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United States Patent Application Publication

20250259830

Kind Code

A1

Publication Date

August 14, 2025

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FILM FORMING APPARATUS

Abstract

A film forming apparatus configured to form a metal oxide film or a metal nitride film through atomic layer deposition by alternately introducing metal compound gas and an OH radical or an NH radical in a reaction container. The film forming apparatus including: the reaction container; and at least one plasma generator provided outside the reaction container and configured to generate a first plasma including an oxygen radical or a nitrogen radical when oxygen or nitrogen is supplied and generate a second plasma including a hydrogen radical when hydrogen is supplied. The OH radical is generated by collision between the oxygen radical and the hydrogen radical or the NH radical is generated by collision between the nitrogen radical and the hydrogen radical in a downstream region from an outlet of the at least one plasma generator to an inner space of the reaction container.

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Appl. No.: 19/169953

Filed: April 03, 2025

Foreign Application Priority Data

JP	2021-140476	Aug. 30, 2021
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Related U.S. Application Data

parent US continuation 17897170 20220828 PENDING child US 19169953

Publication Classification

Int. Cl.: H01J37/32 (20060101); C23C16/44 (20060101); C23C16/455 (20060101)

U.S. Cl.:

CPC H01J37/32871 (20130101); C23C16/4402 (20130101); C23C16/45548 (20130101); C23C16/45553 (20130101); H01J37/3244 (20130101); H01J2237/332 (20130101)

Background/Summary

CROSS REFERENCE TO RELATED APPLICATION [0001] This application is a continuation of U.S. patent application Ser. No. 17/897,170, which was filed Aug. 28, 2022, and was based upon and claims the benefit of priority to Japanese Patent Application No. 2021-140476 filed on Aug. 30, 2021, the entire contents of all of the foregoing applications are incorporated herein by reference.

BACKGROUND

[0002] The present disclosure relates to, for example, a film forming apparatus that forms a metal oxide film or a metal nitride film on a subject in a reaction container by using an OH radical or an NH radical through atomic layer deposition (ALD).

[0003] By using an OH radical, a resist is removed in JP-A-2008-085231 and JP-A-2008-109050, bacteria in water are killed in JP-A-2012-096141, substances to be purged are decomposed to perform clarification in JP-A-2013-086072, nitric acid is produced in JP-A-2016-150888, an organic binder or a protective agent undergoes oxidative destruction from above a conductive layer to improve conductivity in JP-A-2020-113654, and a metal oxide film is formed on powder by ALD in JP-B-6787621 by the present applicant. In JP-A-2008-085231, JP-A-2008-109050, JP-A-2012-096141, JP-A-2013-086072, JP-A-2016-150888, JP-A-2020-113654, JP-B-6787621, and JP-B-4694209, an OH radical is generated by plasma excitation on water vapor. Furthermore, in JP-B-6787621, a metal nitride film is formed by using an NH radical. The NH radical is generated by plasma excitation on NH.sub.3.

[0004] In JP-B-4694209, an oxygen radical necessary for forming an oxide film on a substrate is generated by plasma excitation on oxygen O.sub.2 and hydrogen H.sub.2 in a treatment chamber. Thus, unlike in the use of H.sub.2O or ozone O.sub.3, a moisture generator or an ozone generator is not necessary, contributing to cost reduction.

[0005] According to JP-A-2008-085231, JP-A-2008-109050, JP-A-2012-096141, JP-A-2013-086072, JP-A-2016-150888, JP-A-2020-113654, JP-B-6787621, and JP-B-4694209, a moisture generator for generating an OH radical is necessary, and the introduction of water vapor to a subject of treatment less resistant to moisture may cause damage to a surface of the subject of treatment.

[0006] According to JP-B-6787621, in a process of generating NH* (* indicates a radical) by decompose NH.sub.3 by plasma, it is assumed that the following states are mixed:

$$\text{NH.sub.3} \rightleftharpoons \text{NH}^* + 2\text{H}^* \rightleftharpoons \text{NH}^* + \text{H.sub.2}$$

$$\text{NH.sub.3} \rightleftharpoons \text{NH.sub.2} + \text{N}^* \rightleftharpoons \text{NH}^* + 2\text{H}^* \rightleftharpoons \text{NH}^* + \text{H.sub.2}$$

$$\text{NH.sub.3} \rightleftharpoons \text{N}^* + 3\text{H}^* \rightleftharpoons \text{NH}^* + 2\text{H}^* \rightleftharpoons \text{NH}^* + \text{H.sub.2}$$

[0007] An NH radical is generated with low efficiency because of the mixed states.

[0008] According to JP-B-4694209, in a process of decomposing oxygen O.sub.2 and hydrogen H.sub.2 by heat at 500° C. to 600° C. to generate an oxygen radical O*, thermal reactions occur as follows (paragraph [0032]):

H.sub.2+O.sub.2.fwdarw.H*+HO.sub.2

O.sub.2+H*.fwdarw.OH*+O*

H.sub.2+O*.fwdarw.H*+OH*

H.sub.2+OH*.fwdarw.H*+H.sub.2O

[0009] Although JP-B-4694209 does not aim at generating OH* (OH radical), the thermal excitation of oxygen O.sub.2 and hydrogen H.sub.2 generates OH* (OH radical). However, an OH radical is generated with low efficiency because of the mixed states. This is because in the treatment chamber of JP-B-4694209, a collision of oxygens or hydrogens leads to a reaction that causes transition to a stabilized system as follows:

O+O.fwdarw.O.sub.2

H+H.fwdarw.H.sub.2

O+OH.fwdarw.O.sub.2H

H+OH.fwdarw.H.sub.2O

Description

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 illustrates a first embodiment and a second embodiment of a film forming apparatus according to the present disclosure;

[0011] FIG. 2 is a timing chart indicating the opening/closing operations of valves in the first embodiment;

[0012] FIG. 3 is a timing chart indicating a cycle of ALD performed in the first embodiment;

[0013] FIG. 4 is a timing chart indicating the opening/closing operations of valves in the second embodiment;

[0014] FIG. 5 is a timing chart indicating a cycle of ALD performed in the second embodiment;

[0015] FIG. 6 illustrates a third embodiment of a film forming apparatus according to the present disclosure;

[0016] FIG. 7 illustrates a fourth embodiment of a film forming apparatus according to the present disclosure;

[0017] FIG. 8 is a timing chart indicating the opening/closing operations of valves in the fourth embodiment; and

[0018] FIG. 9 illustrates a structure in which positive ions and negative ions or the like are removed at an intermediate point of a pipe by using charge held by the ions.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0019] The following disclosure provides many different embodiments, or examples, for implementing different features of the provided subject matter. These are, of course, merely examples and are not intended to be limiting. In addition, the disclosure may repeat reference numerals and/or letters in the various examples. This repetition is for the purpose of simplicity and

clarity and does not in itself dictate a relationship between the various embodiments and/or configurations discussed. Further, when a first element is described as being “connected” or “coupled” to a second element, such description includes embodiments in which the first and second elements are directly connected or coupled to each other, and also includes embodiments in which the first and second elements are indirectly connected or coupled to each other with one or more other intervening elements in between.

[0020] In the following disclosure, different embodiments and examples are provided for implementing different characteristics of a presented subject. The embodiments and examples are merely exemplary and are not intended to be limiting. Furthermore, in the present disclosure, reference numerals and/or characters may be repeated in various examples. The repetition is performed for simplicity and clarification and does not need to be associated with various embodiments and/or described configurations. Moreover, a description that a first element is “connected” or “coupled” to a second element includes an embodiment in which the first element and the second element are directly connected or coupled to each other and an embodiment in which the first element and the second element are indirectly connected or coupled to each other with at least one element interposed between the first and second elements. When the first element “moves” relative to the second element in a description, such a description includes an embodiment of a movement of at least one of the first element and the second element relative to the other of the elements.

[0021] The present disclosure provides a film forming apparatus that efficiently generates an OH radical or an NH radical with high reactivity to improve the efficiency of film formation, the OH or NH radical being necessary for forming a metal oxide film or a metal nitride film on a subject in a reaction container by ALD.

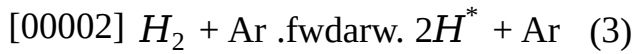
[0022] (1) In accordance with one of some aspect, there is provided a film forming apparatus configured to form a metal oxide film or a metal nitride film through atomic layer deposition by alternately introducing metal compound gas and an OH radical or an NH radical in a reaction container, [0023] the film forming apparatus comprising: [0024] the reaction container; and [0025] at least one plasma generator provided outside the reaction container and configured to generate a first plasma including an oxygen radical or a nitrogen radical when oxygen or nitrogen is supplied and generate a second plasma including a hydrogen radical when hydrogen is supplied, [0026] wherein the OH radical is generated by collision between the oxygen radical and the hydrogen radical or the NH radical is generated by collision between the nitrogen radical and the hydrogen radical in a downstream region from an outlet of the at least one plasma generator to an inner space of the reaction container.

[0027] According to one aspect of the present disclosure, from metal compound gas adsorbed to an object in the reaction container, organic substances or inorganic substances other than metallic components are dissociated by an OH radical, and the metal compound gas is oxidized into metal oxide by the OH radical. Alternatively, from metal compound gas adsorbed to an object in the reaction container, organic substances or inorganic substances other than metallic components are dissociated by an NH radical, and the metal compound gas is nitrified into metal nitride by the NH radical. The metal oxide or the metal nitride is sequentially deposited at an atomic layer level, so that a metal oxide film or a metal nitride film is formed on the object.

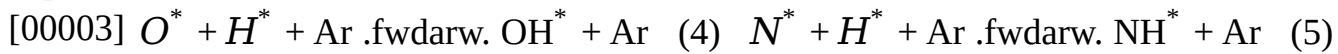
[0028] If the carrier gas is, for example, argon Ar, the first plasma includes an oxygen radical O^* or a nitrogen radical N^* that is dissociated from an oxygen molecule or a nitrogen molecule as indicated in expressions (1) and (2) below. Moreover, electrons and ions are dissociated in the first plasma. It is assumed that many of the electrons and the ions are deactivated downstream of the first plasma and only the oxygen radical and the nitrogen radical, which are protected by carrier gas Ar, are left in the pipe.

[00001] $O_2 + Ar \rightarrow 2O^* + Ar$ (1) $N_2 + Ar \rightarrow 2N^* + Ar$ (2)

[0029] In the second plasma, a hydrogen radical dissociated from a hydrogen molecule is included as indicated by expression (3) below. Also in this case, it is assumed that electrons and ions in the second plasma are deactivated and only the hydrogen radical protected by the carrier gas Ar is left.



[0030] In a downstream region from an outlet of the at least one plasma generator to an inner space of the reaction container, the oxygen radical O^* or the nitrogen radical N^* and the hydrogen radical H^* are in time division or simultaneously introduced and merged each other. With this configuration, the oxygen radical O^* or the nitrogen radical N^* and the hydrogen radical H^* are joined to collide with each other, thereby generating an OH radical or an NH radical by a reaction expressed in (4) or (5) below.



[0031] In other words, in (4), the oxygen radical O^* and the hydrogen radical H^* , which are in time division or simultaneously introduced into the reaction container and are caused to collide and are coupled with each other for the first time in the reaction container so as to mainly generate an OH radical. Thus, as compared with the generation process of JP-B-4694209 in which thermal excitation is simultaneously performed on oxygen O.sub.2 and hydrogen H.sub.2 in a treatment container so as to generate an OH radical, the present disclosure can more efficiently generate an OH radical. Likewise, mainly in (5), a nitrogen radical N^* and a hydrogen radical H^* are coupled to each other to mainly generate an NH radical. Thus, as compared with the generation process of JP-B-6787621 in which NH.sub.3 is excited to generate an NH radical, the present disclosure can more efficiently generate an NH radical.

[0032] (2) In aspect (1) of the present disclosure, the film forming apparatus may further comprises: [0033] a first gas source configured to supply oxygen or nitrogen; [0034] a second gas source configured to supply hydrogen; [0035] a third gas source configured to supply carrier gas; [0036] a first pipe causing the first gas source and the third gas source to communicate with the reaction container; and [0037] a second pipe causing the second gas source and the third gas source to communicate with the reaction container; and [0038] wherein the at least one plasma generator includes: [0039] a first plasma generator attached to the first pipe and configured to generate the first plasma; [0040] a second plasma generator attached to the second pipe and configured to generate the second plasma.

[0041] In this way, oxygen radicals and hydrogen radicals are supplied to the reaction container through separate routes. In this way, oxygen radicals and hydrogen radicals can be simultaneously supplied, for example, to the inner space of the reaction container located downstream of the outlets of the first and second plasma generators.

[0042] (3) In aspect (2) of the present disclosure, at least one of the first pipe and the second pipe includes a first charged particle remover, and the first charged particle remover can remove charged particles including dissociated ions and/or electrons in the plasma in the first plasma generator and the second plasma generator, by using charge of the charged particles. With this configuration, positive ions having positive charge, negative ions having negative charge, and electrons or the like are neutralized by emitting/injecting excessive electrons or additionally required electrons from the metallic pipe. In this way, charged particles including positive ions, negative ions, and electrons that are generated by the first and second plasma generators are removed by using charge held by the charged particles. Thus, an oxygen radical or a nitrogen radical and a hydrogen radical are mainly supplied into the reaction container. This can more efficiently generate an OH radical or an NH radical in the reaction container.

[0043] (4) In aspect (2) of the present disclosure, the first pipe and the second pipe may be coupled to the reaction container via a junction pipe. Thus, the reaction in (4) or (5) can be more efficient in a junction pipe that can be designed with a sufficiently smaller capacity than the reaction container, so that an OH radical or an NH radical that is generated in the junction pipe can be supplied into

the reaction container.

[0044] (5) Also in aspect (3) of the present disclosure, the first pipe and the second pipe may be coupled to the reaction container via the junction pipe. Thus, the same effect can be obtained as in aspects (1) to (3) of the present disclosure.

[0045] (6) Also in aspect (4) or (5) of the present disclosure, the junction pipe includes a second charged particle remover, and the second charged particle remover can remove charged particles including dissociated ions and/or electrons in the plasma in the first plasma generator and the second plasma generator, by using charge of the charged particles. Thus, the same effect can be obtained as in aspects (1), (2) and (4) of the present disclosure. In other words, charged particles including positive ions, negative ions, and electrons that are generated by the first and second plasma generators are removed by using charge held by the charged particles. Thus, an oxygen radical or a nitrogen radical and a hydrogen radical are mainly supplied into the junction pipe. Furthermore, positive ions, negative ions, and electrons or the like that are left in the junction pipe are removed by using charge held by the ions and electrons. This can more efficiently supply an OH radical or an NH radical into the reaction container.

[0046] (7) In aspect (2) or (3) of the present disclosure, the first pipe has a first valve between the first plasma generator and the reaction container, the second pipe has a second valve between the second plasma generator and the reaction container, and one of the first valve and the second valve may be closed while the other of the first valve and the second valve is opened. Thus, when the first valve is opened, an oxygen radical or a nitrogen radical that is generated by the first plasma generator is supplied into the reaction container. At this point, the second valve is closed, thereby preventing the oxygen radical or the nitrogen radical from flowing into the second plasma generator. Before or after this point, when the second valve is opened, a hydrogen radical generated by the second plasma generator is supplied into the reaction container. At this point, the first valve is closed, thereby preventing the hydrogen radical from flowing into the first plasma generator.

[0047] (8) In aspect (1) of the present disclosure, the film forming apparatus further comprising: [0048] a first gas source configured to supply oxygen or nitrogen; [0049] a second gas source configured to supply hydrogen; [0050] a third gas source configured to supply carrier gas; [0051] a first pipe coupled to the first gas source and the third gas source; and [0052] a second pipe coupled to the second gas source and the third gas source; and [0053] a junction pipe having one end coupled to the first pipe and the second pipe and the other end coupled to the reaction container; and [0054] wherein the at least one plasma generator is a plasma generator attached to the junction pipe and configured to generate the first and the second plasma, and wherein: [0055] the first pipe has a first valve upstream of the plasma generator; [0056] the second pipe has a second valve upstream of the plasma generator; [0057] the plasma generator generates plasma including an oxygen radical or a nitrogen radical when the first valve is opened and the second valve is closed, the radical being dissociated from the oxygen or the nitrogen; [0058] the plasma generator generates plasma including a hydrogen radical when the second valve is opened and the first valve is closed, the radical being dissociated from the hydrogen; and [0059] in the reaction container, the OH radical is generated by collision between the oxygen radical and the hydrogen radical, or the NH radical is generated by collision between the nitrogen radical and the hydrogen radical.

[0060] Thus, when the first valve is opened and the second valve is closed, an oxygen radical or a nitrogen radical that is generated by only one plasma generator is supplied into the reaction container. Before or after this point, when the second valve is opened and the first valve is closed, a hydrogen radical generated by one plasma generator is supplied into the reaction container.

[0061] (9) Also in aspect (8) of the present disclosure, the junction pipe includes a charged particle remover, and the charged particle remover can remove charged particles including dissociated ions and/or electrons in the plasma in the plasma generator, by using charge of the charged particles. Thus, the same effect can be obtained as in aspect (5) of the present disclosure.

1. First Embodiment

1.1. ALD Apparatus

[0062] FIG. 1 illustrates an example of an ALD apparatus **10**. The ALD apparatus **10** includes a reaction container **20** and at least one plasma generator provided outside the reaction container **20**. In the present embodiment, at least one plasma generator includes a first plasma generator **44** and a second plasma generator **54**. The ALD apparatus **10** further includes gas sources **30** to **60**. The reaction container **20** is a container for forming a film on a workpiece **1**. The reaction container **20** may include a placement part **21** on which the workpiece **1**, e.g., a substrate is placed. If the workpiece is powder or the like, the powder may be held in a dispersed state in the reaction container **20**. The gas sources **30** to **60** are coupled to the reaction container **20**, and a variety of gas is introduced into the reaction container **20**. An exhaust pipe **70** is coupled to the reaction container **20**, allowing a vacuum pump **71** to evacuate the reaction container **20**.

[0063] A source gas source **30** supplies metal compound gas, e.g., organic metallic gas that is source gas selected for a film deposited on the workpiece **1**. The source gas source **30** and the reaction container **20** are coupled to each other via a pipe **33** including a flow controller (MFC) **31** and a valve **32**. Source gas is supplied from the source gas source **30** into the reaction container **20** through the pipe **33** including the flow controller **31** and the valve **32** while the timing of supply and the flow rate are controlled.

[0064] An oxygen/nitrogen gas source **40** and a hydrogen gas source **50** are reactant gas sources. The oxygen/nitrogen gas source (first gas source) **40** contains oxygen when an oxide film is formed, and contains nitrogen when a nitride film is formed. The oxygen/nitrogen gas source **40** and the reaction container **20** are coupled to each other via a pipe **43** including a flow controller (MFC) **41**, a valve **42**, and a first plasma generator **44**. A valve **47** on the pipe **43** is optional in the first embodiment. If the valve **47** is installed, the valve **47** is fully opened all the time. The hydrogen gas source **50** and the reaction container **20** are coupled to each other via a pipe **53** including a flow controller (MFC) **51**, a valve **52**, and a second plasma generator **54**. A valve **57** on the pipe **53** is optional in the first embodiment. If the valve **57** is installed, the valve **57** is fully opened all the time.

[0065] A carrier gas source **60** contains inert gas, for example, argon Ar. In the present embodiment, argon Ar in the carrier gas source **60** is used as purge gas as well as carrier gas. For the use of gas, the carrier gas source **60** and the reaction container **20** can be coupled to each other via a pipe **63** including a flow controller (MFC) **61**, a valve **62**, and a valve **66**. Thus, argon Ar is supplied as purge gas into the reaction container **20** through the pipe **63** while the timing of supply and the flow rate are controlled. This can substitute argon gas Ar for an atmosphere in the reaction container **20**. The pipe **63** includes first to third branch pipes **63A** to **63C** downstream of the valve **62**. The first branch pipe **63A** is coupled to the pipe **33** via a valve **64**. The second branch pipe **63B** is coupled to the pipe **43** via a valve **65**. The third branch pipe **63C** is coupled to the pipe **53** via the valve **66**. With this configuration, argon Ar can be used as a carrier gas for source gas, oxygen, nitrogen, or hydrogen.

[0066] The first plasma generator **44** includes an induction coil **46** that serves as exciting means of oxygen or nitrogen and is wound around a nonmetallic pipe **45** made of, for example, quartz. A high-frequency power supply, which is not illustrated, is connected to the induction coil **46**. For example, the induction coil **46** applies electromagnetic energy of 20 W at a frequency of 13.56 MHz. The induction coil **46** generates inductively coupled plasma P1 of gas in the first plasma generator **44**. The plasma P1 contains an oxygen radical or a nitrogen radical that is dissociated from an oxygen molecule or a nitrogen molecule.

[0067] Likewise, the second plasma generator **54** includes an induction coil **56** that serves as exciting means of hydrogen and is wound around a nonmetallic pipe **55** made of, for example, quartz. The induction coil **56** generates inductively coupled plasma P2 of gas in the second plasma generator **54**. The plasma P2 contains a hydrogen radical dissociated from a hydrogen molecule.

1.2. ALD Method

[0068] An example of the formation of a metal oxide film, e.g., an Al_2O_3 film on the workpiece **1** will be described below. The oxygen/nitrogen gas source **40** contains oxygen and thus is also referred to as an oxygen gas source **40** hereafter. First, the workpiece **1** is conveyed into the reaction container **20**. In the first embodiment, the valves in FIG. **1** are opened and closed according to a timing chart in FIG. **2**, so that an ALD cycle is performed as indicated in FIG. **3**. The ALD cycle is a cycle including at least four steps of: the supply of a first precursor (source gas).
forward evacuation (including purge).
forward the supply of a second precursor (reactive gas).
forward evacuation (including purge). The evacuation is vacuum pumping through the vacuum pump **71**, and the purge is the supply of inert gas (purge gas) from the carrier gas source **60**. In either way, the atmosphere of the first or second precursor is substituted by a vacuum or purge gas atmosphere in the reaction container **20**. The thickness of a film formed on the workpiece **1** is proportionate to N indicating the number of ALD cycles. Thus, the ALD cycle is repeated N times where N denotes a required number of times.

1.2.1. Supply of source gas

[0069] First, the reaction container **20** is evacuated by the vacuum pump **71** and is set at, for example, 10⁻⁴ Pa. Subsequently, as illustrated in FIG. **2**, the valves **32**, **62**, and **64** are opened over a period T₁. Thus, source gas, for example, TMA ($\text{Al}(\text{CH}_3)_3$) from the source gas source **30** and carrier gas, for example, argon Ar from the carrier gas source **60** are supplied into the reaction container **20**, and the container is filled with the gas with a predetermined pressure, e.g., 1 to 10 Pa. In the first step (period T₁) of the ALD cycle in FIG. **3**, TMA penetrates the exposed surface of the workpiece **1**.

1.2.2. Purge

[0070] Thereafter, as the second step of the ALD cycle, the valves **32** and **64** are closed, the valve **62** is kept opened, and a valve **67** is opened over a period T₂ as indicated in FIG. **2**. Thus, purge gas is introduced into the reaction container **20** as indicated in FIG. **3**, and the purge gas substitutes for trimethylaluminum $\text{Al}(\text{CH}_3)_3$ in the reaction container **20**.

1.2.3. Introduction of Reactant Gas

[0071] Thereafter, as the third step of the ALD cycle, the valve **67** is closed, the valve **62** is kept opened, and the valves **42**, **52**, **65**, and **66** are opened over a period T₃ as indicated in FIG. **2**. Thus, oxygen gas from the oxygen gas source **40** and argon Ar as carrier gas from the carrier gas source **60** are supplied into the first plasma generator **44**. Concurrently, hydrogen gas from the hydrogen gas source **50** and argon Ar as carrier gas from the carrier gas source **60** are supplied into the second plasma generator **54**. In the first plasma generator **44**, the inductively coupled plasma P₁ including an oxygen radical is generated, the oxygen radical being dissociated from oxygen as indicated by the foregoing expression (1). The oxygen radical is supplied with carrier gas into the reaction container **20** through the pipe **43**. In the second plasma generator **54**, the inductively coupled plasma P₂ including a hydrogen radical is generated, the hydrogen radical being dissociated from hydrogen as indicated by the foregoing expression (3). The hydrogen radical is supplied with carrier gas into the reaction container **20** through the pipe **53** by a route different from that of an oxygen radical. Thus, the oxygen radical and the hydrogen radical are simultaneously supplied to the inner space of the reaction container **20** located downstream of the outlets of the first and second plasma generators **44** and **54**, for example.

[0072] In the reaction container **20**, the oxygen radical and the hydrogen radical join for the first time. Thus, in the reaction container **20**, an OH radical is generated by collision and combination of the oxygen radical and the hydrogen radical as indicated by the foregoing expression (4). The reaction container **20** is filled with the OH radical (OH*) as reactant gas with a predetermined pressure, e.g., 1 to 10 Pa (the period T₃ in FIG. **3**), so that the OH radical (OH*) penetrates the exposed surface of the workpiece **1**. Hence, on the exposed surface of the workpiece **1**, an organic substance CH_3 is dissociated from TMA($\text{Al}(\text{CH}_3)_3$) and a metal A₁ is oxidized, so that aluminum oxide Al_2O_3 is generated. This forms a metal oxide film over the exposed

surface of the workpiece **1**. Organic metallic gas can be saturated and adsorbed particularly on a hydroxy group (—OH) of the exposed surface of the workpiece **1** even at room temperature. This eliminates the need for forcibly heating the workpiece **1** during the formation of the film.

1.2.4. Purge

[0073] Thereafter, as the fourth step of the ALD cycle, the valves **42**, **52**, **65**, and **66** are closed, the valve **62** is kept opened, and the valve **67** is opened over a period T_4 as indicated in FIG. **2**. Thus, purge gas is introduced into the reaction container **20**, and the purge gas substitutes for reactant gas in the reaction container **20**. An Al.sub.2O.sub.3 film of 1 angstrom=0.1 nm is formed in each cycle, so that the ALD cycle may be repeated 100 times to form the film with a thickness of, for example, 10 nm. At the completion of all the ALD cycles, the workpiece **1** is conveyed out of the reaction container **20**.

2. Second Embodiment

[0074] In a second embodiment, in the ALD apparatus **10** of FIG. **1**, the valves in FIG. **1** are opened and closed according to a timing chart in FIG. **4**, so that an ALD cycle is performed as indicated in FIG. **5**. Unlike in the first embodiment, a valve **47** acting as a first valve and a valve **57** acting as a second valve are opened and closed in the second embodiment.

2.1. Supply of Source Gas

[0075] As illustrated in FIG. **4**, valves **32**, **62**, and **64** are opened over a period T_1 . Thus, source gas, for example, $\text{TMA(Al(CH.sub.3).sub.3)}$ from a source gas source **30** and carrier gas, for example, argon Ar from a carrier gas source **60** are supplied into a reaction container **20**, and the container is filled with the gas with a predetermined pressure, e.g., 1 to 10 Pa. In the first step (period T_1) of the ALD cycle in FIG. **5**, TMA penetrates the exposed surface of a workpiece **1**.

2.2. Purge

Thereafter, as the second step of the ALD cycle, the valves **32** and **64** are closed, the valve **62** is kept opened, and a valve **67** is opened over a period T_2 as indicated in FIG. **4**. Thus, purge gas is introduced into the reaction container **20** as indicated in FIG. **5**, and the purge gas substitutes for trimethylaluminum $\text{Al(CH.sub.3).sub.3}$ in the reaction container **20**.

2.3. Introduction of Reactant Gas

[0076] Subsequently, as the third step of the ALD cycle, the valve **67** is closed, the valve **62** is kept opened, and a valve **42**, the valve **47**, and a valve **65** are opened over a period T_3 as indicated in FIG. **4**. Thus, oxygen gas from an oxygen gas source **40** and argon Ar as carrier gas from the carrier gas source **60** are supplied into a first plasma generator **44**. In the first plasma generator **44**, an inductively coupled plasma P_1 including an oxygen radical is generated, the oxygen radical being dissociated from oxygen as indicated by the forgoing expression (1). The oxygen radical is supplied with carrier gas into the reaction container **20** through a pipe **43**. In this way, the reaction container **20** is filled with the oxygen radical with a predetermined pressure. At this point, the second valve **57** is closed, thereby preventing the oxygen radical from flowing into a second plasma generator **54**.

[0077] Thereafter, as indicated in FIG. **4**, the valves **42**, **47**, and **65** are closed, and the valve **52**, the valve **57**, and a valve **66** are opened over a period T_4 . Thus, hydrogen gas from a hydrogen gas source **50** is supplied into a second plasma generator **54** with argon Ar serving as carrier gas from the carrier gas source **60**. In the second plasma generator **54**, an inductively coupled plasma P_2 including a hydrogen radical is generated, the hydrogen radical being dissociated from hydrogen as indicated by the forgoing expression (3). The hydrogen radical is supplied with carrier gas into the reaction container **20** through a pipe **53** by a route different from that of an oxygen radical. In this way, the reaction container **20** is filled with the hydrogen radical with a predetermined pressure. At this point, the first valve **47** is closed, thereby preventing the hydrogen radical from flowing into a first plasma generator **44**.

[0078] In the reaction container **20**, the oxygen radical and the hydrogen radical join for the first time. Thus, in the reaction container **20**, an OH radical is generated by collision and combination of

the oxygen radical and the hydrogen radical as indicated by the foregoing expression (4). The reaction container **20** is filled with the OH radical (OH*) as reactant gas with a predetermined pressure, e.g., 1 to 10 Pa (the period T4 in FIG. 5), so that the OH radical (OH*) penetrates the exposed surface of the workpiece **1**. Hence, on the exposed surface of the workpiece **1**, aluminum oxide Al.sub.2O.sub.3 is generated as in the first embodiment.

2.4. Purge

[0079] Thereafter, as the fourth step of the ALD cycle, the valves **52**, **57**, and **66** are closed, the valve **62** is kept opened, and the valve **67** is opened over a period T5 as indicated in FIG. 4. Thus, purge gas is introduced into the reaction container **20**, and the purge gas substitutes for reactant gas in the reaction container **20**.

3. Third Embodiment

3.1. ALD Apparatus

[0080] FIG. 6 illustrates an example of an ALD apparatus **11**. In the ALD apparatus **11**, members having the same functions as the members of the ALD apparatus **10** in FIG. 1 are indicated by the same reference numerals as in FIG. 1, and an explanation thereof is omitted. The ALD apparatus **11** includes a first pipe **43** and a second pipe **53** that are coupled to a reaction container **20** via a junction pipe **80**.

3.2. ALD Method

[0081] In a third embodiment, in the ALD apparatus **11** of FIG. 6, valves in FIG. 6 are opened and closed according to the timing chart in FIG. 2, so that an ALD cycle is performed as indicated in FIG. 3. An ALD method in the third embodiment is different from the first embodiment only in the introduction of reactant gas (third step) in a period T3, and thus operations in the period T3 will be discussed below.

[0082] As the third step of the ALD cycle, a valve **67** is closed, a valve **62** is kept opened, and valves **42**, **52**, **65**, and **66** are opened over the period T3 as indicated in FIG. 2. Thus, oxygen gas from an oxygen gas source **40** and argon Ar as carrier gas from a carrier gas source **60** are supplied into a first plasma generator **44**. Concurrently, hydrogen gas from a hydrogen gas source **50** and argon Ar as carrier gas from the carrier gas source **60** are supplied into a second plasma generator **54**. In the first plasma generator **44**, an inductively coupled plasma P1 including an oxygen radical is generated, the oxygen radical being dissociated from oxygen as indicated by the foregoing expression (1). The oxygen radical is supplied with carrier gas into a junction pipe **80** through a pipe **43**. In the second plasma generator **54**, an inductively coupled plasma P2 including a hydrogen radical is generated, the hydrogen radical being dissociated from hydrogen as indicated by the foregoing expression (3). The hydrogen radical is supplied with carrier gas into the junction pipe **80** through a pipe **53**.

[0083] The oxygen radical and the hydrogen radical join for the first time in the junction pipe **80** located downstream of the outlets of the first and second plasma generators **44** and **54**, for example. Thus, in the junction pipe **80**, an OH radical is generated by collision and combination of the oxygen radical and the hydrogen radical as indicated by the foregoing expression (4). The OH radical (OH*) as reactant gas is supplied from the junction pipe **80** into the reaction container **20**. The reaction container **20** is filled with the OH radical with a predetermined pressure, e.g., 1 to 10 Pa, so that the OH radical (OH*) penetrates the exposed surface of a workpiece **1**. This forms a metal oxide film over the exposed surface of the workpiece **1** as in the first embodiment.

4. Fourth Embodiment

4.1. ALD Apparatus

[0084] FIG. 7 illustrates an example of an ALD apparatus **12**. In the ALD apparatus **12**, members having the same functions as the members of the ALD apparatus **10** in FIG. 1 are indicated by the same reference numerals as in FIG. 1, and an explanation thereof is omitted. The ALD apparatus **12** includes a first pipe **43** and a second pipe **53** that are coupled to a reaction container **20** via a junction pipe **90**. Furthermore, a plasma generator **94** is attached to the junction pipe **90**. The

junction pipe **90** is coupled to a branch pipe **63D**, which is a branch from a pipe **63** of carrier gas, via a valve **68**. In a fourth embodiment, a valve **42** and the valve **68** upstream of the plasma generator **94** act as first valves, and another valve **52** upstream of the plasma generator **94** acts as a second valve.

4.2. ALD Method

[0085] In the fourth embodiment, in the ALD apparatus **12** of FIG. 7, valves in FIG. 7 are opened and closed according to the timing chart in FIG. 8, so that an ALD cycle is performed as indicated in FIG. 5. An ALD method in the fourth embodiment is different from the second embodiment only in the introduction of reactant gas (third step) in periods T3 and T4, and thus operations in the periods T3 and T4 will be discussed below.

[0086] In FIG. 8, valve operations in periods T1, T2, and T5 are identical to those in FIG. 4. As the third step of the ALD cycle, a valve **67** is first closed, a valve **62** is kept opened, and the valves **42** and **68** are opened over the period T3 as indicated in FIG. 8. Thus, oxygen gas from an oxygen gas source **40** and argon Ar as carrier gas from a carrier gas source **60** are supplied into the first plasma generator **94**. In the first plasma generator **94**, an inductively coupled plasma P including an oxygen radical is generated, the oxygen radical being dissociated from oxygen as indicated by the foregoing expression (1). The oxygen radical is supplied with carrier gas into the reaction container **20** through the junction pipe **90**. In this way, the reaction container **20** is filled with the oxygen radical with a predetermined pressure.

[0087] Subsequently, the valve **42** is closed, the valve **62** is kept opened, and a valve **52** and the valve **68** are opened over the period T4 as indicated in FIG. 8. Thus, hydrogen gas from a hydrogen gas source **50** and argon Ar as carrier gas from a carrier gas source **60** are supplied into the plasma generator **94**. In the plasma generator **94**, an inductively coupled plasma P including a hydrogen radical is generated, the hydrogen radical being dissociated from hydrogen as indicated by the foregoing expression (3). The hydrogen radical is supplied with carrier gas into the reaction container **20** through the junction pipe **90**. In this way, the reaction container **20** is filled with the hydrogen radical with a predetermined pressure.

[0088] The oxygen radical and the hydrogen radical join for the first time in the reaction container **20** located downstream of the outlet of the plasma generators **94**, for example. Thus, in the reaction container **20**, an OH radical is generated by collision and combination of the oxygen radical and the hydrogen radical as indicated by the foregoing expression (4). The reaction container **20** is filled with the OH radical (OH*) as reactant gas with a predetermined pressure, e.g., 1 to 10 Pa (the period T4 in FIG. 8), so that the OH radical (OH*) penetrates the exposed surface of the workpiece **1**. Hence, on the exposed surface of the workpiece **1**, aluminum oxide Al.sub.2O.sub.3 is generated as in the first embodiment.

5. Modification

[0089] Instead of reactant gas used for forming a metal oxide film, nitrogen gas can be used to form a metal oxide film. In this case, the oxygen/nitrogen gas source **40** in, for example, FIG. 1 contains oxygen. Thus, an NH radical can be efficiently generated by using a nitride radical (N*) and a hydrogen radical (H*). For example, by using TDMAS(SiH[N(CH.sub.3).sub.2].sub.3) as source gas, a film of SiN can be formed on the surface of the workpiece **1**. For example, by using TDMAS(Ti[N(CH.sub.3).sub.2].sub.4) as source gas, TiN can be deposited on the surface of the workpiece **1**. In either case, a low-temperature process can be achieved by the presence of the NH radical.

[0090] The source gas is not limited to the foregoing organometallic compounds, and an inorganic metal compound may be used instead. For example, if SiCl.sub.4 is supplied as inorganic metal compound gas to the surface of the substrate **1**, the gas is adsorbed by SiCl.sub.2, and then the gas is exhausted after Cl.sub.2 is desorbed.



[0091] When an OH radical is supplied in this state, SiCl.sub.2 is oxidized into SiO.sub.2, and then the gas is exhausted after HCl is desorbed.



[0092] Additionally, a metal oxide film can be similarly formed by using TiCl.sub.4 or SiH.sub.2Cl.sub.2 as another inorganic metal compound gas.

[0093] Downstream of the first and second plasma generator **44** and **54** or the plasma generator **94**, the pipe **43** and the pipe **53**, which supply an oxygen radical, a hydrogen radical, or an OH radical into the reaction container **20** in FIG. **1**, and the junction pipe **80** in FIG. **6** or the junction pipe **90** in FIG. **7** may include, for example, a metallic pipe **100** illustrated in FIG. **9**. For example, an alternating-current power supply **101** that applies an alternating voltage changing from -100 V to +100 V at 10 Hz to 100 Hz may be connected to the metallic pipe **100**. It is particularly preferable to dispose a metallic bending pipe **102** in the metallic pipe **100** in FIG. **9**. With this configuration, positive ions or the like having positive charge are adsorbed by the pipe **100** when a negative voltage is applied to the metallic pipe **100**, whereas charged particles such as negative ions having negative charge are adsorbed by the pipe **100** when a positive voltage is applied to the metallic pipe **100**. Furthermore, the ions and charged particles are neutralized by emitting/injecting excessive electrons or additionally required electrons from the metallic pipe. In this way, positive ions, negative ions, and electrons or the like are removed by using charge held by the ions and electrons. Thus, in the first and second embodiments, an oxygen radical or a nitrogen radical and a hydrogen radical are mainly supplied into the reaction container **20**. In the third embodiment, an oxygen radical or a nitrogen radical and a hydrogen radical are mainly supplied into the junction pipe **80**, and an OH radical or an NH radical is mainly supplied into the reaction container **20**. In the fourth embodiment, an oxygen radical or a nitrogen radical and a hydrogen radical are mainly supplied into the junction pipe **90**, and an OH radical or an NH radical is mainly supplied into the reaction container **20**. The charged particle remover may be the installed metallic pipe **100**. Alternatively, the charged particle remover may be a mesh disposed at an intermediate point of the pipe, the mesh including charge adsorption fibers. The charge adsorption fibers may be grounded or may be connected to an alternating-current power supply.

[0094] Although only some embodiments of the present disclosure have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the embodiments without materially departing from the novel teachings and advantages of this disclosure. Accordingly, all such modifications are intended to be included within scope of this disclosure.

Claims

1. A film forming apparatus configured to form a metal oxide film or a metal nitride film through atomic layer deposition by alternately introducing metal compound gas and an OH radical or an NH radical in a reaction container, the film forming apparatus comprising: the reaction container; a first gas source configured to supply oxygen or nitrogen; a second gas source configured to supply hydrogen; a third gas source configured to supply carrier gas; a fourth gas source configured to supply the metal compound gas; a first pipe causing the first gas source and the third gas source to communicate with the reaction container; a second pipe causing the second gas source and the third gas source to communicate with the reaction container; a third pipe causing the fourth gas source to communicate with the reaction container; a junction pipe provided for joining the first pipe and the second pipe to connect with the reaction container; a first plasma generator attached to the first pipe and configured to generate a first plasma including an oxygen radical or a nitrogen radical when oxygen or nitrogen is supplied; and a second plasma generator attached to the second pipe and configured to generate a second plasma including a hydrogen radical when hydrogen is supplied,

wherein the OH radical is generated by collision between the oxygen radical and the hydrogen radical or the NH radical is generated by collision between the nitrogen radical and the hydrogen radical in the junction pipe.

2. (canceled)

3. The film forming apparatus according to claim 1, wherein at least one of the first pipe and the second pipe includes a first charged particle remover, and the first charged particle remover removes charged particles including dissociated ions and/or electrons generated in the first plasma and/or the second plasma by using charge of the charged particles.

4. (canceled)

5. (canceled)

6. The film forming apparatus according to claim 1, wherein the junction pipe includes a first charged particle remover, and the first second charged particle remover removes charged particles including dissociated ions and/or electrons generated in the first plasma and/or the second plasma by using charge of the charged particles.

7. (canceled)

8. The film forming apparatus according to claim 1, wherein the first pipe has a first valve between the first plasma generator and the reaction container, the second pipe has a second valve between the second plasma generator and the reaction container, and one of the first valve and the second valve is closed while the other of the first valve and the second valve is opened.

9. The film forming apparatus according to claim 3, wherein the first pipe has a first valve between the first plasma generator and the reaction container, the second pipe has a second valve between the second plasma generator and the reaction container, and one of the first valve and the second valve is closed while the other of the first valve and the second valve is opened.

10. The film forming apparatus according to claim 1, wherein: the first pipe is coupled to the first gas source and the third gas source; the second pipe is coupled to the second gas source and the third gas source; and the junction pipe has one end coupled to the first pipe and the second pipe and the other end coupled to the reaction container; the first pipe has a first valve upstream of the first plasma generator; the second pipe has a second valve upstream of the second plasma generator; the first plasma generator generates the first plasma when the first valve is opened and the second valve is closed; the second plasma generator generates the second plasma when the second valve is opened and the first valve is closed.

11. The film forming apparatus according to claim 10, wherein the junction pipe includes a charged particle remover, and the charged particle remover removes charged particles including dissociated ions and/or electrons generated in the first plasma and the second plasma by using charge of the charged particles.
