

WHAT IS CLAIMED IS:

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

etching a first film exposed on a surface of ~~a~~ the substrate by performing a cycle a ~~predetermined number of~~ two or more times, the cycle including non-simultaneously performing:

(a) forming a first modified layer in at least a portion of a surface of the first film by supplying a first gas to the substrate; and

(b) etching at least a portion of the first film with an etching species, ~~the etching species being generated~~ and forming a second modified layer, which is removable by the first gas, in at least a portion of the surface of the first film having at least the portion etched, by supplying a second gas having a molecular structure different from that of the first gas to the substrate ~~to perform~~, wherein the etching species is generated by performing at least one selected from the group of causing the second gas to react with the first modified layer and activating the first modified layer with the second gas.

2. The method of Claim 1, wherein in (a), the first modified layer is formed by causing at least a portion of molecules of the first gas to be physically adsorbed or chemically adsorbed on the at least a portion of the surface of the first film.

3. The method of Claim 1, wherein in (a), the first modified layer is formed by generating a compound by a chemical reaction between at least a portion of molecules of the first gas and atoms or molecules of the at least a portion of the surface of the first film.

4. The method of Claim 1, wherein in (b), the second gas is supplied to the substrate under a condition that the reaction between the second gas and the first modified layer is more predominant than a reaction between the second gas and the first film.

5. The method of Claim 1, wherein in (b), the second gas is supplied to the substrate under a condition that the reaction between the second gas and the first modified layer progresses and a reaction between the second gas and the first film does not progress.

6. The method of Claim 1, wherein in (b), the second gas is supplied to the substrate under a condition that the activation of the first modified layer with the second gas is more predominant than an activation of the first film with the second gas.

7. The method of Claim 1, wherein in (b), the second gas is supplied to the substrate under a condition that the activation of the first modified layer with the second gas progresses and an activation of the first film with the second gas does not progress.

8. The method of Claim 1, wherein in (b), the second gas is supplied to the substrate under a condition that the etching of the at least a portion of the first film with the etching species is more predominant than a reaction between the second gas and the first film.

9. The method of Claim 1, wherein in (b), the second gas is supplied to the substrate under a condition that the etching of the at least a portion of the first film with the etching species progresses and a reaction between the second gas and the first film does not progress.

~~10. The method of Claim 1, wherein (b) includes forming a second modified layer in the at least a portion of the surface of the first film having the at least a portion etched.~~

~~11.~~10. The method of Claim ~~10~~1, wherein the cycle includes a first cycle and at least one subsequent cycle, and

wherein in (a) in the at least one subsequent cycle, the second modified layer is removed by causing the first gas to react with the second modified layer by supplying the first gas to the substrate, and the first modified layer is formed in ~~the~~ at least a portion of the surface of the first film from which the second modified layer is removed.

~~12.11.~~ The method of Claim 1, wherein the first film includes a nitrogen-containing film, a transition metal film, or a semiconductor film.

~~13.12.~~ The method of Claim 1, wherein a second film is further exposed on the surface of the substrate, and

wherein the first film is selectively etched with respect to the second film by performing the cycle ~~the~~ a predetermined number of times.

~~14.13.~~ The method of Claim ~~13~~12, wherein the first film includes a nitrogen-containing film, a transition metal film, or a semiconductor film, and the second film includes an oxygen-containing film or a non-transition metal film.

~~15.14.~~ The method of Claim ~~14~~13, wherein the nitrogen-containing film includes a silicon-based nitrogen-containing film, a boron-based nitrogen-containing film, or a metal-based nitrogen-containing film.

~~16.15.~~ The method of Claim ~~14~~13, wherein the oxygen-containing film includes a silicon-based oxygen-containing film or a metal-based oxygen-containing film.

~~17.16.~~ The method of Claim ~~13~~12, wherein the first film is etched with respect to the second film with a selectivity of 5:1 or more by performing the cycle the predetermined number of times.

~~18.17.~~ The method of Claim 1, wherein the first gas includes one or more selected from the group of a silicon-containing gas, a metal-containing gas, an oxygen-containing gas, a nitrogen- and hydrogen-containing gas, a boron-containing gas, a phosphorus-containing gas, and a halogen-containing gas, and

wherein the second gas includes one or more selected from the group of the halogen-containing gas and an acetylacetone-based gas.

~~19.18.~~ The method of Claim 1, wherein the cycle is performed ~~the predetermined number of times~~ under a non-plasma atmosphere.

~~20.19.~~ The method of Claim 1, wherein the cycle is performed ~~the predetermined number of times~~ under a condition that an etching reaction of the first film is difficult to continue when at least one selected from the group of the first gas and the second gas is present alone.

~~21.20.~~ A substrate processing method of manufacturing a semiconductor device, comprising:
etching a first film exposed on a surface of a substrate by performing a cycle a ~~predetermined number of~~ two or more times, the cycle including non-simultaneously performing:

(a) forming a first modified layer in at least a portion of a surface of the first film by supplying a first gas to the substrate; and

(b) etching at least a portion of the first film with an etching species, ~~the etching species being generated by~~ and forming a second modified layer, which is removable by the first gas, in at least a portion of the surface of the first film having at least the portion etched, by supplying a second gas having a molecular structure different from that of the first gas to the substrate ~~to perform, wherein the etching species is generated by performing~~ at least one selected from the group of causing the second gas to react with the first modified layer and activating the first modified layer with the second gas.

~~22.21.~~ A substrate processing apparatus comprising:

a process chamber in which a substrate is processed;

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

a second gas supply system configured to supply a second gas, which has a molecular structure different from that of the first gas, to the substrate in the process chamber;

a temperature regulator configured to regulate a temperature of the substrate in the

process chamber; and

a controller configured to be capable of controlling the first gas supply system, the second gas supply system, and the temperature regulator so as to etch a first film exposed on a surface of the substrate by performing a cycle ~~a predetermined number of~~ two or more times, the cycle including non-simultaneously performing: (a) forming a first modified layer in at least a portion of a surface of the first film by supplying the first gas to the substrate; and (b) etching at least a portion of the first film with an etching species, ~~the etching species being generated by~~ and forming a second modified layer, which is removable by the first gas, in at least a portion of the surface of the first film having at least the portion etched, by supplying the second gas to the substrate to perform, wherein the etching species is generated by performing at least one selected from the group of causing the second gas to react with the first modified layer and activating the first modified layer with the second gas.

23.22. 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:

etching a first film exposed on a surface of a substrate by performing a cycle ~~a predetermined number of~~ two or more times, the cycle including non-simultaneously performing:

(a) forming a first modified layer in at least a portion of a surface of the first film by supplying a first gas to the substrate; and

(b) etching at least a portion of the first film with an etching species, ~~the etching species being generated~~ and forming a second modified layer, which is removable by the first gas, in at least a portion of the surface of the first film having at least the portion etched, by supplying a second gas having a molecular structure different from that of the first gas to the substrate to perform, wherein the etching species is generated by performing at least one selected from the group of causing the second gas to react with the first modified layer and activating the first modified layer with the second gas.