been found that, by adopting the IPA contact angle or the water contact angle on the surface in the pattern non-formation region as an index, a pattern collapse rate in the pattern formation region can be evaluated stably, and by setting the IPA contact angle or the water contact angle within a specified range, a pattern collapse can be suppressed, and the present disclosure has been completed.

[0006]

In an aspect, a treatment method of treating a main surface of a semiconductor substrate that has, on the main surface of the substrate, a pattern formation region in which a pattern having a concave-convex structure with a pattern dimension of 30 nm or less is formed and a pattern non-formation region in which no pattern is formed, the method comprising a surface treatment step of bringing a surface treatment agent composition including a silylating agent and a solvent into contact with the pattern formation region and the pattern non-formation region on the main surface of the semiconductor substrate, and an evaluation step of determining whether or not, with respect to a surface of the pattern non-formation region after the surface treatment step, an IPA contact angle with 2-propanol is 2° or more at a room temperature of 25°C and/or a water contact angle with pure water is 50° or more at the room temperature of 25°C, which is obtained by dropping 1 μl of droplets of 2-propanol or pure water on the substrate surface of the pattern non-formation region at the room temperature of 25°C in a state in which the semiconductor substrate is stood on a horizontal table, and then measuring after 5 seconds, is provided.

[0007]

In another example, there is provided a surface treatment agent composition used for treating a main surface of a semiconductor substrate that has, on the main surface of the substrate, a pattern formation region in which a pattern having a concave-convex structure with a pattern dimension of 30 nm or less is formed and

CLAIMS

1. A treatment method of treating a main surface of a semiconductor substrate that has, on the main surface of the substrate, a pattern formation region in which a pattern having a concave-convex structure with a pattern dimension of 30 nm or less is formed and a pattern non-formation region in which no pattern is formed, the method comprising:

a surface treatment step of bringing a surface treatment agent composition including a silylating agent and a solvent into contact with the pattern formation region and the pattern non-formation region on the main surface of the semiconductor substrate,and

an evaluation step of determining whether or not, with respect to a surface of the pattern non-formation region after the surface treatment step, an IPA contact angle with 2-propanol is 2° or more at a room temperature of 25°C and/or a water contact angle with pure water is 50° or more at the room temperature of 25°C, which is obtained by dropping 1 μl of droplets of 2-propanol or pure water on the substrate surface of the pattern non-formation region at the room temperature of 25°C in a state in which the semiconductor substrate is stood on a horizontal table, and then measuring after 5 seconds.

2. The treatment method according to Claim 1,

wherein the pattern dimension is at least one dimension in a width direction of an in-plane direction of the main surface and/or at least one dimension in a height direction of a direction perpendicular to the main surface.

3. The treatment method according to Claim 1 or 2,

wherein the surface treatment step is a step of forming a surface treatment agent layer on an entire main surface of the semiconductor substrate, and

on a surface of the surface treatment agent layer, the IPA contact angle is 2° or more at the room temperature of 25°C and/or the water contact angle is 55° or more at the room temperature of 25°C.

4. The treatment method according to any one of Claims 1 to 3,

wherein the concave-convex structure includes one or two or more kinds selected from the group consisting of Si, Ti, Ge, W, Ru, and oxides, nitrides, nitrogen oxides, carbonitrides, or carbide oxides, which include one or more kinds of these elements.

5. The treatment method according to Claim 1 to 4,

wherein the solvent includes an aprotic solvent.

6. The treatment method according to Claim 5,

wherein the solvent includes the aprotic solvent in a content of 100% by mass in 100% by mass of the solvent.

7. The treatment method according to Claim 5 or 6,

wherein the aprotic solvent includes one or two or more kinds selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen element-containing solvents, sulfoxides, carbonate solvents, derivatives of polyhydric alcohol, nitrogen

element-containing solvents, and silicone solvents.

8. The treatment method according to any one of Claims 5 to 7, wherein the solvent includes a carbonate solvent or a lactone.

9. The treatment method according to any one of Claims 5 to 7, wherein the solvent include propylene carbonate or γ-butyrolactone.

10. The treatment method according to any one of Claims 5 to 7, wherein the solvent includes one or two or more kinds selected from the group consisting of derivatives of polyhydric alcohol, hydrocarbons, and ethers.

11. The treatment method according to any one of Claims 1 to 10, wherein the silylating agent includes a silicon compound represented by General Formula [1],

$$R^1_aSi(H)_bX_{4-a-b} \quad [1]$$

(in General Formula [1], R^1's each independently represent an organic group including a hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, X's each independently represent a monovalent functional group in which an element bonded to an Si element is nitrogen, oxygen, carbon, or halogen, a represents an integer of 1 to 3, b represents an integer of 0 to 2, and a sum of a and b is 1 to 3).

12. The treatment method according to any one of Claims 1 to 11, wherein the silylating agent has a trialkylsilyl group.

13. The treatment method according to any one of Claims 1 to 12, wherein, in the silylating agent, an element bonded to an Si element is nitrogen.

14. The treatment method according to any one of Claims 1 to 13, wherein a content of the silylating agent is 0.1% by mass or more and 50% by mass or less in 100% by mass of the surface treatment agent composition.

15. The treatment method according to any one of Claims 1 to 14, wherein the surface treatment agent composition includes a catalyst.

16. The treatment method according to Claim 15,

wherein the catalyst includes one or two or more kinds selected from the group consisting of trimethylsilyltrifluoroacetate,
trimethylsilyltrifluoromethanesulfonate,
dimethylsilyltrifluoroacetate,
dimethylsilyltrifluoromethanesulfonate,
butyldimethylsilyltrifluoroacetate,
butyldimethylsilyltrifluoromethanesulfonate,
hexyldimethylsilyltrifluoroacetate,
hexyldimethylsilyltrifluoromethanesulfonate,
octyldimethylsilyltrifluoroacetate,

octyldimethylsilyltrifluoromethanesulfonate, decyldimethylsilyltrifluoroacetate, decyldimethylsilyltrifluoromethanesulfonate, a sulfonic acid represented by General Formula [3], an anhydride of the sulfonic acid, a salt of the sulfonic acid, a sulfonic acid derivative represented by General Formula [4], a sulfonate represented by General Formula [5], a sulfonimide represented by each of General Formulae [6] and [7], a sulfonimide derivative represented by each of General Formulae [8] and [9], a sulfonmethide represented by General Formula [10], a sulfonmethide derivative represented by General Formula [11], an acid imidized product, a nitrogen-containing compound, a nitrogen-containing heterocyclic compound, and a silylated heterocyclic compound,

$$R^8\text{-}S(=O)_2OH \qquad [3]$$

[in General Formula [3], R^8 represents a group selected from the group consisting of a monovalent hydrocarbon group having 1 to 8 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, and a hydroxyl group]

$$R^{8\prime}\text{-}S(=O)_2O\text{-}Si(H)_{3-r}(R^9)_r \qquad [4]$$

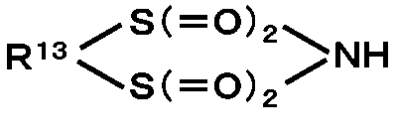
[in General Formula [4], $R^{8\prime}$ represents a monovalent hydrocarbon group having 1 to 8 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, R^9's each independently represent at least one group selected from monovalent hydrocarbon groups having 1 to 18 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, and r represents an integer of 1 to 3]

$$R^{10}\text{-}S(=O)_2OR^{11} \qquad [5]$$

[in General Formula [5], R^{10} represents a group selected from the group consisting of a monovalent hydrocarbon group having 1 to 8 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, and a fluorine element, and R^{11} represents a monovalent alkyl group having 1 to 18 carbon atoms]

$$(R^{12}\text{-}S(=O)_2)_2NH \quad [6]$$

[in General Formula [6], R^{12}'s each independently represent a group selected from the group consisting of a monovalent hydrocarbon group having 1 to 8 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, and a fluorine element]

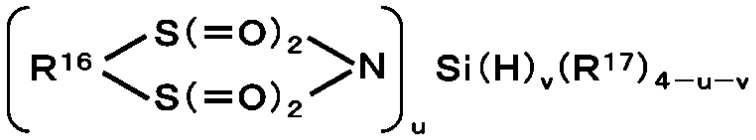


[7]

[in General Formula [7], R^{13} represents a divalent hydrocarbon group having 1 to 8 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements]

$$((R^{14}\text{-}S(=O)_2)_2N)_sSi(H)_t(R^{15})_{4-s-t} \quad [8]$$

[in General Formula [8], R^{14}'s each independently represent a group selected from the group consisting of a monovalent hydrocarbon group having 1 to 8 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, and a fluorine element, R^{15}'s each independently represent a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, s represents an integer of 1 to 3, t represents an integer of 0 to 2, and a sum of s and t is 3 or less]



[9]

[in General Formula [9], R^{16}'s each independently represent a divalent hydrocarbon group having 1 to 8 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, R^{17}'s each independently represent a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, u represents an integer of 1 to 3, v represents an integer of 0 to 2, and a sum of u and v is 3 or less]

$(R^{18}\text{-}S(=O)_2)_3CH$ [10]

[in General Formula [10], R^{18}'s each independently represent a group selected from the group consisting of a monovalent hydrocarbon group having 1 to 8 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, and a fluorine element]

$((R^{19}\text{-}S(=O)_2)_3C)_wSi(H)_x(R^{20})_{4-w-x}$ [11]

[in General Formula [11], R^{19}'s each independently represent a group selected from the group consisting of a monovalent hydrocarbon group having 1 to 8 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, and a fluorine element, R^{20}'s each independently represent a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, w represents an integer of 1 to 3, x represents an integer of 0 to 2, and a sum of w and x is 3 or less].

17. The treatment method according to Claim 15 or 16,

wherein a content of the catalyst is 0.005% by mass or more and 20% by mass or less in 100% by mass of the surface treatment agent composition.

18. The treatment method according to any one of Claims 1 to 17,

wherein the surface treatment agent composition does not contain water or contains water in a content of 2% by mass or less in 100% by mass of the surface treatment agent composition.

19. The treatment method according to any one of Claims 1 to 18,

wherein, in the surface treatment step, the surface treatment agent composition is brought into contact with the main surface by a spin coating method.

20. The treatment method according to any one of Claims 1 to 19, further comprising, before the surface treatment step:

at least one or more cleaning steps of bringing the main surface of the semiconductor substrate into contact with an aqueous cleaning solution.

21. The treatment method according to Claim 20,

wherein the aqueous cleaning solution includes one or two or more kinds selected from the group consisting of water, alcohol, an ammonium hydroxide aqueous solution, a tetramethylammonium aqueous solution, a hydrochloric acid aqueous solution, a hydrogen peroxide

aqueous solution, a sulfuric acid aqueous solution, and an organic solvent.

22. The treatment method according to Claim 20 or 21, further comprising, after the cleaning step before the surface treatment step:

a first rinsing step of bringing the main surface of the semiconductor substrate into contact with a first rinsing solution.

23. The treatment method according to any one of Claims 1 to 22, further comprising, after the surface treatment step:

a second rinsing step of bringing the main surface of the semiconductor substrate into contact with a second rinsing solution.

24. The treatment method according to any one of Claims 1 to 23, further comprising, after the surface treatment step:

a drying step of drying the main surface of the semiconductor substrate.

25. The treatment method according to any one of Claims 1 to 24, further comprising, after the surface treatment step:

a removal step of removing a surface treatment agent layer formed on the main surface of the semiconductor substrate from the main surface, the surface treatment agent layer being formed by the surface treatment step.