the rinsing solution to a back surface along with the inclined surface.

[0006]

As a result of intensive studies based on such findings, it has been found that, by performing a surface treatment using a surface treatment agent composition which sets a receding contact angle of 2-propanol (hereinafter, also referred to as "IPA") and/or a receding contact angle of pure water to predetermined values on a bevel region formed on a periphery of the semiconductor substrate, liquid drainage characteristics of the rinsing solution in the bevel region can be controlled, and by adopting the IPA receding contact angle and/or the water receding contact angle as indexes, it is possible to stably evaluate the liquid drainage characteristics. Further, it has been found that, by setting the IPA receding contact angle and/or the water receding contact angle to a predetermined value or more, it is possible to suppress the rinsing solution from wrapping around to the back surface of the semiconductor substrate during the manufacturing process, and the present disclosure has been completed.

[0006a]

In an aspect of the present disclosure, there is provided 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 bevel region which is formed on a periphery of the pattern formation region and includes an inclined surface formed on the main surface, 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 bevel region on the main surface of the semiconductor substrate by a spin method, and

a step of, after the surface treatment step, bringing the main surface of the semiconductor substrate into contact with a rinsing solution, and shaking off the rinsing solution using a spin method,

wherein the surface treatment agent composition is a liquid; and

wherein the surface treatment agent composition exhibits an IPA receding contact angle obtained by the following procedure is 3° or more at a room temperature of 25°C, and/or

the surface treatment agent composition exhibits a water receding contact angle obtained by the following procedure is 40° or more at the room temperature of 25°C,

(procedure)

the surface treatment agent composition is brought into contact with a smooth surface of a silicon oxide substrate of which surface is composed of silicon oxide to perform a surface treatment, and

with respect to the surface-treated surface of the silicon oxide substrate in a state of being stood on a horizontal table, 3 μl of 2-propanol is dropped on the surface at the room temperature of 25°C and a value of a contact angle 60 seconds later after the dropping is measured and defined as the IPA receding contact angle (°), and

30 μl of pure water is dropped on the surface at the room temperature of 25°C, the pure water is sucked at a rate of 6 μl/sec, and a value of a contact angle while a droplet size is decreasing is measured and

defined as the water receding contact angle (°).

[0007]

According to the present disclosure, there is provided 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 bevel region which is formed on a periphery of the pattern formation region, the method including a surface treatment step of bringing a surface treatment agent composition including a silylating agent into contact with the pattern formation region and the bevel region on the main

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 bevel region which is formed on a periphery of the pattern formation region and includes an inclined surface formed on the main surface, 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 bevel region on the main surface of the semiconductor substrate by a spin method, and

a step of, after the surface treatment step, bringing the main surface of the semiconductor substrate into contact with a rinsing solution, and shaking off the rinsing solution using a spin method,

wherein the surface treatment agent composition is a liquid; and

wherein the surface treatment agent composition exhibits an IPA receding contact angle obtained by the following procedure is 3° or more at a room temperature of 25°C, and/or

the surface treatment agent composition exhibits a water receding contact angle obtained by the following procedure is 40° or more at the room temperature of 25°C,

(procedure)

the surface treatment agent composition is brought into contact with a smooth surface of a silicon oxide substrate of which surface

is composed of silicon oxide to perform a surface treatment, and

with respect to the surface-treated surface of the silicon oxide substrate in a state of being stood on a horizontal table, 3 μl of 2-propanol is dropped on the surface at the room temperature of 25°C and a value of a contact angle 60 seconds later after the dropping is measured and defined as the IPA receding contact angle (°), and

30 μl of pure water is dropped on the surface at the room temperature of 25°C, the pure water is sucked at a rate of 6 μl/sec, and a value of a contact angle while a droplet size is decreasing is measured and defined as the water receding contact angle (°).

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 of the semiconductor substrate and/or at least one dimension in a height direction of a direction perpendicular to the main surface of the semiconductor substrate.

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

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.

4. The treatment method according to Claim 1 to 3,

wherein the solvent includes an aprotic solvent.

5. The treatment method according to Claim 4,

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

6. The treatment method according to Claim 4 or 5,

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.

7. The treatment method according to any one of Claims 4 to 6,

wherein the solvent includes a carbonate solvent or a lactone.

8. The treatment method according to any one of Claims 4 to 6,

wherein the solvent includes propylene carbonate or γ-butyrolactone.

9. The treatment method according to any one of Claims 4 to 6,

wherein the solvent includes a derivative of polyhydric alcohol.

10. The treatment method according to any one of Claims 1 to 9,

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).

11. The treatment method according to any one of Claims 1 to 10, wherein the silylating agent has a trialkylsilyl group.

12. The treatment method according to any one of Claims 1 to 11, wherein, in the silylating agent, an element bonded to an Si element is nitrogen.

13. The treatment method according to any one of Claims 1 to 12, 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.

14. The treatment method according to any one of Claims 1 to 13, wherein the surface treatment agent composition includes a catalyst.

15. The treatment method according to Claim 14,

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]

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

[in General Formula [4], $R^{8'}$ represents a monovalent hydrocarbon

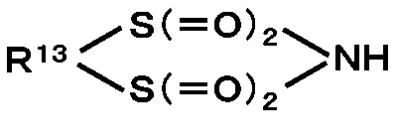
group having 1 to 8 carbon atoms, in which a part or all of hydrogen elements may be replaced with fluorine elements, R^9's each independently represent at least one group selected from monovalent hydrocarbon groups having 1 to 18 carbon atoms, in which a part or all of hydrogen elements may be replaced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

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

[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]

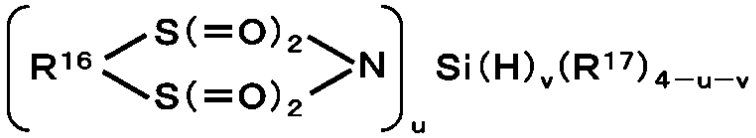

[7]

[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]



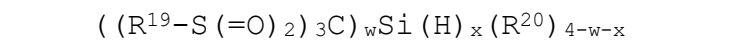
[9]

[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]



[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]



[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].

16. The treatment method according to Claim 14 or 15,

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.

17. The treatment method according to any one of Claims 1 to 16,

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.

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

wherein the IPA receding contact angle is 5° or more at the room temperature of 25°C, and/or

the water receding contact angle is 50° or more at the room temperature of 25°C.

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

wherein an IPA contact angle measured by the following procedure is 2° or more and 10° or less at the room temperature of 25°C, and/or

a water contact angle measured by the following procedure is 50° or more at the room temperature of 25°C,

(procedure)

the surface treatment agent composition is brought into contact with a smooth surface of a silicon oxide substrate of which surface is composed of silicon oxide to perform a surface treatment, and

with respect to the surface-treated surface of the silicon oxide substrate in a state of being stood on a horizontal table, 1 μl of 2-propanol is dropped on the surface at the room temperature of 25°C in a state of a droplet and a value of a contact angle 5 seconds later after the dropping is measured and defined as the IPA contact angle (°), and

1 μl of pure water is dropped on the surface at the room temperature of 25°C and a value of a contact angle 5 seconds later after the dropping is measured and defined as the water contact angle (°).

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

24. The treatment method according to any one of Claims 1 to 23, 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.