllability of the film thickness.

[0054] Moreover, in order to efficiently achieve the aforementioned effects, it is desirable that step 1 be performed under a condition in which the active intermediates generated by the pyrolysis of the BDEAS gas collide with the NH_3 gas before colliding with the surface of the wafer 200. That is, it is desirable that step 1 be performed under a condition in which the state is changed to a state that is difficult to be adsorbed on the surface of the wafer 200 before the portion of the aforementioned intermediates collide with the surface of the wafer 200.

[0055] In other words, in order to efficiently achieve the aforementioned effects, it is desirable that step 1 be performed under a condition in which a mean free path λ where the active intermediates generated by the pyrolysis of the BDEAS gas and the NH_3 gas collide with each other is smaller than a distance (interval) between an object on which an intermediate at a position closest to the surface of the wafer 200 is adsorbed and the surface of the wafer 200, that is, a wafer pitch. That is, it is desirable that step 1 be performed under a condition in which the aforementioned mean free path λ where the intermediates and NH_3 collide with each other is smaller than a distance (interval) between adjacent wafers 200, that is, a wafer pitch. The aforementioned mean free path λ can be obtained by using an equation of $\lambda=kT/(21/2\cdot P\sigma)$ where k is a Boltzmann constant, T is a processing temperature, P is a processing pressure and σ (= $4\pi r^2$) is a collision cross sectional area determined by a molecular radius r.

[0056] In addition, the NH_3 gas supplied together with the BDEAS gas is consumed by the reaction with the intermediates, or the like. Therefore, the supply flow rate of the NH_3 gas at step 1 may be set at a flow rate of 4 times or more and 30 times or less, specifically 10 times or more and 20 times or less, the supply flow rate of the BDEAS gas, in consideration of the consumption due to the reaction with the intermediates, or the like. By setting the supply flow rate of the NH_3 gas at a predetermined flow rate which falls within such a range, it is possible to more efficiently achieve the aforementioned effects.

[0057] After the first layer is formed on the wafer 200, the valves 243a and 243b are closed to stop the supply of each of the BDEAS gas and the NH_3 gas into the process chamber 201.

Then, the interior of the process chamber 201 is vacuum-exhausted and the gas or the like, which remains within the process chamber 201, is removed from the interior of the process chamber 201. At this time, the valves 243c and 243d are opened to supply an N_2 gas into the process chamber 201. The N_2 gas acts as a purge gas.

[0058] As the precursor, it may be possible to use, in addition to the BDEAS gas, a diaminosilane gas such as a bis (tertiary-butylamino) silane ($SiH_2[NH(C_4H_9)]_2$, abbreviation: BTBAS) gas, a bis (diethylpiperidino) silane ($SiH_2[NC_5H_8(C_2H_5)_2]_2$, abbreviation: BDEPS) gas or the like. Furthermore, as the precursor gas, it may be possible to use a monoaminosilane gas such as an (ethylmethylamino) silane ($SiH_3[N(CH_3)(C_2H_5)]$, abbreviation: EMAS gas, a (dimethylamino) silane ($SiH_3[N(CH_3)_2]$, abbreviation: DMAS) gas or the like, or a triaminosilane gas such as a trisdimethylaminosilane ($SiH[N(CH_3)_2]_3$, abbreviation: 3DEAS) gas, a tris (diethylamino) silane ($SiH[N(C_2H_5)_2)_3$ or the like. These gases are halogen-free gases including Si-N bonds and Si-H bonds and containing an amino group. When these substances are used as the precursor, there may be a case that the formation of the first layer goes ahead under a situation in which the supply rate controlling of the intermediates is more dominant than the surface reaction rate controlling of the intermediates. In this case, the supply rate controlling of the intermediates can be appropriately reduced by deactivating the active intermediates generated by the pyrolysis of the precursor by the action of the aforementioned deactivating agent. As a result, it is possible to achieve the aforementioned effects, such as improving the step coverage of the film formed on the wafer 200.

[0059] As the deactivating agent, it may be possible to use, in addition to the NH_3 gas, an ethylamine-based gas such as a triethylamine ($(C_2H_5)_3N$, abbreviation: TEA) gas, a diethylamine ($(C_2H_5)_2NH$, abbreviation: DEA) gas, a monoethylamine ($C_2H_5NH_2$, Abbreviation: MEA) gas or the like, a methylamine-based gases such as a trimethylamine ($(CH_3)_3N$, abbreviation: TMA) gas, a dimethylamine ($(CH_3)_2NH$, abbreviation: DMA) gas, a monomethylamine (CH_3NH_2, abbreviation: MMA) gas or the like, a propylamine-based gas such as a tripropylamine ($(C_3H_7)_3N$, abbreviation: TPA) gas, a dipropylamine ($(C_3H_7)_2NH$, abbreviation: DPA) gas, a monopropylamine ($C_3H_7NH_2$, abbreviation: MPA) gas or the like, an isopropylamine-based gas

such as a triisopropylamine ($[(CH_3)_2CH]_3N$, abbreviation: TIPA) gas, a diisopropylamine ($[(CH_3)_2CH]_2NH$, abbreviation: DIPA) gas, a monoisopropylamine ($(CH_3)_2CHNH_2$, (abbreviation: MIPA) gas or the like, a butylamine-based gas such as a tributylamine ($(C_4H_9)_3N$, abbreviation: TBA) gas, a dibutylamine ($(C_4H_9)_2NH$, abbreviation: DBA) gas, a monobutylamine ($C_4H_9NH_2$, abbreviation: MBA) gas or the like, or an isopropylamine-based gas such as a triisobutylamine ($[(CH_3)_2CHCH_2]_3N$, abbreviation: TIBA) gas, a diisobutylamine ($[(CH_3)_2CHCH_2]_2NH$, abbreviation: DIBA) gas, a monoisobutylamine ($(CH_3)_2CHCH_2NH_2$, abbreviation: MIBA) gas or the like. These gases are N-containing gases expressed by a general formula NR_3 (where R is a hydrogen atom, or various kinds of alkyl groups described above), and act to deactivate a portion of the active intermediates generated by the pyrolysis of various kinds of precursors described above so as to modify them into deactivators which are difficult to be adsorbed on the surface of the wafer 200.

[0060] As the inert gas, it may be possible to use, in addition to the N_2 gas, for example, a rare gas such as an Ar gas, a He gas, a Ne gas, a Xe gas or the like. This also applies to step 2 which will be described later.

[Step 2]

[0061] After step 1 is completed, an O_2 gas is supplied to the wafer 200 in the process chamber 201, namely, to the first layer formed on the wafer 200. Specifically, the opening/closing control of the valves 243b to 243d is performed in the same procedure as the opening/closing control of the valves 243a, 243c and 243d at step 1. The flow rate of the O_2 gas is adjusted by the MFC 241b. The O_2 gas is supplied into the process chamber 201 via the nozzle 249b and is exhausted from the exhaust pipe 231. At this time, the O_2 gas is supplied to the wafer 200.

[0062] The processing conditions at this step may be exemplified as follows:

Processing pressure: 133 to 3,999 Pa

O_2 gas supply flow rate: 1,000 to 10,000 sccm

Gas supply time: 1 to 120 seconds.

[0063] Other processing conditions such as the processing temperature and the like may be

similar to the processing conditions of step 1.

[0064] By supplying the O_2 gas to the wafer 200 under the aforementioned conditions, at least a portion of the first layer formed on the wafer 200 at step 1 can be modified (oxidized). This makes it possible to desorb H or the like from the first layer and to incorporate the O component contained in the O_2 gas into the first layer. By oxidizing the first layer, a silicon oxycarbonitride layer (SiOCN layer), which is a layer containing Si, O, C, and N, is formed as a second layer on the wafer 200.

[0065] After the second layer is formed on the wafer 200, the valve 243b is closed to stop the supply of the O_2 gas into the process chamber 201. Then, the gas or the like remaining within the process chamber 201 is removed from the interior of the process chamber 201 according to the same processing procedures as those of step 1.

[0066] As the oxidizing agent, it may be possible to use, in addition to the O_2 gas, a nitrous oxide (N_2O) gas, a nitrogen monoxide (NO) gas, a nitrogen dioxide (NO_2) gas, a carbon monoxide (CO) gas, a carbon dioxide (CO_2) gas, an ozone (O_3) gas, a hydrogen peroxide (H_2O_2) gas, water vapor (H_2O gas), an O_2 gas+hydrogen (H_2) gas, or the like.

[Performing a Predetermined Number of Times]

[0067] A cycle which non-simultaneously, that is, non-synchronously and alternately, performs steps 1 and 2 is implemented a predetermined number of times (n times, where n is an integer of 1 or more), whereby a SiOCN film having a predetermined composition and a predetermined thickness can be formed on the wafer 200. The aforementioned cycle may be repeated multiple times. That is, the thickness of the second layer formed per one cycle may be set smaller than a desired thickness and the aforementioned cycle may be repeated multiple times until the thickness of the SiOCN film formed by laminating the second layer becomes equal to the desired thickness.

(After-Purge and Atmospheric Pressure Return)

[0068] After the aforementioned film-forming step is completed, the N_2 gas is supplied from the

respective gas supply pipes 232c and 232d into the process chamber 201 and is exhausted from the exhaust pipe 231. Thus, the interior of the process chamber 201 is purged and the gas or the reaction byproduct, which remains within the process chamber 201, is removed from the interior of the process chamber 201 (after-purge). Thereafter, the internal atmosphere of the process chamber 201 is substituted by an inert gas (inert gas substitution). The internal pressure of the process chamber 201 is returned to an atmospheric pressure (atmospheric pressure return).

(Boat Unloading and Wafer Discharging)

[0069] Thereafter, the seal cap 219 is moved down by the boat elevator 115 to open the lower end of the reaction tube 203. Then, the processed wafers 200 supported on the boat 217 are unloaded from the lower end of the reaction tube 203 to the outside of the reaction tube 203 (boat unloading). The processed wafers 200 are discharged from the boat 217 (wafer discharging).

(3) Effects according to the Present Embodiment

[0070] According to the present embodiment, one or more effects as set forth below may be achieved.

[0071] (a) By supplying the BDEAS gas to the wafer 200 under the condition in which the BDEAS gas is pyrolyzed when the BDEAS gas exists alone in the process chamber 201 at step 1, it is possible to generate active intermediates. This makes it possible to allow the formation of the first layer on the wafer 200 to go ahead efficiently, and to allow the formation of the SiOCN film on the wafer 200 to go ahead at a practical rate.

[0072] (b) By performing the film-forming process under the condition in which the BDEAS gas is pyrolyzed when the BDEAS gas exists alone in the process chamber 201, that is, under a relatively high temperature condition in which the pyrolysis of the BDEAS gas occurs, at step 1, it is possible to allow the SiOCN film formed on the wafer 200 to become a high-quality film having a small amount of impurity and excellent ashing resistance or etching resistance.

[0073] (c) By supplying the NH_3 gas together with the BDEAS gas to the wafer 200 at step 1, it

is possible to modify a portion of the active intermediates generated by the pyrolysis of the BDEAS gas into deactivators. Thus, even in a situation in which the supply rate controlling of the intermediates is more dominant than the surface reaction rate controlling of the intermediates, and further in a situation of the supply rate controlling of the intermediates rather than the surface reaction rate controlling of the intermediates, it becomes possible to appropriately reduce the degree of the supply rate of the intermediates. As a result, it is possible to improve the step coverage of the SiOCN film formed on the wafer 200, to improve the in-plane film thickness uniformity of the wafer, and to improve the controllability of the film thickness. This film-forming method is particularly effective when the underlying surface under the film-forming process has a 3D structure such as a line and space shape, a hole shape, a fin shape or the like.

[0074] In addition, by performing step 1 under the condition in which a portion of the active intermediates generated by the pyrolysis of the BDEAS gas collide with the NH_3 gas before colliding with the surface of the wafer 200 and the remainder of the active intermediates described above collide with the surface of the wafer 200, it is possible to more reliably achieve the aforementioned effects of reducing the degree of the supply rate controlling of the intermediates. That is, by performing step 1 under the condition in which the mean free path λ where the active intermediates generated by the pyrolysis of the BDEAS gas and the NH_3 gas collide with each other is smaller than the wafer pitch, it is possible to more reliably achieve the aforementioned effects, such as appropriately lowering the probability of adsorption to the wafer 200 and improving the step coverage of the SiOCN film formed on the wafer 200.

[0075] (d) By using an alternate supply method in which steps 1 and 2 are non-simultaneously performed a predetermined number of times, it is possible to further improve the step coverage, the in-plane film thickness uniformity, the film thickness controllability and the like of the SiOCN film formed on the wafer 200, compared with a case of using a simultaneous supply method in which steps 1 and 2 are simultaneously performed a predetermined number of times.

[0076] (e) By using a Cl-free BDEAS gas as the precursor, it is possible to prevent Cl from being mixed into the SiOCN film formed on the wafer 200. This makes it possible to allow the

SiOCN film formed on the wafer 200 to become, for example, a high-quality film having excellent ashing resistance or etching resistance.

[0077] (f) The effects mentioned above can be similarly achieved in the case where the aforementioned precursor other than the BDEAS gas is used, or in the case where the aforementioned deactivating agent other than the NH_3 gas is used, or in the case where the aforementioned oxidizing agent other than the O_2 gas is used, or in the case where the aforementioned inert gas other than the N_2 gas is used.

<Other Embodiments>

[0078] While one embodiment of the present disclosure has been specifically described above, the present disclosure is not limited to the aforementioned embodiment but may be variously modified without departing from the spirit of the present disclosure.

[0079] For example, in the aforementioned embodiment, there has been described an example in which steps 1 and 2 are sequentially performed, for example, an example in which the reactant is supplied after the precursor is supplied. However, the present disclosure is not limited the aforementioned embodiment, and the supply order of the precursor and the reactant may be reversed. That is, the precursor may be supplied after the reactant is supplied. By changing the supply order, it is possible to change the quality and composition ratio of a film as formed.

[0080] Furthermore, for example, in the aforementioned embodiment, there has been described an example in which a cycle which non-simultaneously performs steps 1 and 2 is performed a predetermined number of times to form a SiOCN film on the wafer 200, but step 2 may be omitted. That is, by performing step 1 a predetermined number of times (once or more), a silicon carbonitride film (SiCN film), which is a film containing Si, C, and N, may be formed on wafer 200. When step 1 is performed, the aforementioned precursor such as the BDEAS gas or the like is supplied to the wafer 200 under the condition in which the precursor is pyrolyzed when the precursor exists alone in the process chamber 201. Thus, it is possible to allow the formation of the first layer on the wafer 200 to go ahead efficiently, and to allow the formation of the SiCN film on the wafer 200 to go ahead at a practical rate. In addition, when step 1 is

performed, the aforementioned deactivating agent such as the NH_3 gas is supplied to the wafer 200 together with the precursor. Thus, even in a situation in which the supply rate controlling of the intermediates is more dominant than the surface reaction rate controlling of the intermediates, it is possible to appropriately reduce the supply rate of the intermediates. Thus, it is possible to effectively achieve the aforementioned effects, such as improving the step coverage of the SiCN film formed on the wafer 200.

[0081] Recipes used in substrate processing may be prepared individually according to the processing contents and may be stored in the memory device 121c via a telecommunication line or an external memory device 123. Moreover, at the start of substrate processing, the CPU 121a may properly select an appropriate recipe from the recipes stored in the memory device 121c according to the processing contents. Thus, it is possible for a single substrate processing apparatus to form films of different kinds, composition ratios, qualities and thicknesses with enhanced reproducibility. In addition, it is possible to reduce an operator's burden and to quickly start the substrate processing while avoiding an operation error.

[0082] The recipes mentioned above are not limited to newly-prepared ones but may be prepared by, for example, modifying the existing recipes already installed in the substrate processing apparatus. When modifying the recipes, the modified recipes may be installed in the substrate processing apparatus via a telecommunication line or a recording medium storing the recipes. In addition, the existing recipes already installed in the substrate processing apparatus may be directly modified by operating the input/output device 122 of the existing substrate processing apparatus.

[0083] In the aforementioned embodiment, there has been described an example in which films are formed using a batch-type substrate processing apparatus capable of processing a plurality of substrates at a time. The present disclosure is not limited to the aforementioned embodiment but may be appropriately applied to, for example, a case where films are formed using a single-wafer-type substrate processing apparatus capable of processing a single substrate or several substrates at a time. In addition, in the aforementioned embodiment, there has been described an example in which films are formed using a substrate processing apparatus provided with a

hot-wall-type process furnace. The present disclosure is not limited to the aforementioned embodiment but may be appropriately applied to a case where films are formed using a substrate processing apparatus provided with a cold-wall-type process furnace.

[0084] In the case of using these substrate processing apparatuses, a film-forming process may be performed by the processing procedures and processing conditions similar to those of the embodiment described above. Effects similar to those of the embodiment described above may be achieved.

[0085] The embodiment, other embodiments and the like described above may be appropriately combined with one another. The processing procedures and processing conditions at this time may be similar to, for example, the processing procedures and processing conditions of the aforementioned embodiment.

Example

[0086] In an example, a SiOCN film was formed on a wafer using the substrate processing apparatus illustrated in FIG. 1 and by the film-forming sequence illustrated in FIG. 4. When performing step 1, an NH_3 gas was supplied to the wafer as a deactivating agent together with a BDEAS gas. The processing conditions at steps 1 and 2 were set to predetermined conditions which fall within the processing condition range described in the aforementioned embodiment.

[0087] In a comparative example, a cycle which alternately performs a step of supplying a BDEAS gas to a wafer and a step of supplying an O_2 gas to the wafer was implemented a predetermined number of times using the substrate processing apparatus illustrated in FIG. 1 to form a SiOCN film on the wafer. At the step of supplying the BDEAS gas, the supply of the NH_3 gas to the wafer was not performed, and the BDEAS gas was supplied alone. Except for this point, the processing procedures and processing conditions in the comparative example were set similar to those of the example.

[0088] In a reference example, a cycle which alternately performs a step of supplying a BDEAS gas to a wafer and a step of supplying an O_2 gas to the wafer was implemented a predetermined number of times using the substrate processing apparatus illustrated in FIG. 1 to form a SiOCN

film on the wafer. When the step of supplying the BDEAS gas was performed, an H_2 gas was supplied to the wafer together with the BDEAS gas. The supply flow rate of the H_2 gas was set similar to the supply flow rate of the NH_3 gas of the example. Except for this point, the processing procedures and processing conditions in the reference example were set similar to those of the example.

[0089] Then, the step coverages (step coverage characteristics, hereinafter also referred to as S/C) of the SiOCN films of the example, the comparative example, and the reference example were each measured. The S/C means that the larger the value, the better the step coverage. As a result of the measurements, it was found that the S/C of these films were 86%, 75%, and 68% in the order of the example, the comparative example, and the reference example. That is, it was found that the example in which the NH_3 gas acting as a deactivating agent when the BDEAS gas was supplied to the wafer together with the NH_3 gas can have more improved S/C of the film formed on the wafer than the comparative example and the reference example in which the supply of the NH_3 gas was not performed. Furthermore, it could be seen that the reference example in which the H_2 gas was supplied together with the BDEAS gas when the BDEAS gas was supplied to the wafer has more reduced S/C of the film formed on the wafer than the comparative example in which the BDEAS gas was supplied alone to the wafer.

EXPLANATION OF REFERENCE NUMERALS

[0090] 200: wafer (substrate)

WHAT IS CLAIMED IS:

1. A method of manufacturing a semiconductor device, comprising:

forming a film on a substrate by performing, a predetermined number of times, forming a first layer by supplying a halogen-free precursor, which includes Si-N bonds and Si-H bonds and contains an amino group, to the substrate under a condition in which the precursor is pyrolyzed when the precursor exists alone,

wherein in the act of forming the first layer, a deactivating agent for deactivating intermediates generated by pyrolyzing the precursor is supplied to the substrate together with the precursor,.

2. The method of Claim 1, wherein in the act of forming the first layer, a portion of the intermediates is deactivated by the deactivating agent, and another portion of the intermediates other than the portion of the intermediates is adsorbed on a surface of the substrate.

3. The method of Claim 1, wherein in the act of forming the first layer, the intermediates deactivated by the deactivating agent are discharged from a space in which the substrate exists, without contributing to a reaction for forming the first layer.

4. The method of Claim 1, wherein the act of forming the first layer is performed under a condition in which a supply rate controlling of the intermediates becomes more dominant than a surface reaction rate controlling of the intermediates.

5. The method of Claim 1, wherein the act of forming the first layer is performed under a condition of a supply rate controlling of the intermediates.

6. The method of Claim 1, wherein a degree of a supply rate controlling of the intermediates in the act of forming the first layer becomes lower by the deactivating agent than a

degree of the supply rate controlling of the intermediates when the precursor exists alone.

7. The method of Claim 1, wherein in the act of forming the first layer, the deactivating agent is caused to collide with a portion of the intermediates, and another portion of the intermediates other than the portion of the intermediates is caused to collide with a surface of the substrate without colliding with the deactivating agent.

8. The method of Claim 1, wherein the act of forming the first layer is performed under a condition in which a portion of the intermediates collides with the deactivating agent, and another portion of the intermediates other than the portion of the intermediates collides with a surface of the substrate without colliding with the deactivating agent.

9. The method of Claim 1, wherein in the act of forming the first layer, a portion of the intermediates is changed to a state in which the portion is difficult to be adsorbed on a surface of the substrate, and another portion of the intermediates other than the portion of the intermediates is adsorbed on the surface of the substrate.

10. The method of Claim 1, wherein the act of forming the first layer is performed under a condition in which a portion of the intermediates is changed to a state in which the portion is difficult to be adsorbed on a surface of the substrate and another portion of the intermediates other than the portion of the intermediates is adsorbed on the surface of the substrate.

11. The method of Claim 1, wherein the act of forming the first layer is performed under a condition in which a mean free path where the intermediates and the deactivating agent collide with each other is smaller than a distance between an object on which an intermediate located at a position closest to a surface of the substrate is adsorbed and the surface of the substrate.

12. The method of Claim 1, wherein in the act of forming the film, the film is formed on

each of a plurality of substrates at a time, and

wherein the act of forming the film is performed under a condition in which a mean free path where the intermediates and the deactivating agent collide with other is smaller than a distance between adjacent substrates.

13. The method of Claim 1, wherein the deactivating agent includes an N-containing gas expressed by a general formula NR_3, wherein R is a hydrogen atom or an alkyl group.

14. The method of Claim 13, wherein in the act of forming the first layer, N of the NR_3 is bonded to an element constituting a portion of the intermediates, and another portion of the intermediates other than the portion of the intermediates is adsorbed on a surface of the substrate.

15. The method of any one of Claims 1 to 14, further comprising forming a second layer by supplying a reactant to the substrate to modify the first layer,

wherein the act of forming the film includes performing, the predetermined number of times, a cycle which non-simultaneously performs the act of forming the first layer and the act of forming the second layer.

16. The method of Claim 13, wherein the precursor further contains C,

wherein the reactant is an oxidizing agent,

wherein the first layer is a layer containing Si, C, and N,

wherein the second layer is a layer containing Si, O, C, and N, and

wherein the film is a film containing Si, O, C, and N.

17. A substrate processing apparatus, comprising:

a process chamber in which a substrate is processed;

a heater configured to heat the substrate in the process chamber;

a precursor supply system configured to supply a halogen-free precursor, which includes

Si-N bonds and Si-H bonds and contains an amino group, to the substrate in the process chamber;

a deactivating agent supply system configured to supply a deactivating agent for deactivating intermediates generated by pyrolyzing the precursor to the substrate in the process chamber; and

a controller configured to control the heater, the precursor supply system, and the deactivating agent supply system so as to perform a process in the process chamber, the process including:

forming a film on the substrate by performing, a predetermined number of times, forming a first layer by supplying the precursor to the substrate under a condition in which the precursor is pyrolyzed when the precursor exists alone,

wherein in the act of forming the first layer, the deactivating agent is supplied to the substrate together with the precursor.

18. A program that causes, by a computer, a substrate processing apparatus to perform a process in a process chamber of the substrate processing apparatus, the process comprising:

forming a film on a substrate by performing, a predetermined number of times, forming a first layer by supplying a halogen-free precursor, which includes Si-N bonds and Si-H bonds and contains an amino group, to the substrate under a condition in which the precursor is pyrolyzed when the precursor exists alone,

wherein in the act of forming the first layer, a deactivating agent for deactivating intermediates generated by pyrolyzing the precursor is supplied to the substrate together with the precursor.