# METHOD OF MANUFACTURING SEMICONDUCTOR DEVICE, SUBSTRATE PROCESSING APPARATUS, RECORDING MEDIUM, AND PROGRAM

## TECHNICAL FIELD

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

## BACKGROUND

**[0002]** A patterning technique is also becoming miniaturized according to miniaturization of large scale integrated circuits (hereinafter, referred to as "LSIs"). As the patterning technique, for example, a hard mask or the like is used, but it is difficult to apply a method of exposing a resist to separate an etching region and a non-etching region due to the miniaturization of the patterning technique. For this reason, an epitaxial film such as silicon (Si) or silicon germanium (SiGe) is selectively grown and formed on a substrate such as a silicon (Si) wafer (for example, see Patent Documents 1 and 2).

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

**[0003]** Patent Document 1: Japanese laid-open publication No. 2003-100746

Patent Document 2: Japanese laid-open publication No. 2015-122481

## SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

**[0004]** Some embodiments of the present disclosure provide a technique capable of selectively forming a film on a substrate.

MEANS TO SOLVE PROBLEM

layer and a $SiO_2$ layer by supplying a HMDSN gas as an adsorption control agent containing an organic ligand to a wafer 200 while regulating a temperature of the wafer 200 including the Si layer, a SiN layer, and the $SiO_2$ layer on a surface of the wafer 200 depending on a composition of the Si layer and the $SiO_2$ layer; and a step of selectively growing a TiN film on the SiN layer by supplying a $TiCl_4$ gas as a precursor gas and a $NH_3$ gas as a reaction gas, as deposition gases, to the wafer 200.

**[0038]** Further, the step of organically terminating the surfaces of the Si layer and the $SiO_2$ layer may be performed multiple times. In addition, the step of organically terminating the surfaces of the Si layer and the $SiO_2$ layer will be referred to as "pre-processing." The step of selectively growing the TiN film on the SiN layer will be referred to as a film-forming process.

**[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 a 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 film formed on a wafer". Further, when the term "substrate" is used herein, it may be synonymous with the term "wafer."

(Wafer Loading)

**[0040]** When a plurality of wafers 200 is charged on the boat 217 (wafer charging), 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 a lower end opening of the outer tube 203 via the O-ring 220.

(Pressure Regulation and Temperature Regulation)

**[0041]** The interior of the process chamber 201 is vacuum-exhausted by the vacuum pump 246 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 243 is feedback-controlled based on the measured pressure information (pressure regulation). The vacuum

(After-Purge and Atmospheric Pressure Return)

**[0075]** The $N_2$ gas is supplied from each of the gas supply pipes 510, 520 and 530 into the process chamber 201 and is exhausted from the exhaust pipe 231. The $N_2$ gas acts as a purge gas. Thus, the interior of the process chamber 201 is purged with an inert gas and the gas or the 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 the inert gas (inert gas substitution). The internal pressure of the process chamber 201 is returned to an atmospheric pressure (atmospheric pressure return).

(Wafer Unloading)

**[0076]** Next, the seal cap 219 is moved down by the boat elevator 115 to open the lower end of the outer tube 203. Then, the processed wafers 200 supported on the boat 217 are unloaded from the lower end of the outer tube 203 to the outside of the outer tube 203 (boat unloading). Thereafter, the processed wafers 200 are discharged from the boat 217 (wafer discharging).

(3) Effects according to Embodiments of the Present Disclosure

**[0077]** In the present embodiment, the surface of the wafer 200 is first exposed to the HMDSN gas to organically terminate the surfaces of the Si layer and the $SiO_2$ layer. Thus, the precursor molecules are adsorbed only on the SiN layer which is not organically terminated. That is, the precursor molecules may not be easily adsorbed on the Si layer and the $SiO_2$ layer on which the organic ligand contained in the HMDSN gas is adsorbed, such that the TiN film may not be formed. Further, the precursor molecules are adsorbed on the SiN layer on which the organic ligand contained in the HMDSN gas is not adsorbed, thereby selectively growing the TiN film.

**[0078]** That is, the kind of the surface of the wafer 200 on which the organic ligand contained in the adsorption control agent is adsorbed may be set different by controlling the temperature of

WHAT IS CLAIMED IS:

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

organically terminating a first region of a substrate by supplying an adsorption control agent containing an organic ligand to the substrate while regulating a temperature of the substrate including the first region and a second region different from the first region formed on a surface of the substrate depending on a composition of the first region; and

selectively growing a film on the second region by supplying a deposition gas to the substrate.

2. The method according to Claim 1, wherein the organic ligand contains an alkyl group.

3. The method according to Claim 1, wherein the organic ligand is alkylamine.

4. The method according to Claim 1, wherein the first region includes a silicon layer and a silicon oxide layer, and

wherein, in the act of organically terminating the first region, the temperature of the substrate is regulated to 100 degrees C or higher and 250 degrees C or lower.

5. The method according to Claim 1, wherein the first region includes a silicon layer,

wherein the second region includes a silicon oxide layer and a silicon nitride layer, and

wherein, in the act of organically terminating the first region, the temperature of the substrate is regulated to 300 degrees C or higher and 500 degrees C or lower.

6. The method according to Claim 1, wherein a ligand contained in the deposition gas and the organic ligand are respectively selected from electrically negative ligands.

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

causing a ligand to be adsorbed on a first region of a substrate by supplying a pre-processing gas containing the ligand to the substrate without a deposition gas being adsorbed on the substrate while regulating a temperature of the substrate including the first region and a second region different from the first region formed on a surface of the substrate depending on a composition of the first region; and

selectively growing a film only on the second region by supplying the deposition gas to the substrate.

8. The method according to Claim 7, wherein the ligand contains an alkyl group.

9. The method according to Claim 7, wherein the ligand is alkylamine.

10. The method according to Claim 7, wherein the first region includes a silicon layer and a silicon oxide layer, and

wherein, in the act of causing the ligand to be adsorbed on the first region, the temperature of the substrate is regulated to 100 degrees C or higher and 250 degrees C or lower.

11. The method according to Claim 7, wherein the first region includes a silicon layer,

wherein the second region includes a silicon oxide layer and a silicon nitride layer, and

wherein, in the act of causing the ligand to be adsorbed on the first region, the temperature of the substrate is regulated to 300 degrees C or higher and 500 degrees C or lower.

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

organically terminating a first region of a substrate by supplying an adsorption control agent containing an organic ligand to the substrate including the first region and a second region different from the first region formed on a surface of the substrate; and

selectively growing a film on the second region by supplying a deposition gas to the substrate,

wherein in the act of organically terminating the first region, a kind of the organic ligand is selected depending on a composition of the first region.

13. The method according to Claim 12, wherein the first region includes a silicon layer and a silicon oxide layer, and

wherein, in the act of organically terminating the first region, the temperature of the substrate is regulated to 100 degrees C or higher and 250 degrees C or lower.

14. The method according to Claim 12, wherein the first region includes a silicon layer,

wherein the second region includes a silicon oxide layer and a silicon nitride layer, and

wherein, in the act of organically terminating the first region, the temperature of the substrate is regulated to 300 degrees C or higher and 500 degrees C or lower.

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

organically terminating a first region of a substrate by supplying an adsorption control agent containing an organic ligand to the substrate while regulating a temperature of the substrate including the first region and a second region different from the first region formed on a surface of the substrate depending on a composition of the first region; and

selectively growing a film on the second region by supplying a deposition gas to the substrate,

wherein the first region includes a silicon oxide layer, and

wherein, in the act of organically terminating the first region, the temperature of the substrate is regulated to 100 degrees C or higher and 250 degrees C or lower.

16. The method according to Claim 15, wherein the second region includes a silicon nitride layer.

17. A substrate processing apparatus, comprising:

a process chamber configured to accommodate a substrate;

a heating system configured to heat the process chamber;

a first gas supply system configured to supply an adsorption control agent containing an organic ligand to the process chamber;

a second gas supply system configured to supply a deposition gas to the process chamber; and

a controller configured to be capable of controlling the first gas supply system, the second gas supply system, and the heating system to perform a process, the process comprising:

organically terminating a first region of the substrate by supplying the adsorption control agent to the process chamber accommodating the substrate including the first region and a second region different from the first region formed on a surface of the substrate while regulating a temperature of the process chamber depending on a composition of the first region; and

selectively growing a film on the second region by supplying the deposition gas to the process chamber.

18. The method according to Claim 17, wherein the first region includes a silicon layer and a silicon oxide layer, and

wherein, in the act of organically terminating the first region, the temperature of the substrate is regulated to 100 degrees C or higher and 250 degrees C or lower.

19. The method according to Claim 17, wherein the first region includes a silicon layer,

wherein the second region includes a silicon oxide layer and a silicon nitride layer, and

wherein, in the act of organically terminating the first region, the temperature of the substrate is regulated to 300 degrees C or higher and 500 degrees C or lower.

20. A substrate processing apparatus, comprising:

a process chamber configured to accommodate a substrate;

a heating system configured to heat the process chamber;

a first gas supply system configured to supply an adsorption control agent containing an organic ligand to the process chamber;

a second gas supply system configured to supply a deposition gas to the process chamber; and

a controller configured to be capable of controlling the first gas supply system, the second gas supply system, and the heating system to perform a process in the process chamber, the process comprising:

organically terminating a first region of a substrate by supplying the adsorption control agent to the substrate while regulating a temperature of the substrate including the first region and a second region different from the first region formed on a surface of the substrate depending on a composition of the first region; and

selectively growing a film on the second region by supplying the deposition gas to the substrate,

wherein the first region includes a silicon oxide layer, and

wherein, in the act of organically terminating the first region, the temperature of the substrate is regulated to 100 degrees C or higher and 250 degrees C or lower.

21. A computer-readable recording medium storing a program that causes, by a computer, a substrate processing apparatus to perform a process comprising:

organically terminating a first region of a substrate by supplying an adsorption control agent containing an organic ligand to a process chamber of the substrate processing apparatus while regulating a temperature of the substrate accommodated in the process chamber and including the first region and a second region different from the first region formed on a surface of the substrate depending on a composition of the first region; and

selectively growing a film on the second region by supplying a deposition gas to the process chamber.

22. A program that is stored in a computer-readable recording medium and causes, by a computer, a substrate processing apparatus to perform a process in a process chamber of the substrate processing apparatus, the process comprising:

organically terminating a first region of a substrate by supplying an adsorption control agent containing an organic ligand to the substrate while regulating a temperature of the substrate including the first region and a second region different from the first region formed on a surface of the substrate depending on a composition of the first region; and

selectively growing a film on the second region by supplying a deposition gas to the process chamber,

wherein the first region includes a silicon oxide layer, and

wherein, in the act of organically terminating the first region, the temperature of the substrate is regulated to 100 degrees C or higher and 250 degrees C or lower.