CLAIMS

1. A bevel portion treatment agent composition which is used for treating a bevel portion of a wafer, the composition comprising:

a silylating agent,

wherein a surface modification index Y and a surface modification index Z measured in the following procedures (1) to (4) satisfy $0.5 \leq Y/Z \leq 1.0$,

(procedure)

(1) a substrate having a silicon oxide film (SiO_2 film) having a thickness of 1 μm on a surface is treated with the bevel portion treatment agent composition,

treatment conditions are as follows: the substrate is immersed in 1% by mass of a hydrofluoric acid aqueous solution at room temperature for 10 minutes, subsequently, immersed in pure water for 1 minute, and in 2-propanol (iPA) for 1 minute, subsequently, immersed in the bevel portion treatment agent composition at 25°C for 1 minute, subsequently, immersed in iPA for 1 minute, finally the substrate was removed from the iPA, and air is blown to remove the iPA on the surface of the substrate,

(2) a critical surface tension of the silicon oxide film after the treatment (1) is obtained by a Zisman plot method using a plurality of measuring liquids having different mixing ratios of water and iPA, and a value of the obtained critical surface tension (mN/m) is defined as the “surface modification index Y”,

(3) a substrate having a silicon nitride film (SiN film) having a thickness of 50 nm on a surface is treated with the bevel portion treatment agent composition,

the treatment conditions are as follows: the substrate is immersed in 1% by mass of a hydrofluoric acid aqueous solution at room temperature for 10 minutes, subsequently, immersed in pure water for 1 minute, and in iPA for 1 minute, subsequently, immersed in the bevel portion treatment agent composition at 25°C for 1 minute, subsequently, immersed in iPA for 1 minute, finally, the substrate is removed from iPA, and air is blown to remove iPA on the surface of the substrate, and

(4) a critical surface tension of the silicon nitride film after the treatment (3) is obtained by the Zisman plot method using a plurality of measuring liquids having different mixing ratios of water and iPA, and an obtained value (mN/m) of the critical surface tension is defined as the “surface modification index Z”.

2. The bevel portion treatment agent composition according to claim 1,

wherein the surface modification index Y satisfies

15 mN/m ≤ Y ≤ 26mN/m.

3. The bevel portion treatment agent composition according to claim 1 or 2,

wherein the silylating agent contains a silicon compound represented by General Formula[1],

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

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

4. The bevel portion treatment agent composition according to any one of claims 1 to 3,

wherein the silylating agent contains a silicon compound having a trialkylsilyl group.

5. The bevel portion treatment agent composition according to any one of claims 1 to 4, further comprising:

an organic solvent.

6. The bevel portion treatment agent composition according to ~~any one of claims 1 to 5~~claim 3, further comprising:

an accelerator of the silicon compound,

wherein the accelerator includes one or more selected from the group consisting of trimethylsilyl trifluoroacetate, trimethylsilyltrifluoromethane sulfonate, dimethylsilyl trifluoroacetate, dimethylsilyltrifluoromethane sulfonate, butyldimethylsilyl trifluoroacetate, butyldimethylsilyltrifluoromethane sulfonate, hexyldimethylsilyl trifluoroacetate, hexyldimethylsilyltrifluoromethane sulfonate,

octyldimethylsilyl trifluoroacetate, octyldimethylsilyltrifluoromethane sulfonate, decyldimethylsilyl trifluoroacetate, decyldimethylsilyltrifluoromethane sulfonate, 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 sulfonic acid ester represented by General Formula [5], a sulfonimide represented by General Formulas [6] and [7], a sulfonimide derivative represented by General Formulas [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-S(=O)$_2$OH[3]

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

R^8-S(=O)$_2$O-Si(H)$_{3-r}$(R^9)$_r$[4]

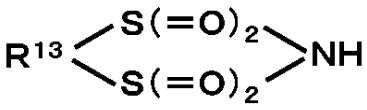
[in General Formula [4], R^8 is a monovalent hydrocarbon group having 1 to 8 carbon atoms in which part or all of hydrogen elements may be substituted with fluorine elements, R^9 each independently is at least one group selected from monovalent hydrocarbon groups having 1 to 18 carbon atoms in which part or all of hydrogen elements may be substituted with fluorine elements, and r is an integer of 1 to 3],

R^{10}-S(=O)$_2$OR^{11}[5]

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

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

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

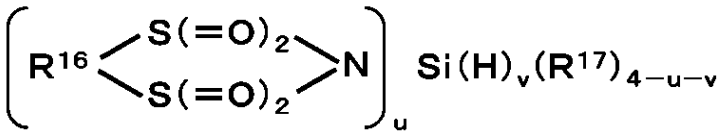


[7]

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

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

[in General Formula [8], R^{14} each independently is a group selected from the group consisting of a monovalent hydrocarbon group having 1 to 8 carbon atoms in which part or all of hydrogen elements may be substituted with fluorine elements, and a fluorine element, R^{15} each independently is a monovalent hydrocarbon group having 1 to 18 carbon atoms in which part or all of hydrogen elements may be substituted with fluorine elements, s is an integer of 1 to 3, t is an integer of 0 to 2, and the sum of s and t is equal to or less than 3],



[9]

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

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

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

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

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

7. The bevel portion treatment agent composition according to ~~any one of claims 1 to 6~~claim 1,

wherein Y and Z satisfy $0.86 \leq Y/Z \leq 0.95$.

8. A method of manufacturing a wafer having a bevel portion, comprising:

a wafer surface modification step; and

a wafer processing step,

wherein in the surface modification step, the bevel portion treatment agent composition according to any one of claims 1 to 7 is applied to the bevel portion.

9. The method of manufacturing the wafer according to claim 8,

wherein the wafer processing step includes at least one of steps consisting of a step of forming a fine pattern having an uneven shape in an element forming region on the wafer, a step of dicing or grinding the wafer, a step of forming an insulating film and/or a metal film, and a step of cleaning the wafer, and

the wafer surface modification step is performed before and after the wafer processing step and between each of a plurality of steps during the processing step.

10. The method of manufacturing the wafer according to claim 9,

wherein the insulating film is a heterogenous film that is exposed on the surface of the bevel portion in a state where a plurality of heterogenous materials is mixed.

11. The method of manufacturing the wafer according to claim 9 or claim 10, wherein the insulating film includes a silicon oxide film and a silicon nitride film.

12. The method of manufacturing the wafer according to any one of claims ~~9~~ 8 to 11, wherein in the wafer surface modification step, the bevel portion treatment agent composition is used within 30 minutes after its preparation.

13. The method of manufacturing the wafer according to any one of claims ~~9~~ 8 to 12, wherein in the wafer surface modification step, the bevel portion treatment agent composition is prepared at a liquid temperature of 25°C.

14. A use of the bevel portion treatment agent composition according to any one of claims 1 to 7 for modifying a surface of a bevel portion of a wafer.