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

CROSS-REFERENCE TO RELATED APPLICATION(S)

[0001] This application is based upon and claims the benefit of priority from Japanese Patent Application No. 2020-159426, filed on September 24, 2020, the entire contents of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to a method of manufacturing a semiconductor device, a substrate processing method, a substrate processing apparatus, and a program.

BACKGROUND

[0003] As one of processes for manufacturing a semiconductor device, there may be performed a substrate-processing process in which an oxide film is formed on a substrate by alternately repeating a step of supplying a precursor to the substrate and a step of supplying an oxidizing agent to the substrate.

SUMMARY

[0004] Some embodiments of the present disclosure provide a technique capable of improving the characteristics of an oxide film formed on a substrate.

[0005] According to one or more embodiments of the present disclosure, there is provided a technique that includes forming an oxide film in which a first oxide film and a second oxide film are alternately laminated on a substrate by alternately performing, a predetermined number of times: (a) forming the first oxide film containing an atom X by performing a first cycle n_1 times (n_1 is an integer of 1 or more), the first cycle including non-simultaneously performing (a1) forming a first layer including a component in which a first functional group is bonded to the atom X by supplying a precursor, which includes a partial structure in which the first functional

WHAT IS CLAIMED IS:

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

forming an oxide film in which a first oxide film and a second oxide film are alternately laminated on the~~a~~ substrate by alternately performing, a predetermined number of times:

(a) forming the first oxide film containing an atom X by performing a first cycle n_1 times (n_1 is an integer of 1 or more), the first cycle including non-simultaneously performing (a1) forming a first layer including a component in which a first functional group is bonded to the atom X by supplying a precursor, which includes a partial structure in which the first functional group and a second functional group are directly bonded to the atom X and has a bonding energy between the first functional group and the atom X higher than a bonding energy between the second functional group and the atom X, to the substrate, and (a2) forming a second layer containing the atom X and oxygen by supplying a first oxidizing agent to the substrate to oxidize the first layer; and

(b) forming the second oxide film containing the atom X by performing a second cycle n_2 times (n_2 is an integer of 1 or more), the second cycle including non-simultaneously performing (b1) forming a third layer including a component in which the first functional group is bonded to the atom X by supplying the precursor to the substrate, and (b2) forming a fourth layer containing the atom X and oxygen by supplying a second oxidizing agent to the substrate to oxidize the third layer, under a processing condition that an oxidizing power is higher than an oxidizing power when oxidizing the first layer in (a2),

wherein in the act of forming the oxide film, (a) and (b) are alternately repeated such that the first oxide film that is first formed is made thicker than the second oxide film that is first formed.

2. The method of Claim 1, wherein the atom X includes four bonds, the first functional group is bonded to each of three bonds of the four bonds of the atom X, and the second functional group is bonded to a remaining one bond of the four bonds of the atom X, and

wherein in (a1) and (b1), the precursor is supplied under a processing condition that the atom X is adsorbed to a surface of the substrate in a state in which the first functional group is bonded to each of the three

bonds of the atom X.

3. The method of Claim 1, wherein in (a1) and (b1), the precursor is supplied under a processing condition that the first functional group is not desorbed and the second functional group is desorbed from the atom X contained in the precursor, and under a processing condition that the atom X, in a state in which the first functional group is bonded to the atom X and the second functional group is desorbed from the atom X, is adsorbed to a surface of the substrate.

4. The method of Claim 3, wherein in (a1) and (b1), the precursor is supplied under a processing condition that the adsorption of the atom X, in the state in which the first functional group is bonded to the atom X and the second functional group is desorbed from the atom X, to the surface of the substrate is more dominant than the adsorption of the second functional group, which is desorbed from the atom X, to the surface of the substrate.

5. The method of Claim 2, wherein in (a1) and (b1), the first functional group bonded to the atom X adsorbed to the surface of the substrate inhibits adsorption of at least one selected from the group of an atom and a molecule to the atom X adsorbed to the surface of the substrate, and inhibits adsorption of at least one selected from the group of an atom and a molecule to an adsorption site on the surface of the substrate that is located in a vicinity of the first functional group.

6. The method of Claim 2, wherein in (a1) and (b1), an adsorption site on the surface of the substrate that is located in a vicinity of the first functional group is held by the first functional group bonded to the atom X adsorbed to the surface of the substrate.

7. The method of Claim 2, wherein in (a1) and (b1), the atom X is discontinuously adsorbed to the surface of the substrate.

8. The method of Claim 2, wherein in (a1) and (b1), the supply of the precursor is continued until adsorption

reaction of the atom X to the surface of the substrate is saturated.

9. The method of Claim 8, wherein in a state in which the adsorption reaction of the atom X to the surface of the substrate is saturated, a layer composed of the atom X adsorbed to the surface of the substrate has a thickness of less than one atomic layer.

10. The method of Claim 8, wherein in a state where the adsorption reaction of the atom X to the surface of the substrate is saturated, an adsorption site is held on a part of the surface of the substrate.

11. The method of Claim 8, wherein in a state in which the adsorption reaction of the atom X to the surface of the substrate is saturated, the surface of the substrate is covered with the first functional group.

12. The method of Claim 1, wherein in (a2), the first oxidizing agent is supplied under a processing condition that at least one selected from the group of a third functional group included in the first functional group bonded to the atom X contained in the first layer and the first functional group bonded to the atom X is desorbed, and

wherein in (b2), the second oxidizing agent is supplied under a processing condition that the third functional group included in the first functional group bonded to the atom X contained in the third layer and the first functional group bonded to the atom X are desorbed.

13. The method of Claim 1, wherein the first functional group includes an alkoxy group, and

wherein the second functional group includes at least one selected from the group of an amino group, an alkyl group, a halogeno group, a hydroxy group, a hydro group, an aryl group, a vinyl group, and a nitro group.

14. The method of Claim 1, wherein the first oxidizing agent includes at least one selected from the group of an O_2 gas, a NO gas, a N_2O gas, and a NO_2 gas, and the second oxidizing agent includes at least one selected from the group of O_2 gas + H_2 gas, O_3 gas + H_2 gas, H_2O_2 gas + H_2 gas, H_2O + H_2 gas, an O_3 gas, a H_2O_2 gas, a H_2O gas, and a plasma-excited O_2 gas.

15. The method of Claim 1, wherein a processing temperature in (a) is set to 550 degrees C or higher and 700 degrees C or lower, and

wherein a processing temperature in (b) is set to 550 degrees C or higher and 700 degrees C or lower.

16. The method of Claim 1, wherein in the act of forming the oxide film, the first oxide film is first formed.

17. The method of Claim 1, wherein in the act of forming the oxide film, the second oxide film is formed lastly.

~~18. The method of Claim 1, wherein in the act of forming the oxide film, (a) and (b) are alternately repeated such that the first oxide film that is first formed is made thicker than the second oxide film that is first formed.~~

18~~9~~. The method of Claim 1, wherein in the act of forming the oxide film, (a) and (b) are alternately repeated such that the second oxide film formed lastly is made thicker than the first oxide film formed lastly.

19~~20~~. The method of Claim 1~~8~~, wherein (a) and (b) are alternately repeated such that a ratio of a thickness of the first oxide film to a thickness of the second oxide film is gradually reduced.

20~~1~~. A ~~substrate processing~~ method of manufacturing a semiconductor device, comprising:

forming an oxide film in which a first oxide film and a second oxide film are alternately laminated on a substrate by alternately performing, a predetermined number of times:

(a) forming the first oxide film containing an atom X by performing a first cycle n_1 times (n_1 is an integer of 1 or more), the first cycle including non-simultaneously performing (a1) forming a first layer including a component in which a first functional group is bonded to the atom X by supplying a precursor, which includes a partial structure in which the first functional group and a second functional group are directly bonded to the atom X and has a bonding energy between the first functional group and the atom X

higher than a bonding energy between the second functional group and the atom X, to the substrate, and (a2) forming a second layer containing the atom X and oxygen by supplying a first oxidizing agent to the substrate to oxidize the first layer; and

(b) forming the second oxide film containing the atom X by performing a second cycle n_2 times (n_2 is an integer of 1 or more), the second cycle including non-simultaneously performing (b1) forming a third layer including a component in which the first functional group is bonded to the atom X by supplying the precursor to the substrate, and (b2) forming a fourth layer containing the atom X and oxygen by supplying a second oxidizing agent to the substrate to oxidize the third layer, under a processing condition that an oxidizing power is higher than an oxidizing power when oxidizing the first layer in (a2),

wherein in the act of forming the oxide film, (a) and (b) are alternately repeated such that the first oxide film that is first formed is made thicker than the second oxide film that is first formed.

212. A substrate processing apparatus, comprising:

a process chamber in which a substrate is processed;

a precursor supply system configured to supply a precursor, which includes a partial structure in which a first functional group and a second functional group are directly bonded to an atom X and has a bonding energy between the first functional group and the atom X higher than a bonding energy between the second functional group and the atom X, to the substrate in the process chamber;

a first oxidizing agent supply system configured to supply a first oxidizing agent to the substrate in the process chamber;

a second oxidizing agent supply system configured to supply a second oxidizing agent to the substrate in the process chamber;

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

a controller configured to be capable of controlling the precursor supply system, the first oxidizing agent supply system, the second oxidizing agent supply system, and the heater so as to perform, in the process chamber:

forming an oxide film in which a first oxide film and a second oxide film are alternately laminated on the substrate by alternately performing, a predetermined number of times:

(a) forming the first oxide film containing the atom X by performing a first cycle n_1 times (n_1 is an integer of 1 or more), the first cycle including non-simultaneously performing (a1) forming a first layer including a component in which the first functional group is bonded to the atom X by supplying the precursor to the substrate, and (a2) forming a second layer containing the atom X and oxygen by supplying the first oxidizing agent to the substrate to oxidize the first layer; and

(b) forming the second oxide film containing the atom X by performing a second cycle n_2 times (n_2 is an integer of 1 or more), the second cycle including non-simultaneously performing (b1) forming a third layer including a component in which the first functional group is bonded to the atom X by supplying the precursor to the substrate, and (b2) forming a fourth layer containing the atom X and oxygen by supplying the second oxidizing agent to the substrate to oxidize the third layer, under a processing condition that an oxidizing power is higher than an oxidizing power when oxidizing the first layer in (a2),

wherein in the act of forming the oxide film, (a) and (b) are alternately repeated such that the first oxide film that is first formed is made thicker than the second oxide film that is first formed.

22~~3~~. 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 an oxide film in which a first oxide film and a second oxide film are alternately laminated on a substrate by alternately performing, a predetermined number of times:

(a) forming the first oxide film containing an atom X by performing a first cycle n_1 times (n_1 is an integer of 1 or more), the first cycle including non-simultaneously performing (a1) forming a first layer including a component in which a first functional group is bonded to the atom X by supplying a precursor, which includes a partial structure in which the first functional group and a second functional group are directly bonded to the atom X and has a bonding energy between the first functional group and the atom X higher than a bonding energy between the second functional group and the atom X, to the substrate, and (a2) forming a second layer containing the atom X and oxygen by supplying a first oxidizing agent to the substrate to oxidize the first layer; and

(b) forming the second oxide film containing the atom X by performing a second cycle n_2 times

(n_2 is an integer of 1 or more), the second cycle including non-simultaneously performing (b1) forming a third layer including a component in which the first functional group is bonded to the atom X by supplying the precursor to the substrate, and (b2) forming a fourth layer containing the atom X and oxygen by supplying a second oxidizing agent to the substrate to oxidize the third layer, under a processing condition that an oxidizing power is higher than an oxidizing power when oxidizing the first layer in (a2),

wherein in the act of forming the oxide film, (a) and (b) are alternately repeated such that the first oxide film that is first formed is made thicker than the second oxide film that is first formed.