SPECIFICATION

TITLE OF INVENTION: COMPOSITION FOR FILM FORMATION, METHOD FOR MANUFACTURING SUBSTRATE, AND METHOD FOR MANUFACTURING COMPOSITION FOR FILM FORMATION

TECHNICAL FIELD

[0001]

The present disclosure relates to a composition for film formation, a method for manufacturing a substrate, and a method for manufacturing a composition for film formation.

BACKGROUND ART

[0002]

In recent years, there has been a tendency for semiconductor devices to be highly integrated and miniaturized, and the miniaturization and high aspect ratio of resin patterns serving as a mask and inorganic patterns produced by etching have been advanced. However, on the other hand, a problem of so-called pattern collapse has occurred. The pattern collapse is a phenomenon that, in a case where a large number of resin patterns or inorganic patterns are formed in parallel on a substrate, the patterns are brought close to each other so as to be in contact with each other, and in some cases, the patterns are broken or peeled off from a base portion. In a case where such pattern collapse occurs, a desired product cannot be obtained, and thus the yield and reliability of the product are

reduced.

It has been known that the pattern collapse occurs when a cleaning liquid is dried in a cleaning treatment after pattern formation due to a surface tension of the cleaning liquid. That is, when the cleaning liquid is removed in the drying process, stress based on the surface tension of the cleaning liquid acts on the patterns, and thus the pattern collapse occurs.

Therefore, a chemical solution that imparts water repellency to the pattern surface by a silylating agent and suppresses pattern collapse is used in a semiconductor manufacturing site.

Patent Document 1 describes a surface treatment agent including a silylating agent including at least one compound having a disilazane structure and a solvent.

RELATED DOCUMENT

PATENT DOCUMENT

[0003]

Patent Document 1: Japanese Unexamined Patent Publication No. 2011-091349

Patent Document 2: Pamphlet of International Publication No. WO2011/155407

SUMMARY OF THE INVENTION

TECHNICAL PROBLEM

[0004]

A method of adding an accelerator to the chemical solution

has been carried out for the purpose of further improving the effect of imparting water repellency by the silylating agent. However, it has been found that the chemical solution using a chlorine-containing accelerator as the accelerator has not been sufficiently studied so far.

SOLUTION TO PROBLEM

[0005]

As a result of intensive studies in view of the above circumstances, the inventors of the present invention found a new chemical solution containing a chlorine-containing accelerator since a chemical solution containing a silylating agent, a chlorine-containing silyl ester compound, and an aprotic solvent can impart excellent water repellency to a substrate surface, and thus completed the present disclosure.

[0006]

According to one aspect of the present disclosure, the following composition for film formation, a method for manufacturing a substrate, and a method for manufacturing a composition for film formation are provided.

[0007]

1. A composition for film formation, which is used for forming a water-repellent film, containing: (I) a silylating agent; (II) a silyl ester compound represented by General Formula [2]; and (III) an aprotic solvent.

$(R^2\text{-}C(=O)O)_i\text{-}Si(H)_{4-i-h}(R^3)_h$ [2]

(in General Formula [2], R^2 is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of

hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms, R^3's are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, i is an integer of 1 to 3, h is an integer of 1 to 3, and i + h is an integer of 2 to 4)

2. The composition for film formation according to 1., in which 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's are each independently an organic group including a hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, X's are each independently a monovalent group in which an atom bonded to an Si atom is nitrogen, oxygen, carbon, or halogen, a is an integer of 1 to 3, b is an integer of 0 to 2, and a sum of a and b is 1 to 3)

3. The composition for film formation according to 1. or 2., contains the silyl ester compound which R^2 in General Formula [2] is represented by $-C_qY_{(2q+1-r)}Cl_r$ (where Y's are each independently a hydrogen atom or a fluorine atom bonded to carbon, Cl is a chlorine atom, q is an integer of 1 to 5, and r is 1 to 2q).

4. The composition for film formation according to any one

of 1. to 3., in which the aprotic solvent contains one or two or more selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen atom-containing solvents, sulfoxide-based solvents, carbonate-based solvents, a derivative of a polyhydric alcohol that does not have an OH group, a nitrogen atom-containing solvent that does not have an N-H group, and a silicone solvent.

5. The composition for film formation according to any one of 1. to 4., in which a content of the silylating agent is 0.1% by mass or more and 35% by mass or less in 100% by mass of the composition for film formation.

6. The composition for film formation according to any one of 1. to 5., in which a content of the silyl ester compound is 0.01% by mass or more and 10% by mass or less in 100% by mass of the composition for film formation.

7. The composition for film formation according to any one of 1. to 6., in which a water contact angle of a film formed from the composition for film formation, which is measured in accordance with JIS R 3257:1999, is 70° or more.

8. The composition for film formation according to any one of 1. to 7., in which the composition for film formation contains (III) the aprotic solvent having a polarity.

9. The composition for film formation according to any one of 1. to 8., in which the composition for film formation does not contain an amide compound represented by General Formula [4] or a content of the amide compound is 0.1% by mass or less in 100% by mass of the composition for film formation.

R^{b1}-C(=O)N(H)Z[4]

(in General Formula [4], R^{b1} is a hydrocarbon group having a Cl_3C moiety, a Cl_2HC moiety, or a Cl_2FC moiety, and Z is a hydrogen atom or a monovalent hydrocarbon group having 1 to 3 carbon atoms, which is bonded to a nitrogen atom)

10. The composition for film formation according to 9., in which the composition for film formation contains an amide compound having a structure in which R^{b1} is a hydrocarbon group that does not have a Cl_3C moiety, a Cl_2HC moiety, or a Cl_2FC moiety in General Formula [4].

11. The composition for film formation according to any one of 1. to 10., in which the composition for film formation contains one or two or more selected from the group consisting of a silylamide compound represented by General Formula [5] and an aminosilane compound represented by General Formula [6].

$(R^{b2}$-C(=O)N(H))$_j$-Si(H)$_{4-j-t}(R^{b3})_t$[5]

(in General Formula [5], R^{b2} is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms, R^{b3}'s are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, j is an integer of 1 to 3, t is an integer of 1 to 3, and j + t is an integer of 2 to 4)

$(R^{b4})_u$Si(H)$_v(NH_2)_{4-u-v}$[6]

(in General Formula [6], R^{b4}'s are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, u is an integer of 1 to 3, v is an integer of 0 to 2, and a sum of u and v is 1 to 3)

12. A method for manufacturing a substrate, including: a step of preparing a substrate; and a step of supplying a composition for film formation to the substrate to form a water-repellent film on at least a part of a surface of the substrate, in which the composition for film formation contains (I) a silylating agent, (II) a silyl ester compound represented by General Formula [2], and (III) an aprotic solvent.

$(R^2\text{-}C(=O)O)_i\text{-}Si(H)_{4-i-h}(R^3)_h$ [2]

(in General Formula [2], R^2 is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms, R^3's are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, i is an integer of 1 to 3, h is an integer of 1 to 3, and i + h is an integer of 2 to 4)

13. The method for manufacturing a substrate according to 12., further including: a step of cleaning the substrate prior to supplying the composition for film formation.

14. A method for manufacturing a composition for film formation, including: a step of mixing (I) a silylating agent, (II) a silyl ester compound, and (III) an aprotic solvent.

15. A method for manufacturing a composition for film formation, including: a reaction step of reacting (I) a silylating agent with a chlorocarboxylic acid compound containing at least one of a chlorocarboxylic acid and a chlorocarboxylic acid anhydride to obtain (II) a silyl ester compound.

16. The method for manufacturing a composition for film formation according to 15., in which the chlorocarboxylic acid contains one or two or more of compounds represented by General Formula [7], and the chlorocarboxylic acid anhydride contains one or two or more of compounds represented by General Formula [8].

R^{C2}-C(=O)OH[7]

R^{C2}-C(=O)O-C(=O)-R^{C2}[8]

(in General Formulae [7] and [8], R^{C2}'s are each a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms)

17. The method for manufacturing a composition for film formation according to 15. or 16., in which the chlorocarboxylic acid compound contains at least one of the chlorocarboxylic acid having a pKa of -0.2 or more and 4.5 or less and an anhydride of

the chlorocarboxylic acid.

18. The method for manufacturing a composition for film formation according to any one of 15. to 17., in which the reaction step is carried out in (III) an aprotic solvent.

19. The method for manufacturing a composition for film formation according to any one of 15. to 18., in which in the reaction step, the chlorocarboxylic acid compound contains the chlorocarboxylic acid and does not contain the chlorocarboxylic acid anhydride.

20. The method for manufacturing a composition for film formation according to any one of 15. to 19., in which (I) the silylating agent is not a silazane compound.

21. The method for manufacturing a composition for film formation according to any one of 15. to 20., in which the reaction step is carried out in an inert atmosphere.

ADVANTAGEOUS EFFECTS OF INVENTION

[0008]

According to the present disclosure, it is possible to provide a composition for film formation, which can realize a novel chemical solution containing a chlorine-containing accelerator, a method for manufacturing a substrate using the composition for film formation, and a method for manufacturing a composition for film formation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

FIG. 1 is a top view schematically showing a configuration of a substrate.

FIG. 2 is a cross-sectional view schematically showing a configuration of a substrate.

FIG. 3A to FIG.3C are cross-sectional views of a step schematically illustrating a step of manufacturing a substrate.

DESCRIPTION OF EMBODIMENTS

[0010]

Hereinafter, embodiments of the present disclosure will be described with reference to the drawings. It is noted that in all the drawings, the same constitutional elements are denoted as the same reference numerals and explanations thereof will not be repeated, as appropriate. In addition, the figures are schematic views and do not correspond to the actual dimensional ratios.

[0011]

An outline of the composition for film formation according to the present embodiment will be described.

[0012]

The composition for film formation according to the present embodiment contains (I) a silylating agent, (II) a silyl ester compound represented by General Formula [2], and (III) an aprotic solvent.

$(R^2\text{-}C(=O)O)_i\text{-}Si(H)_{4-i-h}(R^3)_h$ [2]

(in General Formula [2], R^2 is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of

hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms, R^3's are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, i is an integer of 1 to 3, h is an integer of 1 to 3, and i + h is an integer of 2 to 4)

[0013]

According to the findings of the inventors of the present invention, it has been found that excellent water repellency can be imparted to a substrate surface by a composition for film formation, which contains the above-described silylating agent, chlorine-containing silyl ester compound, and aprotic solvent.

[0014]

The composition for film formation according to the present embodiment is a surface reforming agent solution used for forming a water-repellent film on at least a part of a substrate surface.

The water repellency can be defined using a water contact angle measured by the following coupon test as an index.

In the water-repellent film in a case where the composition for film formation is formed into a film, the water contact angle measured in accordance with JIS R 3257:1999 is, for example, 70° or more, preferably 75° or more, and more preferably 81° or more.

(Procedure of Coupon Test)

A silicon wafer having no uneven pattern on a surface and having a silicon oxide film with a thickness of 1 μm on the surface is cut to prepare a coupon consisting of a silicon substrate having dimensions of a length of 4 cm, a width of 1 cm, and a thickness of 0.75 mm.

The coupon is immersed in 1% by mass of hydrofluoric acid at room temperature, then immersed in water at room temperature, then immersed in 2-propanol at room temperature, and then immersed in propylene glycol monomethyl ether acetate at room temperature for cleaning. In addition, at this time, the "room temperature" is set to 25°C.

An evaluation solution consisting of the composition for film formation is prepared, and the cleaned coupon is immersed in the evaluation solution at room temperature. An immersion time in the evaluation solution is set to 20 seconds.

The coupon taken out from the evaluation solution is cleaned by being immersed in 2-propanol at room temperature, and then the surface of the coupon is dried with nitrogen gas.

In a state in which the dried coupon is placed on a horizontal plane, 2 μl of pure water is placed on the surface of the coupon on which the silicon oxide film has formed at room temperature, and a water contact angle (°) is measured in accordance with JIS R 3257:1999.

[0015]

Patent Document 2 discloses a chemical solution for forming a protective film, which is a chemical solution for forming a water-repellent protective film on at least a surface of a

concave portion of a fine uneven pattern during cleaning a wafer having the uneven pattern on a surface thereof, in which at least a part of the uneven pattern contains a silicon element, and contains a silicon compound A having a predetermined structure and an acid A, in which the acid A is at least one selected from the group consisting of trimethylsilyl trifluoroacetate, trimethylsilyl trifluoromethanesulfonate, dimethylsilyl trifluoroacetate, dimethylsilyl trifluoromethanesulfonate, butyldimethylsilyl trifluoroacetate, butyldimethylsilyl trifluoromethanesulfonate, octyldimethylsilyl trifluoroacetate, and octyldimethylsilyl trifluoromethanesulfonate.

In Patent Document 2, the result is disclosed that in a case where a perfluoroalkyl derivative such as trimethylsilyl trifluoroacetate (TMSTFA) is used as an accelerator, excellent water repellency can be imparted, but in a case where unsubstituted sulfuric acid, nitric acid, or acetic acid is used, water repellency is significantly deteriorated.

From there, it was predicted that in a compound such as trimethylsilyl chlorodifluoroacetate (TMSCDFA) or trimethylsilyl dichlorofluoroacetate (TMSDCFA), in which at least a part of the fluorine atoms of the perfluoroalkyl derivative is substituted with chlorine atoms, the electron-withdrawing property of the chlorine atom is insufficient, and thus the water repellency imparted is decreased. However, in a case where the compound containing a chlorine atom as described above is applied to the accelerator, contrary to expectations, the water repellency

equivalent to that of a perfluoroalkyl derivative such as TMSTFA can be achieved. Here, the equivalent water repellency refers that the water repellency is significantly superior to that in a case where unsubstituted sulfuric acid, nitric acid, or acetic acid is used, specifically, the water repellency standard of the water contact angle of 70° or more is satisfied.

According to the present embodiment, it is possible to provide a composition for film formation having the same water repellency by substituting at least a part of the fluorine atoms of the perfluoroalkyl derivative with chlorine atoms.

In addition, in view of the situation where the natural fluorine resource is in a depleted state, it is preferable that the fluorine is substituted with chlorine in the accelerator from the viewpoint of resource saving.

[0016]

It is noted that in the “water-repellent film” in the present specification, both a compound having a silyl group derived from a silylating agent chemically bonded to the substrate surface and a group of such compounds are referred to, and the presence or absence of interaction between the compounds or the presence or absence of bonding between the compounds does not matter. It is noted that the above-described binding is not required to be a direct bonding and includes a case of bonding through another element, a substituent, or the like.

[0017]

Hereinafter, each composition of the composition for film formation of the present embodiment will be described in detail.

[0018]

((I) Silylating Agent)

As the silylating agent, a publicly known silylating agent can be used.

The silylating agent may include, for example, a silicon compound represented by General Formula [1]. These may be used alone, or two or more thereof may be used in combination.

[0019]

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

[0020]

In General Formula [1], R^1's are each independently an organic group including a hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, X's are each independently a monovalent group in which an atom bonded to an Si atom is nitrogen, oxygen, carbon, or halogen, a is an integer of 1 to 3, b is an integer of 0 to 2, and a sum of a and b is 1 to 3.

In a case where all hydrogen atoms of the above-described hydrocarbon group are substituted with atoms other than hydrogen atoms, the hydrocarbon group is also referred to as a hydrocarbon group.

[0021]

R^1 in General Formula [1] may include not only a hydrogen atom, a carbon atom, a nitrogen atom, an oxygen atom, a fluorine atom, and a chlorine atom, but also a silicon atom, a sulfur atom, a halogen atom (other than fluorine), and the like. In

addition, R^1 in General Formula [1] may contain an unsaturated bond, an aromatic ring, or a cyclic structure.

[0022]

Examples of R^1's in General Formula [1] each independently include at least one group selected from C_eH_{2e+1} (e = 1 to 18) and $C_fF_{2f+1}CH_2CH_2$ (f = 1 to 8).

[0023]

In addition, in a case where R^1 in General Formula [1] includes a silicon atom, a structure of General Formula [1-1] shown below may be adopted.

$$R^1_mX_{3-m-n}(H)_nSi-(CH_2)_p-Si(H)_nX_{3-m-n}R^1_m \quad [1-1]$$

In General Formula [1-1], R^1's and X are the same as in General Formula [1] (however, a silicon atom is not included in R^1's), m is an integer of 1 or 2, n is an integer of 0 or 1, a sum of m and n is 1 or 2, p is an integer of 1 to 18, and a methylene chain represented by $-(CH_2)_p-$ may be substituted with halogen.

[0024]

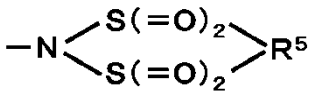
In X in General Formula [1], a monovalent group in which an atom bonded to an Si atom is nitrogen, oxygen, or carbon may include not only a hydrogen, carbon, nitrogen, or oxygen atom but also a silicon, sulfur, or halogen atom.

[0025]

In X in General Formula [1], examples of the above-described monovalent group in which the atom bonded to the Si atom is nitrogen include an isocyanate group, an amino group, a dialkylamino group, an isothiocyanate group, an azido group, an

acetamide group, $-NHC(=O)CF_3$, $-N(CH_3)C(=O)CH_3$, $-N(CH_3)C(=O)CF_3$, $-N=C(CH_3)OSi(CH_3)_3$, $-N=C(CF_3)OSi(CH_3)_3$, $-NHC(=O)-OSi(CH_3)_3$, $-NHC(=O)-NH-Si(CH_3)_3$, an imidazole ring, a triazole ring, a tetrazole ring, an oxazolidinone ring, a morpholine ring, $-NH-C(=O)-Si(CH_3)_3$, $-N(S(=O)_2R^4)_2$ (here, R^4'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 atoms may be substituted with fluorine atoms, and a fluorine atom), and a substituent having a structure of General Formula [1-2].

[chem. 1]



[1-2]

(In General Formula [1-2], R^5's each independently is a divalent hydrocarbon group having 1 to 8 carbon atoms in which a part or all of the hydrogen atoms may be substituted with fluorine atoms), $-N=C(NR^6_2)_2$, $-N=C(NR^6_2)R^6$ (here, R^6's each independently is selected from a hydrogen group, a $-C\equiv N$ group, a $-NO_2$ group, and a hydrocarbon group in which a part or all of hydrogen atoms may be substituted with fluorine atoms, and the hydrocarbon group may have an oxygen atom and/or a nitrogen atom), $-N(R^{a1})(R^{a2})$ (Here, R^{a1} represents a hydrogen atom, or a saturated or unsaturated alkyl group, and R^{a2} is a saturated or unsaturated alkyl group, a saturated or unsaturated cycloalkyl group, or a saturated or unsaturated heterocycloalkyl group. R^{a1} and R^{a2} may be bonded to each other to form a saturated or unsaturated heterocycloalkyl group having a nitrogen atom), -

$N(R^{a3})-Si(R^{a4})(R^{a5})(R^{a6})$ (here, R^{a3} represents a hydrogen atom, a hydrocarbon group having 1 to 4 carbon atoms, a trimethylsilyl group, or a dimethylsilyl group, R^{a4}, R^{a5}, and R^{a6} each independently represent a hydrogen atom or an organic group, the total number of carbon atoms contained in R^{a4}, R^{a5}, and R^{a6} is equal to or more than 1), $-N(R^{a7})-C(=O)R^{a8}$ (here, R^{a7} represents a hydrogen atom, a methyl group, a trimethylsilyl group, or a dimethylsilyl group, and R^{a8} is a hydrogen atom, a saturated or unsaturated alkyl group, or a fluorine-containing alkyl group, or a trialkylsilylamino group), and the like.

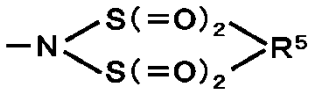
[0026]

Examples of the silylating agent in which X in General Formula [1] is a monovalent group in which an atom bonded to an Si atom is nitrogen include aminosilanes such as $CH_3Si(NH_2)_3$, $C_2H_5Si(NH_2)_3$, $C_3H_7Si(NH_2)_3$, $C_4H_9Si(NH_2)_3$, $C_5H_{11}Si(NH_2)_3$, $C_6H_{13}Si(NH_2)_3$, $C_7H_{15}Si(NH_2)_3$, $C_8H_{17}Si(NH_2)_3$, $C_9H_{19}Si(NH_2)_3$, $C_{10}H_{21}Si(NH_2)_3$, $C_{11}H_{23}Si(NH_2)_3$, $C_{12}H_{25}Si(NH_2)_3$, $C_{13}H_{27}Si(NH_2)_3$, $C_{14}H_{29}Si(NH_2)_3$, $C_{15}H_{31}Si(NH_2)_3$, $C_{16}H_{33}Si(NH_2)_3$, $C_{17}H_{35}Si(NH_2)_3$, $C_{18}H_{37}Si(NH_2)_3$, $(CH_3)_2Si(NH_2)_2$, $C_2H_5Si(CH_3)(NH_2)_2$, $(C_2H_5)_2Si(NH_2)_2$, $C_3H_7Si(CH_3)(NH_2)_2$, $(C_3H_7)_2Si(NH_2)_2$, $C_4H_9Si(CH_3)(NH_2)_2$, $(C_4H_9)_2Si(NH_2)_2$, $C_5H_{11}Si(CH_3)(NH_2)_2$, $C_6H_{13}Si(CH_3)(NH_2)_2$, $C_7H_{15}Si(CH_3)(NH_2)_2$, $C_8H_{17}Si(CH_3)(NH_2)_2$, $C_9H_{19}Si(CH_3)(NH_2)_2$, $C_{10}H_{21}Si(CH_3)(NH_2)_2$, $C_{11}H_{23}Si(CH_3)(NH_2)_2$, $C_{12}H_{25}Si(CH_3)(NH_2)_2$, $C_{13}H_{27}Si(CH_3)(NH_2)_2$, $C_{14}H_{29}Si(CH_3)(NH_2)_2$, $C_{15}H_{31}Si(CH_3)(NH_2)_2$, $C_{16}H_{33}Si(CH_3)(NH_2)_2$, $C_{17}H_{35}Si(CH_3)(NH_2)_2$, $C_{18}H_{37}Si(CH_3)(NH_2)_2$, $(CH_3)_3SiNH_2$, $C_2H_5Si(CH_3)_2NH_2$, $(C_2H_5)_2Si(CH_3)NH_2$, $(C_2H_5)_3SiNH_2$, $C_3H_7Si(CH_3)_2NH_2$, $(C_3H_7)_2Si(CH_3)NH_2$, $(C_3H_7)_3SiNH_2$, $C_4H_9Si(CH_3)_2NH_2$, $(C_4H_9)_3SiNH_2$, $C_5H_{11}Si(CH_3)_2NH_2$,

$C_6H_{13}Si(CH_3)_2NH_2$, $C_7H_{15}Si(CH_3)_2NH_2$, $C_8H_{17}Si(CH_3)_2NH_2$, $C_9H_{19}Si(CH_3)_2NH_2$, $C_{10}H_{21}Si(CH_3)_2NH_2$, $C_{11}H_{23}Si(CH_3)_2NH_2$, $C_{12}H_{25}Si(CH_3)_2NH_2$, $C_{13}H_{27}Si(CH_3)_2NH_2$, $C_{14}H_{29}Si(CH_3)_2NH_2$, $C_{15}H_{31}Si(CH_3)_2NH_2$, $C_{16}H_{33}Si(CH_3)_2NH_2$, $C_{17}H_{35}Si(CH_3)_2NH_2$, $C_{18}H_{37}Si(CH_3)_2NH_2$, $(CH_3)_2Si(H)NH_2$, $CH_3Si(H)_2NH_2$, $(C_2H_5)_2Si(H)NH_2$, $C_2H_5Si(H)_2NH_2$, $C_2H_5Si(CH_3)(H)NH_2$, $(C_3H_7)_2Si(H)NH_2$, $C_3H_7Si(H)_2NH_2$, $CF_3CH_2CH_2Si(NH_2)_3$, $C_2F_5CH_2CH_2Si(NH_2)_3$, $C_3F_7CH_2CH_2Si(NH_2)_3$, $C_4F_9CH_2CH_2Si(NH_2)_3$, $C_5F_{11}CH_2CH_2Si(NH_2)_3$, $C_6F_{13}CH_2CH_2Si(NH_2)_3$, $C_7F_{15}CH_2CH_2Si(NH_2)_3$, $C_8F_{17}CH_2CH_2Si(NH_2)_3$, $CF_3CH_2CH_2Si(CH_3)(NH_2)_2$, $C_2F_5CH_2CH_2Si(CH_3)(NH_2)_2$, $C_3F_7CH_2CH_2Si(CH_3)(NH_2)_2$, $C_4F_9CH_2CH_2Si(CH_3)(NH_2)_2$, $C_5F_{11}CH_2CH_2Si(CH_3)(NH_2)_2$, $C_6F_{13}CH_2CH_2Si(CH_3)(NH_2)_2$, $C_7F_{15}CH_2CH_2Si(CH_3)(NH_2)_2$, $C_8F_{17}CH_2CH_2Si(CH_3)(NH_2)_2$, $CF_3CH_2CH_2Si(CH_3)_2NH_2$, $C_2F_5CH_2CH_2Si(CH_3)_2NH_2$, $C_3F_7CH_2CH_2Si(CH_3)_2NH_2$, $C_4F_9CH_2CH_2Si(CH_3)_2NH_2$, $C_5F_{11}CH_2CH_2Si(CH_3)_2NH_2$, $C_6F_{13}CH_2CH_2Si(CH_3)_2NH_2$, $C_7F_{15}CH_2CH_2Si(CH_3)_2NH_2$, $C_8F_{17}CH_2CH_2Si(CH_3)_2NH_2$, $CF_3CH_2CH_2Si(CH_3)(H)NH_2$, aminodimethylvinylsilane, aminodimethylphenylethylsilane, aminodimethylphenylsilane, aminomethyldiphenylsilane, and aminodimethyl-t-butylsilane, or those obtained by substituting an amino group ($-NH_2$ group) of the aminosilane with $-N=NC=O$, a dialkylamino group ($-N(CH_3)_2$, $-N(C_2H_5)_2$, or the like), a t-butylamino group, an allylamino group, $-N=NC=S$, $-N_3$, $-NHC(=O)CH_3$, $-NHC(=O)CF_3$, $-N(CH_3)C(=O)CH_3$, $-N(CH_3)C(=O)CF_3$, $-N=C(CH_3)OSi(CH_3)_3$, $-N=C(CF_3)OSi(CH_3)_3$, $-NHC(=O)-OSi(CH_3)_3$, $-NHC(=O)-NH-Si(CH_3)_3$ (for example, N,N'-bis(trimethylsilyl)urea or the like), an imidazole ring (for example, N-trimethylsilylimidazole or the like), a triazole ring (for example, N-trimethylsilyltriazole or the like), a tetrazole ring, an oxazolidinone ring, a morpholine

ring, $-NH-C(=O)-Si(CH_3)_3$, $-N(S(=O)_2R^4)_2$ (R^4 is as described above, for example, N-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide and the like), a substituent having a structure of General Formula [1-2]

[chem. 2]



[1-2]

(in General Formula [1-2], R^5 is as described above, for example, N-(trimethylsilyl)N,N-difluoromethane-1,3-bis(sulfonyl)imide, and the like) $-N=C(NR^6_2)_2$, $-N=C(NR^6_2)R^6$ (R^6 is as described above, for example, 2-trimethylsilyl-1,1,3,3-tetramethylguanidine), $-N(R^{a1})R^{a2}$ (R^{a1} and R^{a2} are as described above), $-N(R^{a3})-Si(R^{a4})(R^{a5})(R^{a6})$ (R^{a3}, R^{a4}, R^{a5}, and R^{a6} are as described above, for example, hexamethyldisilazane, N-methylhexamethyldisilazane, 1,1,3,3-tetramethyldisilazane, 1,3-dimethyldisilazane, 1,3-di-N-octyltetramethyldisilazane, 1,3-divinyltetramethyldisilazane, heptamethyldisilazane, N-allyl-N,N-bis(trimethylsilyl)amine, 1,3-diphenyltetramethyldisilazane, 1,1,3,3-tetraphenyl-1,3-dimethyldisilazane, nonamethyldisilazane, pentamethylethyldisilazane, pentamethylvinyldisilazane, pentamethylpropyldisilazane, pentamethylethyldisilazane, pentamethyl-t-butyldisilazane, pentamethylphenyldisilazane, trimethyltriethyldisilazane, and the like), and $-N(R^{a7})-C(=O)R^{a8}$ (R^{a7} and R^{a8} are as described above. for example, N-trimethylsilylacetamide, N-trimethylsilyltrifluoroacetamide, N-methyl-N-trimethylsilylacetamide, N-methyl-N-

trimethylsilyltrifluoroacetamide, bis(trimethylsilyl) acetamide, bis(trimethylsilyl) trifluoroacetamide, and the like).

[0027]

Examples of the silylating agent in which X in General Formula [1] is a monovalent group in which the atom bonded to the Si atom is oxygen include those obtained by substituting an amino group ($-NH_2$ group) of the aminosilane with $-O-C(=A)R^{a9}$ (Here, A represents O, CHR^{a10}, $CHOR^{a10}$, $CR^{a10}R^{a10}$, or NR^{a11}, where R^{a9} and R^{a10} each independently are a hydrogen atom, a saturated or unsaturated alkyl group, a chlorine-containing alkyl group a saturated or unsaturated cycloalkyl group, a fluorine-containing alkyl group, a trialkylsilyl group, a trialkylsiloxy group, an alkoxy group, a phenyl group, a phenyl ethyl group, or an acetyl group, and R^{a11} represents a hydrogen atom, an alkyl group, or a trialkylsilyl group. For example, trimethylsilyl acetate, dimethylsilyl acetate, monomethylsilyl acetate, trimethylsilyl trifluoroacetate, dimethylsilyl trifluoroacetate, monomethylsilyl trifluoroacetate, trimethylsilyl trichloroacetate, trimethylsilyl propionate, trimethylsilyl butyrate, and the like), $-O-C(R^{a12})=N(R^{a13})$ (here, R^{a12} represents a hydrogen atom, a saturated or unsaturated alkyl group, a fluorine-containing alkyl group, or a trialkylsilylamino group, and R^{a13} represents a hydrogen atom, an alkyl group, and a trialkylsilyl group), $-O-C(R^{a14})=CH-C(=O)\ R^{a15}$ (Here, R^{a14} and R^{a15} each independently represents a hydrogen atom or an organic group. For example, trimethylsilyloxy-3-pentene-2-on, 2-trimethylsiloxypenta-2-en-4-on, and the like), $-OR^{a16}$ (here, R^{a16}

represents a saturated or unsaturated alkyl group, a saturated or unsaturated cycloalkyl group, or a fluorine-containing alkyl group. for example, alkylmethoxysilanes such as $CH_3Si(OCH_3)_3$, $C_2H_5Si(OCH_3)_3$, $C_3H_7Si(OCH_3)_3$, $C_4H_9Si(OCH_3)_3$, $C_5H_{11}Si(OCH_3)_3$, $C_6H_{13}Si(OCH_3)_3$, $C_7H_{15}Si(OCH_3)_3$, $C_8H_{17}Si(OCH_3)_3$, $C_9H_{19}Si(OCH_3)_3$, $C_{10}H_{21}Si(OCH_3)_3$, $C_{11}H_{23}Si(OCH_3)_3$, $C_{12}H_{25}Si(OCH_3)_3$, $C_{13}H_{27}Si(OCH_3)_3$, $C_{14}H_{29}Si(OCH_3)_3$, $C_{15}H_{31}Si(OCH_3)_3$, $C_{16}H_{33}Si(OCH_3)_3$, $C_{17}H_{35}Si(OCH_3)_3$, $C_{18}H_{37}Si(OCH_3)_3$, $(CH_3)_2Si(OCH_3)_2$, $C_2H_5Si(CH_3)(OCH_3)_2$, $(C_2H_5)_2Si(OCH_3)_2$, $C_3H_7Si(CH_3)(OCH_3)_2$, $(C_3H_7)_2Si(OCH_3)_2$, $C_4H_9Si(CH_3)(OCH_3)_2$, $(C_4H_9)_2Si(OCH_3)_2$, $C_5H_{11}Si(CH_3)(OCH_3)_2$, $C_6H_{13}Si(CH_3)(OCH_3)_2$, $C_7H_{15}Si(CH_3)(OCH_3)_2$, $C_8H_{17}Si(CH_3)(OCH_3)_2$, $C_9H_{19}Si(CH_3)(OCH_3)_2$, $C_{10}H_{21}Si(CH_3)(OCH_3)_2$, $C_{11}H_{23}Si(CH_3)(OCH_3)_2$, $C_{12}H_{25}Si(CH_3)(OCH_3)_2$, $C_{13}H_{27}Si(CH_3)(OCH_3)_2$, $C_{14}H_{29}Si(CH_3)(OCH_3)_2$, $C_{15}H_{31}Si(CH_3)(OCH_3)_2$, $C_{16}H_{33}Si(CH_3)(OCH_3)_2$, $C_{17}H_{35}Si(CH_3)(OCH_3)_2$, $C_{18}H_{37}Si(CH_3)(OCH_3)_2$, $(CH_3)_3SiOCH_3$, $C_2H_5Si(CH_3)_2OCH_3$, $(C_2H_5)_2Si(CH_3)OCH_3$, $(C_2H_5)_3SiOCH_3$, $C_3H_7Si(CH_3)_2OCH_3$, $(C_3H_7)_2Si(CH_3)OCH_3$, $(C_3H_7)_3SiOCH_3$, $C_4H_9Si(CH_3)_2OCH_3$, $(C_4H_9)_3SiOCH_3$, $C_5H_{11}Si(CH_3)_2OCH_3$, $C_6H_{13}Si(CH_3)_2OCH_3$, $C_7H_{15}Si(CH_3)_2OCH_3$, $C_8H_{17}Si(CH_3)_2OCH_3$, $C_9H_{19}Si(CH_3)_2OCH_3$, $C_{10}H_{21}Si(CH_3)_2OCH_3$, $C_{11}H_{23}Si(CH_3)_2OCH_3$, $C_{12}H_{25}Si(CH_3)_2OCH_3$, $C_{13}H_{27}Si(CH_3)_2OCH_3$, $C_{14}H_{29}Si(CH_3)_2OCH_3$, $C_{15}H_{31}Si(CH_3)_2OCH_3$, $C_{16}H_{33}Si(CH_3)_2OCH_3$, $C_{17}H_{35}Si(CH_3)_2OCH_3$, $C_{18}H_{37}Si(CH_3)_2OCH_3$, $(CH_3)_2Si(H)OCH_3$, $CH_3Si(H)_2OCH_3$, $(C_2H_5)_2Si(H)OCH_3$, $C_2H_5Si(H)_2OCH_3$, $C_2H_5Si(CH_3)(H)OCH_3$, and $(C_3H_7)_2Si(H)OCH_3$, or fluoroalkyl methoxysilanes such as $CF_3CH_2CH_2Si(OCH_3)_3$, $C_2F_5CH_2CH_2Si(OCH_3)_3$, $C_3F_7CH_2CH_2Si(OCH_3)_3$, $C_4F_9CH_2CH_2Si(OCH_3)_3$, $C_5F_{11}CH_2CH_2Si(OCH_3)_3$, $C_6F_{13}CH_2CH_2Si(OCH_3)_3$, $C_7F_{15}CH_2CH_2Si(OCH_3)_3$, $C_8F_{17}CH_2CH_2Si(OCH_3)_3$, $CF_3CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_2F_5CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_3F_7CH_2CH_2Si(CH_3)(OCH_3)_2$,

$C_4F_9CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_5F_{11}CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_6F_{13}CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_7F_{15}CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_8F_{17}CH_2CH_2Si(CH_3)(OCH_3)_2$, $CF_3CH_2CH_2Si(CH_3)_2OCH_3$, $C_2F_5CH_2CH_2Si(CH_3)_2OCH_3$, $C_3F_7CH_2CH_2Si(CH_3)_2OCH_3$, $C_4F_9CH_2CH_2Si(CH_3)_2OCH_3$, $C_5F_{11}CH_2CH_2Si(CH_3)_2OCH_3$, $C_6F_{13}CH_2CH_2Si(CH_3)_2OCH_3$, $C_7F_{15}CH_2CH_2Si(CH_3)_2OCH_3$, $C_8F_{17}CH_2CH_2Si(CH_3)_2OCH_3$, $CF_3CH_2CH_2Si(CH_3)(H)OCH_3$, or the like, or a compound in which a methyl group moiety of a methoxy group of the above-described methoxysilane is substituted with a monovalent hydrocarbon group having 2 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms), $-O-S(=O)_2-R^{a17}$ (here, R^{a17} represents an alkyl group having 1 to 6 carbon atoms, a perfluoroalkyl group, a phenyl group, a tolyl group, or an $-O-Si(CH_3)_3$ group. For example, a trimethylsilyl sulfonate, a trimethylsilyl benzene sulfonate, a trimethylsilyl toluene sulfonate, a trimethylsilyl trifluoromethanesulfonate, a trimethylsilyl perfluorobutane sulfonate, a bistrimethylsilyl sulfate, or the like), and $-O-P(-O-Si(CH_3)_3)_2$ (for example, tristrimethylsilylphosphite and the like).

[0028]

In addition, specific examples of the silylating agent in which X in General Formula [1] is a monovalent group in which an atom bonded to an Si atom is oxygen, other than those described above, include siloxane compounds such as hexamethyl disiloxane, 1,3-diphenyl-1,3-dimethyl disiloxane, 1,1,3,3-tetramethyl disiloxane, 1,1,1-triethyl-3,3-dimethyl disiloxane, 1,1,3,3-tetra-n-octyl dimethyl disiloxane,

bis(nonafluorohexyl)tetramethyl disiloxane, 1,3-bis(trifluoropropyl)tetramethyl disiloxane, 1,3-di-n-butyl tetramethyl disiloxane, 1,3-di-n-octyl tetramethyl disiloxane, 1,3-diethyl tetramethyl disiloxane, 1,3-diphenyl tetramethyl disiloxane, hexa-n-butyl disiloxane, hexaethyl disiloxane, hexavinyl disiloxane, 1,1,3,3-tetraisopropyl disiloxane, vinyl pentamethyl disiloxane, 1,3-bis(3-chloroisobutyl)tetramethyl disiloxane, hexaphenyl disiloxane, 1,1,1-triethyl-3,3,3-trimethyl disiloxane, 1,3-bis(chloromethyl)tetramethyl disiloxane, 1,1,3,3-tetraphenyl dimethyl disiloxane, pentamethyl disiloxane, 1,3-bis(3-chloropropyl)tetramethyl disiloxane, 1,3-dichloro-1,3-diphenyl-1,3-dimethyl disiloxane, n-butyl-1,1,3,3-tetramethyl disiloxane, 1,3-di-t-butyl disiloxane, vinyl-1,1,3,3,-tetramethyl disiloxane, 1,1,1-trimethyl-3,3,3-triphenyl disiloxane, 3,3-diphenyl tetramethyl trisiloxane, 3-phenyl heptamethyl trisiloxane, hexamethylcyclotrisiloxane, n-propylheptamethyltrisiloxane, 3-ethylheptamethyltrisiloxane, 3-(3,3,3-trifluoropropyl)heptamethyltrisiloxane, 1,1,3,5,5-pentaphenyl-1,3,5-trimethyltrisiloxane, octamethyltrisiloxane, 1,1,5,5-tetraphenyl-1,3,3,5-tetramethyltrisiloxane, hexaphenylcyclotrisiloxane, 1,1,1,5,5,5-hexamethyltrisiloxane, 3-phenyl-1,1,3,5,5-pentamethyltrisiloxane, 1,3,5-trivinyl-1,1,3,5,5-pentamethyltrisiloxane, 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane, 3-octylheptamethyltrisiloxane, 1,3,5-triphenyltrimethylcyclotrisiloxane, 1,1,1,3,3,5,5-heptamethyltrisiloxane, 1,1,3,3,5,5-hexamethyltrisiloxane, 1,1,1,5,5,5-hexaethyl-3-methyltrisiloxane,

furfuryloxytrisiloxane, tetrakis(dimethylsiloxy)silane, 1,1,3,3,5,5,7,7-octamethyltetrasiloxane, diphenylsiloxane-dimethylsiloxane copolymer, 1,3-diphenyl-1,3-dimethyl disiloxane, octamethylcyclotetrasiloxane, 1,3-bis(trimethylsiloxy)-1,3-dimethyldisiloxane, tetra-n-propyltetramethylcyclotetrasiloxane, octaethylcyclotetrasiloxane, decamethyltetrasiloxane, dodecamethylcyclohexasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane, hexaphenylcyclotrisiloxane, polydimethylsiloxane, polyoctadecylmethylsiloxane, decamethylcyclopentasiloxane, poly(3,3,3-trifluoropropylmethylsiloxane), polydimethylsiloxane terminated with trimethylsiloxy, and 1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane.

[0029]

Examples of the silylating agent in which X in General Formula [1] is a monovalent group in which the atom bonded to the Si atom is carbon include those obtained by substituting the amino group ($-NH_2$ group) of the above-described aminosilane with $-C(S(=O)_2R^7)_3$ (here, R^7's are each independently 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 atoms may be substituted with fluorine atoms, and a fluorine atom). For example, (trimethylsilyl) tris(trifluoromethanesulfonyl) methide, and the like).

[0030]

In addition, examples of a silylating agent that X in

General Formula [1] is a monovalent group in which the atom bonded to the Si atom is halogen include a group in which the amino group ($-NH_2$ group) in the above-described aminosilane is substituted with a chloro group, a bromo group, or an iodo group (for example, chlorotrimethylsilane, bromotrimethylsilane, and the like).

[0031]

A silicon compound represented by General Formula [1] is preferably a silicon compound having a trialkylsilyl group. In addition, R^1 is preferably a methyl group. In addition, b is preferably 0. In addition, X is more preferably a monovalent group in which an atom bonded to an Si atom is nitrogen or oxygen, and it may be even more preferable that an atom bonded to an Si atom is nitrogen.

[0032]

As the silylating agent in which the atom bonded to the Si atom of X in General Formula [1] is nitrogen, it is more preferable to use a silazane compound. Examples of the silazane compound include acyclic disilazane compounds such as hexamethyldisilazane, heptamethyldisilazane, tetramethyldisilazane, diethyltetramethyldisilazane, dipropyltetramethyldisilazane, dibutyltetramethyldisilazane, dihexyltetramethyldisilazane, dioctyltetramethyldisilazane, and didodecyltetramethyldisilazane; cyclic disilazane compounds such as 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane and 2,2,6,6-tetramethyl-2,6-disila-1-azacyclohexane; cyclic trisilazane compounds such as 2,2,4,4,6,6-hexamethylcyclotrisilazane and

2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane; and cyclic tetrasilazane compounds such as 2,2,4,4,6,6,8,8-octamethylcyclotetrasilazane.

[0033]

In addition, more suitable specific examples of the silylating agent include one or two or more selected from the group consisting of hexamethyldisilazane, heptamethyldisilazane, N-(trimethylsilyl)dimethylamine, bis(dimethylamino)dimethylsilane, bis(trimethylsilyl)trifluoroacetamide, N-methyl-N-trimethylsilyltrifluoroacetamide, N-trimethylsilylacetamide, N-trimethylsilylimidazole, trimethylsilyltriazole, bistrimethylsilylsulfate, 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane, and 2,2,4,4,6,6-hexamethylcyclotrisilazane.

[0034]

The content of the silylating agent in 100% by mass of the composition for film formation is not particularly limited as long as the substrate can be imparted with desired water repellency.

In addition, the lower limit of the content of the silylating agent may be, for example, 0.1% by mass or more, preferably 0.2% by mass or more, more preferably 0.3% by mass or more, and still more preferably 0.5% by mass or more. In this manner, the water repellency of the substrate is easily improved.

On the other hand, the upper limit of the content of the silylating agent may be, for example, 35% by mass or less,

preferably 33% by mass or less, and more preferably 30% by mass or less. In a case where the content is within the above-described range, the water repellency can be more efficiently imparted with respect to the content of the silylating agent.

[0035]

In a case where two or more kinds of the silylating agents are used, the total content of the silylating agents may be within the above-described content range. In addition, in a case where a silylamide compound and an aminosilane compound described later are used in combination, the total amount of the silylating agent, the silylamide compound, and the aminosilane compound is preferably within the above-described content range.

In addition, in a case where two or more kinds are used, when the content of any one of hexamethyldisilazane, heptamethyldisilazane, N-(trimethylsilyl)dimethylamine, bis(dimethylamino)dimethylsilane, bis(trimethylsilyl)trifluoroacetamide, N-methyl-N-trimethylsilyltrifluoroacetamide, N-trimethylsilylacetamide, N-trimethylsilylimidazole, trimethylsilyltriazole, bistrimethylsilylsulfate, 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane, and 2,2,4,4,6,6-hexamethylcyclotrisilazane among the silylating agents contained in the composition for film formation is the highest, the water repellency is easily improved, which is suitable.

[0036]

((II) Silyl Ester Compound)

The silyl ester compound is a chlorine-containing

accelerator that acts as an accelerator in the chemical solution of the composition for film formation. The silyl ester compound includes one or more kinds of compounds represented by General Formula [2].

$$(R^2\text{-}C(=O)O)_i\text{-}Si(H)_{4-i-h}(R^3)_h \quad [2]$$

In General Formula [2], R^2 is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms, R^3's are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, i is an integer of 1 to 3, h is an integer of 1 to 3, and i + h is an integer of 2 to 4.

[0037]

In the monovalent hydrocarbon group of R^2 in General Formula [2], the number of carbon atoms is 1 to 5, preferably 1 to 3, and more preferably 1 or 2. In this manner, the water repellency can be enhanced. In addition, R^2 also includes a case where all hydrogen atoms are substituted with chlorine atoms, and is also described as a hydrocarbon group in a case where all hydrogen atoms are substituted with atoms other than hydrogen atoms.

In addition, in the monovalent hydrocarbon group of R^2 in General Formula [2], it is preferable that at least one hydrogen atom bonded to a carbon atom closest to the "C(=O)O" skeleton is

substituted with a chlorine atom. In this manner, the catalytic performance of the silyl ester compound can be improved.

In addition, in General Formula [2], in a case where R^2 is a hydrocarbon group having 2 or more carbon atoms, it is more preferable that at least one hydrogen atom of each hydrocarbon group is substituted with a chlorine atom.

[0038]

R^2 in General Formula [2] may be a group represented by $-C_qY_{(2q+1-r)}Cl_r$ (here, Y's are each independently a hydrogen atom or a fluorine atom bonded to carbon, Cl is a chlorine atom, q is an integer of 1 to 5, and r is 1 to 2q).

In addition, when the total number of chlorine atoms and fluorine atoms is larger than the total number of hydrogen atoms as the atom bonded to the carbon contained in R^2, it is easy to improve the water repellency of the composition for film formation, which is preferable.

More preferably, the atom bonded to the carbon contained in R^2 may be only a fluorine atom and a chlorine atom (provided that R^2 does not include $-CF_3$ and $-CF_2-$), or the atom bonded to the carbon contained in R^2 may be only a hydrogen atom and a chlorine atom (provided that the total number of chlorine atoms is larger than the total number of hydrogen atoms).

[0039]

From the viewpoint of obtaining good water repellency, as R^2, $-CHClF$, $-CClF_2$, $-CHCl_2$, $-CCl_2F$, $-CHClCH_3$, $-CCl_2CH_3$, $-CH_2CHCl_2$, $-CHClCH_2Cl$, $-CHClCCl_3$, $-CCl_2CHCl_2$, $-CCl_2CCl_3$, $-CClFCF_3$, $-CF_2CClF_2$, CCl_2CF_3, $-CClFCCl_2F$, $-CF_2CCl_3$, $-CClFCCl_3$, $-CCl_2CCl_2F$, $-CClFCH_3$, -

CCl_2CH_2F, $-CHFCHCl_2$, $-CClFCH_2Cl$, $-CHClCHClF$, $-CCl_2CHClF$, $-CF_2CH_2Cl$, $-CHClCF_3$, $-CClFCHF_2$, $-CF_2CHClF$, $-CHFCClF_2$, or the like is preferably used, and $-CHClF$, $-CClF_2$, $-CHCl_2$, $-CCl_2F$, $-CHClCH_3$, $-CCl_2CH_3$, $-CH_2CHCl_2$, $-CHClCH_2Cl$, $-CHClCCl_3$, $-CCl_2CHCl_2$, $-CCl_2CCl_3$, $-CClFCCl_2F$, $-CClFCCl_3$, $-CCl_2CCl_2F$, $-CClFCH_3$, $-CCl_2CH_2F$, $-CHFCHCl_2$, $-CClFCH_2Cl$, $-CHClCHClF$, $-CCl_2CHClF$, $-CClFCHF_2$, $-CHFCClF_2$, or the like is more preferably used.

[0040]

R^3 in General Formula [2] may include not only a hydrogen atom, a carbon atom, a nitrogen atom, an oxygen atom, a fluorine atom, and a chlorine atom, but also a silicon atom, a sulfur atom, a halogen atom (other than fluorine), and the like. In addition, R^3 in General Formula [2] may contain an unsaturated bond, an aromatic ring, or a cyclic structure.

[0041]

Examples of R^3 in General Formula [2] each independently include at least one group selected from $C_{ee}H_{2ee+1}$ (ee = 1 to 18) and $C_{ff}F_{2ff+1}CH_2CH_2$ (ff = 1 to 8).

[0042]

Specific examples of the silyl ester compound include trimethylsilyl chloroacetate, trimethylsilyl dichloroacetate, trimethylsilyl chlorodifluoroacetate, trimethylsilyl dichlorofluoroacetate, trimethylsilyl chlorofluoroacetate, dimethylsilyl chloroacetate, dimethylsilyl dichloroacetate, dimethylsilyl chlorodifluoroacetate, butyldimethylsilyl chloroacetate, trimethylsilyl-2-chloropropionate, trimethylsilyl-3-chloropropionate, trimethylsilyl-2,2-

dichloropropionate, trimethylsilyl-2,3-dichloropropionate, triethylsilyl-2-chloropropionate, and trimethylsilyl trichloroacetate. These may be used alone, or two or more thereof may be used in combination. Among the above, trimethylsilyl dichloroacetate, trimethylsilyl chlorodifluoroacetate, trimethylsilyl dichlorofluoroacetate, trimethylsilyl-2,2-dichloropropionate, and trimethylsilyl-2,3-dichloropropionate are more preferable.

[0043]

The content of the silyl ester compound in 100% by mass of the composition for film formation is not particularly limited as long as the substrate can be imparted with desired water repellency.

The lower limit of the content of the silyl ester compound is, for example, 0.01% by mass or more, preferably 0.05% by mass or more, and more preferably 0.2% by mass or more.

On the other hand, the upper limit of the content of the silyl ester compound is, for example, 10% by mass or less, preferably 5% by mass or less, and more preferably 3% by mass or less.

The above range is suitable since the water repellency of the substrate is easily improved.

[0044]

In addition, in a case where the content of the silylating agent in 100% by mass of the composition for film formation is defined as C_{Si} and the content of the silyl ester compound is defined as C_{es}, the lower limit of C_{Si}/C_{es} is, for example, 1.0 or

more, preferably 5.0 or more, and more preferably 10 or more. In this manner, water repellency can be imparted in a shorter time of processing.

On the other hand, the upper limit of C_{Si}/C_{es} is not particularly limited as long as desired water repellency can be obtained, but may be, for example, 40 or less. The upper limit is preferably 30 or less.

[0045]

In a case where two or more kinds of silyl ester compounds are used, the total amount of the content of the silyl ester compounds contained in the composition for film formation is set to the content of the silyl ester compound. In addition, in a case where two or more kinds of silyl ester compounds are used, it is preferable that the silyl ester compound having the highest content is trimethylsilyl chloroacetate, trimethylsilyl dichloroacetate, trimethylsilyl chlorodifluoroacetate, trimethylsilyl dichlorofluoroacetate, trimethylsilyl chlorofluoroacetate, dimethylsilyl chloroacetate, dimethylsilyl dichloroacetate, dimethylsilyl chlorodifluoroacetate, butyldimethylsilyl chloroacetate, trimethylsilyl-2-chloropropionate, trimethylsilyl-3-chloropropionate, trimethylsilyl-2,3-dichloropropionate, triethylsilyl-2-chloropropionate, or trimethylsilyl trichloroacetate. Among the above, trimethylsilyl dichloroacetate, trimethylsilyl chlorodifluoroacetate, trimethylsilyl dichlorofluoroacetate, trimethylsilyl-2,2-dichloropropionate, and trimethylsilyl-2,3-dichloropropionate are more preferable.

[0046]

((III) Aprotic Solvent)

The aprotic solvent refers to a solvent which does not contain a group in which a hydrogen atom is bonded to an oxygen atom or a nitrogen atom, such as a hydroxyl group or an amino group. However, the aprotic solvent is not particularly limited as long as it dissolves the above-described silylating agent and silyl ester compound.

[0047]

Examples of the aprotic solvent may include one or two or more selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen atom-containing solvents, sulfoxide-based solvents, carbonate-based solvents, solvents containing no OH group among derivatives of polyhydric alcohols, nitrogen atom-containing solvents containing no N-H group, and silicone solvents.

Among these, hydrocarbons, esters, ethers, halogen atom-containing solvents, sulfoxide-based solvents, or derivatives of polyhydric alcohol not having an OH group are preferable.

[0048]

Examples of the above-described hydrocarbons include linear, branched, or cyclic hydrocarbon-based solvents, aromatic hydrocarbon-based solvents, and terpene-based solvents, and specific examples thereof include n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tetradecane, n-hexadecane, n-octadecane, n-icosane, branched hydrocarbon corresponding to the carbon numbers thereof (for example,

isododecane, isocetane, and the like), cyclohexane, methylcyclohexane, decalin, benzene, toluene, xylene, (ortho-, meta-, or para-)diethylbenzene, 1,3,5-trimethylbenzene, butylbenzene, naphthalene, p-menthane, o-menthane, m-menthane, diphenylmenthane, limonene, α-terpinene, β-terpinene, γ-terpinene, bornane, norbornane, pinane, α-pinene, β-pinene, carane, longifolene, and abietane.

[0049]

Examples of the above-described esters include ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, n-pentyl acetate, i-pentyl acetate, n-hexyl acetate, n-heptyl acetate, n-octyl acetate, n-pentyl formate, n-butyl propionate, ethyl butyrate, n-propyl butyrate, i-propyl butyrate, n-butyl butyrate, methyl n-octanate, methyl decanoate, methyl pyruvate, ethyl pyruvate, n-propyl pyruvate, methyl acetoacetate, ethyl acetoacetate, ethyl 2-oxobutanoate, dimethyl adipate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, and ethyl ethoxyacetate.

[0050]

In addition, as the above-described esters, cyclic esters such as a lactone compound may be used. Examples of the lactone compound include β-propiolactone, γ-butyrolactone, γ-valerolactone, γ-hexanolactone, γ-heptanolactone, γ-octanolactone, γ-nonanolactone, γ-decanolactone, γ-undecanolactone, γ-dodecanolactone, δ-valerolactone, δ-hexanolactone, δ-octanolactone, δ-nonanolactone, δ-

decanolactone, δ-undecanolactone, δ-dodecanolactone, and ε-hexanolactone.

[0051]

Examples of the above-described ethers include di-n-propyl ether, ethyl-n-butyl ether, di-n-butyl ether, ethyl-n-amyl ether, di-n-amyl ether, ethyl-n-hexyl ether, di-n-hexyl ether, di-n-octyl ether, diisopropyl ethers corresponding to the number of carbon atoms thereof, ethers with branched hydrocarbon groups, such as diisoamyl ether, dimethyl ether, diethyl ether, methyl ethyl ether, methyl cyclopentyl ether, diphenyl ether, tetrahydrofuran, and dioxane.

[0052]

Examples of the above-described ketones include acetone, acetylacetone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, 2-heptanone, 3-heptanone, cyclohexanenone, and isophorone.

[0053]

Examples of the above-described halogen atom-containing solvent include perfluorocarbons such as perfluorooctane, perfluorononane, perfluorocyclopentane, perfluorocyclohexane, and hexafluorobenzene; hydrofluorocarbons such as 1,1,1,3,3-pentafluorobutane, octafluorocyclopentane, 2,3-dihydrodecafluoropentane, and ZEORORA H (manufactured by ZEON CORPORATION); hydrofluoroethers such as methyl perfluoropropyl ether, methyl perfluoroisobutyl ether, methyl perfluorobutyl ether, ethyl perfluorobutyl ether, ethyl perfluoroisobutyl ether, methyl perfluorohexyl ether, ethyl perfluorohexyl ether,

Asahiklin AE-3000 (manufactured by Asahi Glass Co., Ltd.), Novec HFE-7100, Novec HFE-7200, Novec 7300, and Novec 7600 (all manufactured by 3M); chlorocarbons such as tetrachloromethane; hydrochlorocarbons such as chloroform; chlorofluorocarbons such as dichlorodifluoromethane; hydrochlorofluorocarbons such as 1,1-dichloro-2,2,3,3,3-pentafluoropropane, 1,3-dichloro-1,1,2,2,3-pentafluoropropane, 1-chloro-3,3,3-trifluoropropene, and 1,2-dichloro-3,3,3-trifluoropropene; perfluoroether, and perfluoropolyether.

[0054]

Examples of the above-described sulfoxide-based solvent include dimethyl sulfoxide.

[0055]

Examples of the above-described carbonate-based solvent include dimethyl carbonate, ethylmethyl carbonate, diethyl carbonate, and propylene carbonate.

[0056]

Examples of the derivative of the polyhydric alcohol which does not have an OH group include ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, ethylene glycol diacetate, diethylene glycol dimethyl ether, diethylene glycol ethyl methyl ether, diethylene glycol diethyl ether, diethylene glycol butyl methyl ether, diethylene glycol dibutyl ether, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene

glycol monobutyl ether acetate, diethylene glycol diacetate, triethylene glycol dimethyl ether, triethylene glycol diethyl ether, triethylene glycol dibutyl ether, triethylene glycol butyl methyl ether, triethylene glycol monomethyl ether acetate, triethylene glycol monoethyl ether acetate, triethylene glycol monobutyl ether acetate, triethylene glycol diacetate, tetraethylene glycol dimethyl ether, tetraethylene glycol diethyl ether, tetraethylene glycol dibutyl ether, tetraethylene glycol monomethyl ether acetate, tetraethylene glycol monoethyl ether acetate, tetraethylene glycol monobutyl ether acetate, tetraethylene glycol diacetate, propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol dibutyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monobutyl ether acetate, propylene glycol diacetate, dipropylene glycol dimethyl ether, dipropylene glycol methyl propyl ether, dipropylene glycol diethyl ether, dipropylene glycol dibutyl ether, dipropylene glycol monomethyl ether acetate, dipropylene glycol monoethyl ether acetate, dipropylene glycol monobutyl ether acetate, dipropylene glycol diacetate, tripropylene glycol dimethyl ether, tripropylene glycol diethyl ether, tripropylene glycol dibutyl ether, tripropylene glycol monomethyl ether acetate, tripropylene glycol monoethyl ether acetate, tripropylene glycol monobutyl ether acetate, tripropylene glycol diacetate, tetrapropylene glycol dimethyl ether, tetrapropylene glycol monomethyl ether acetate, tetrapropylene glycol diacetate, butylene glycol dimethyl ether, butylene glycol

monomethyl ether acetate, butylene glycol diacetate, glycerin triacetate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, and 3-methyl-3-methoxybutyl propionate.

[0057]

Examples of the acyclic nitrogen atom-containing solvent which does not have the N-H group include N,N-dimethylacetamide and triethylamine.

[0058]

Examples of the above-described silicone solvent include hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, and dodecamethylpentasiloxane.

[0059]

From the viewpoint of cost and solubility, a derivative of polyhydric alcohol (however, those having no OH group in the molecule) are preferable, and for example, at least one selected from the group consisting of diethylene glycol monoethyl ether acetate, ethylene glycol monomethyl ether acetate, propylene glycol monomethyl ether acetate, diethylene glycol dimethyl ether, diethylene glycol ethyl methyl ether, diethylene glycol diethyl ether, diethylene glycol monomethyl ether acetate, diethylene glycol diacetate, triethylene glycol dimethyl ether, ethylene glycol diacetate, ethylene glycol dimethyl ether, 3-methoxy-3-methyl-1-butyl acetate, propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol dibutyl ether, propylene glycol monoethyl ether acetate, propylene glycol monobutyl ether acetate, propylene glycol diacetate, dipropylene glycol dimethyl ether, dipropylene glycol methyl

propyl ether, dipropylene glycol diethyl ether, dipropylene glycol dibutyl ether, dipropylene glycol monomethyl ether acetate, dipropylene glycol monoethyl ether acetate, dipropylene glycol monobutyl ether acetate, and dipropylene glycol diacetate is preferable. In addition, propylene carbonate, a linear or branched hydrocarbon-based solvent having 6 to 12 carbon atoms, p-menthane, diphenylmenthane, limonene, terpinene, bornane, norbornane, pinane, or the like is also preferable.

[0060]

Among the above-described aprotic solvents, a solvent having polarity (hereinafter, also referred to as an aprotic polar solvent) may be used. Examples of the aprotic polar solvent include an acyclic nitrogen atom-containing solvent represented by N,N-dimethylacetamide, a lactone compound represented by γ-butyrolactone, and a sulfoxide-based solvent represented by dimethyl sulfoxide.

[0061]

It is preferable that the solvent contained in the composition for film formation is substantially only an aprotic solvent. In addition, a plurality of aprotic solvents may be used. Specifically, in a case where the total amount of the solvents contained in the composition for film formation is 100% by mass, the amount of the aprotic solvent is preferably 90% by mass or more, more preferably 95% by mass or more, still more preferably 98% by mass or more, and still more preferably 99.5% by mass or more, in terms of mass ratio. The “aprotic solvent” includes an aprotic polar solvent, and in a case where two or

more solvents are used, the total amount of the content thereof is defined as the content of the aprotic solvent.

[0062]

It is desirable that the composition for film formation does not contain water substantially. In addition, a composition for film formation substantially containing no water, which is obtained by not adding water at the time of preparing the composition for film formation or using a composition for film formation, containing no water or having a low water content as a raw material of each component, is more preferable. For example, the water contained in the composition for film formation may be 0.3% by mass or less, preferably 0.1% by mass or less. In addition, the content of water may be less than the measurement limit of the Karl Fischer titration method, for example, less than 10 ppm by mass. By using such a composition for film formation, it is possible to suppress the deactivation of the silylating agent.

[0063]

The composition for film formation may further include one or two or more selected from the group consisting of a silylamide compound represented by General Formula [5] and an aminosilane compound represented by General Formula [6]. By using the above-described (I) silylating agent in combination, it is easy to suppress a change in the composition of the composition, and it is easy to impart water repellency with good reproducibility. The following General Formula [5] and General Formula [6] are included in the above-described General Formula

[1] of the (I) silylating agent, and both of them can be used as the (I) silylating agent in a case where they are used alone. The compound of General Formula [6] may be generated by the contact of the composition for film formation of the present disclosure with a protonic substance such as water. For example, the compound may be generated by moisture in the atmosphere in a case where the composition for film formation is prepared in the atmosphere.

The following description will be made for a case where the (I) silylating agent is used in combination. Specifically, General Formula [5] having a content lower than the content of the compound used as the (I) silylating agent contained in the composition for film formation is referred to as an "silylamide compound used in combination", and General Formula [6] having a content lower than the content of the compound used as the (I) silylating agent contained in the composition for film formation is referred to as a "aminosilane compound used in combination". In the composition for film formation in which General Formula [6] having a content lower than the content of the compound used as the (I) silylating agent contained in the composition for film formation corresponds to the "aminosilane compound used in combination", it is easy to impart more excellent water repellency to the substrate surface, which is preferable.

[0064]

$$(R^{b2}\text{-}C(=O)N(H))_j\text{-}Si(H)_{4-j-t}(R^{b3})_t \quad [5]$$

[0065]

In General Formula [5], R^{b2} is a monovalent hydrocarbon

group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms, R^{b3}'s are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, j is an integer of 1 to 3, t is an integer of 1 to 3, and j + t is an integer of 2 to 4.

[0066]

$$(R^{b4})_uSi(H)_v(NH_2)_{4-u-v} \quad [6]$$

[0067]

In General Formula [6], R^{b4}'s are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, u is an integer of 1 to 3, v is an integer of 0 to 2, and a sum of u and v is 1 to 3.

[0068]

R^{b2} in General Formula [5] is the same as R^2 in General Formula [2] described above, and the details thereof will not be repeated below since they are the same as those for R^2. In addition, R^{b3} of General Formula [5] is the same as R^3 of General Formula [2] described above, and the details thereof will not be repeated below as they are the same as those for R^3.

R^{b4} in General Formula [6] is the same as R^1 in General Formula [1] described above, and the details thereof will not be

repeated below since they are the same as those for R^1.

[0069]

Examples of the silylamide compound represented by General Formula [5] include N-(trimethylsilyl)chloroacetamide, N-(trimethylsilyl)dichloroacetamide, N-(trimethylsilyl)-2-chloropropionamide, N-(trimethylsilyl)-3-chloropropionamide, N-(trimethylsilyl)-2,3-dichloropropionamide, N-(trimethylsilyl)-2,2-dichloropropionamide, N-(trimethylsilyl)-2,2,3-trichloropropionamide, N-(trimethylsilyl)-2,3,3,3-tetrachloropropionamide, N-(trimethylsilyl)-2,2,3,3,3-pentachloropropionamide, N-(trimethylsilyl)chlorodifluoroacetamide, N-(trimethylsilyl)dichlorofluoroacetamide, N-(trimethylsilyl)chlorofluoroacetamide, N-(trimethylsilyl)-3-chloro-2,2-difluoropropionamide, N-(trimethylsilyl)-3-chloro-2,2,3,3-tetrafluoropropionamide, N-(trimethylsilyl)-2-chloro-2,3,3,3-tetrafluoropropionamide, N-(trimethylsilyl)-2,3-dichloro-2,3-difluoropropionamide, N-(trimethylsilyl)-3,3-dichloro-2,2-difluoropropionamide, N-(trimethylsilyl)-2,2-dichloro-3,3,3-trifluoropropionamide, N-(trimethylsilyl)-2,3-dichloro-2,3,3-trifluoropropionamide, N-(trimethylsilyl)-2,2,3-trichloro-3,3-difluoropropionamide, N-(trimethylsilyl)-2,3,3-trichloro-2,3-difluoropropionamide, N-(trimethylsilyl)-3,3,3-trichloro-2,2-difluoropropionamide, N-(trimethylsilyl)-2,3,3,3-tetrachloro-2-fluoropropionamide, and N-(trimethylsilyl)-2,2,3,3-tetrachloro-3-fluoropropionamide.

[0070]

Specific examples of the aminosilane compound represented by General Formula [6] include, for example, $CH_3Si(NH_2)_3$, $C_2H_5Si(NH_2)_3$, $C_3H_7Si(NH_2)_3$, $C_4H_9Si(NH_2)_3$, $C_5H_{11}Si(NH_2)_3$, $C_6H_{13}Si(NH_2)_3$, $C_7H_{15}Si(NH_2)_3$, $C_8H_{17}Si(NH_2)_3$, $C_9H_{19}Si(NH_2)_3$, $C_{10}H_{21}Si(NH_2)_3$, $C_{11}H_{23}Si(NH_2)_3$, $C_{12}H_{25}Si(NH_2)_3$, $C_{13}H_{27}Si(NH_2)_3$, $C_{14}H_{29}Si(NH_2)_3$, $C_{15}H_{31}Si(NH_2)_3$, $C_{16}H_{33}Si(NH_2)_3$, $C_{17}H_{35}Si(NH_2)_3$, $C_{18}H_{37}Si(NH_2)_3$, $(CH_3)_2Si(NH_2)_2$, $C_2H_5Si(CH_3)(NH_2)_2$, $(C_2H_5)_2Si(NH_2)_2$, $C_3H_7Si(CH_3)(NH_2)_2$, $(C_3H_7)_2Si(NH_2)_2$, $C_4H_9Si(CH_3)(NH_2)_2$, $(C_4H_9)_2Si(NH_2)_2$, $C_5H_{11}Si(CH_3)(NH_2)_2$, $C_6H_{13}Si(CH_3)(NH_2)_2$, $C_7H_{15}Si(CH_3)(NH_2)_2$, $C_8H_{17}Si(CH_3)(NH_2)_2$, $C_9H_{19}Si(CH_3)(NH_2)_2$, $C_{10}H_{21}Si(CH_3)(NH_2)_2$, $C_{11}H_{23}Si(CH_3)(NH_2)_2$, $C_{12}H_{25}Si(CH_3)(NH_2)_2$, $C_{13}H_{27}Si(CH_3)(NH_2)_2$, $C_{14}H_{29}Si(CH_3)(NH_2)_2$, $C_{15}H_{31}Si(CH_3)(NH_2)_2$, $C_{16}H_{33}Si(CH_3)(NH_2)_2$, $C_{17}H_{35}Si(CH_3)(NH_2)_2$, $C_{18}H_{37}Si(CH_3)(NH_2)_2$, $(CH_3)_3SiNH_2$, $C_2H_5Si(CH_3)_2NH_2$, $(C_2H_5)_2Si(CH_3)NH_2$, $(C_2H_5)_3SiNH_2$, $C_3H_7Si(CH_3)_2NH_2$, $(C_3H_7)_2Si(CH_3)NH_2$, $(C_3H_7)_3SiNH_2$, $C_4H_9Si(CH_3)_2NH_2$, $(C_4H_9)_3SiNH_2$, $C_5H_{11}Si(CH_3)_2NH_2$, $C_6H_{13}Si(CH_3)_2NH_2$, $C_7H_{15}Si(CH_3)_2NH_2$, $C_8H_{17}Si(CH_3)_2NH_2$, $C_9H_{19}Si(CH_3)_2NH_2$, $C_{10}H_{21}Si(CH_3)_2NH_2$, $C_{11}H_{23}Si(CH_3)_2NH_2$, $C_{12}H_{25}Si(CH_3)_2NH_2$, $C_{13}H_{27}Si(CH_3)_2NH_2$,$C_{14}H_{29}Si(CH_3)_2NH_2$, $C_{15}H_{31}Si(CH_3)_2NH_2$, $C_{16}H_{33}Si(CH_3)_2NH_2$, $C_{17}H_{35}Si(CH_3)_2NH_2$, $C_{18}H_{37}Si(CH_3)_2NH_2$, $(CH_3)_2Si(H)NH_2$, $CH_3Si(H)_2NH_2$, $(C_2H_5)_2Si(H)NH_2$, $C_2H_5Si(H)_2NH_2$, $C_2H_5Si(CH_3)(H)NH_2$, $(C_3H_7)_2Si(H)NH_2$, $C_3H_7Si(H)_2NH_2$, $CF_3CH_2CH_2Si(NH_2)_3$, $C_2F_5CH_2CH_2Si(NH_2)_3$, $C_3F_7CH_2CH_2Si(NH_2)_3$, $C_4F_9CH_2CH_2Si(NH_2)_3$, $C_5F_{11}CH_2CH_2Si(NH_2)_3$, $C_6F_{13}CH_2CH_2Si(NH_2)_3$, $C_7F_{15}CH_2CH_2Si(NH_2)_3$, $C_8F_{17}CH_2CH_2Si(NH_2)_3$, $CF_3CH_2CH_2Si(CH_3)(NH_2)_2$, $C_2F_5CH_2CH_2Si(CH_3)(NH_2)_2$, $C_3F_7CH_2CH_2Si(CH_3)(NH_2)_2$, $C_4F_9CH_2CH_2Si(CH_3)(NH_2)_2$, $C_5F_{11}CH_2CH_2Si(CH_3)(NH_2)_2$, $C_6F_{13}CH_2CH_2Si(CH_3)(NH_2)_2$, $C_7F_{15}CH_2CH_2Si(CH_3)(NH_2)_2$, $C_8F_{17}CH_2CH_2Si(CH_3)(NH_2)_2$,

$CF_3CH_2CH_2Si(CH_3)_2NH_2$, $C_2F_5CH_2CH_2Si(CH_3)_2NH_2$, $C_3F_7CH_2CH_2Si(CH_3)_2NH_2$, $C_4F_9CH_2CH_2Si(CH_3)_2NH_2$, $C_5F_{11}CH_2CH_2Si(CH_3)_2NH_2$, $C_6F_{13}CH_2CH_2Si(CH_3)_2NH_2$, $C_7F_{15}CH_2CH_2Si(CH_3)_2NH_2$, $C_8F_{17}CH_2CH_2Si(CH_3)_2NH_2$, $CF_3CH_2CH_2Si(CH_3)(H)NH_2$, and the like.

[0071]

(I) The content of the silylamide compound and the aminosilane compound described above, which are used in combination with the silylating agent, is not particularly limited as long as the performance of the composition for film formation is not impaired. For example, the silylamide compound and the aminosilane compound used in combination with the (I) silylating agent may be each present in an amount of 10% by mass or less in 100% by mass of the composition for film formation. The lower limit is not particularly limited, but may be, for example, 0.01% by mass or more.

[0072]

According to the experiment by the inventors of the present invention, it has been confirmed that the composition for film formation may be cloudy.

As a result of further studies, it was found that one of the causes of the occurrence of the cloudiness is that a part of the amide compound (in particular, an amide compound having a hydrocarbon group having a Cl_3C moiety, a Cl_2HC moiety, or a Cl_2FC moiety) is present in an insoluble state in the composition for film formation.

[0073]

In a case where the composition for film formation contains

the above-described silylamide compound, a part of amide compound described above (particularly, an amide compound having a hydrocarbon group having a Cl_3C moiety, a Cl_2HC moiety, or a Cl_2FC moiety), which is presumed to be a decomposition product of the silylamide compound, may also be contained in the composition.

[0074]

Here, a part of amide compound described above (particularly, an amide compound having a hydrocarbon group having a Cl_3C moiety, a Cl_2HC moiety, or a Cl_2FC moiety) is defined by an amide compound represented by General Formula [4].

R^{b1}-C(=O)N(H)Z[4]

In General Formula [4], R^{b1} is a hydrocarbon group having a Cl_3C moiety, a Cl_2HC moiety, or a Cl_2FC moiety, and Z is a hydrogen atom or a monovalent hydrocarbon group having 1 to 3 carbon atoms, which is bonded to a nitrogen atom.

[0075]

The composition for film formation may contain one or two or more kinds of the amide compounds represented by General Formula [4], but from the viewpoint of suppressing the cloudiness of the composition for film formation, the content of the amide compound represented by General Formula [4] in the composition for film formation is preferably lower.

Examples of the amide compound represented by General Formula [4] include 2,2-dichloroacetamide, 2,2,2-trichloroacetamide, 2,3,3,3-tetrachloropropionamide, 2,2,3,3,3-pentachloropropionamide, 2,2-dichloro-2-fluoroacetamide, 3,3-

dichloro-2,2-difluoropropionamide, 2,3,3-trichloro-2,3-difluoropropionamide, 3,3,3-trichloro-2,2-difluoropropionamide, 2,3,3,3-tetrachloro-2-fluoropropionamide, and 2,2,3,3-tetrachloro-3-fluoropropionamide.

[0076]

As a result of intensive studies based on such findings, it was found that the cloudiness of the composition for film formation can be suppressed by the following methods (i) to (iv). Each method may be used alone, or any two or more methods may be used in combination.

[0077]

(i) The composition for film formation does not contain the amide compound represented by General Formula [4].

An example of the step of manufacturing the composition for film formation described later includes a reaction step of reacting (I) a silylating agent with a chlorocarboxylic acid compound to obtain (II) a silyl ester compound.

(ia) In the reaction step, it is preferable that a chlorocarboxylic acid is used as the chlorocarboxylic acid compound and a chlorocarboxylic acid anhydride is not used. By not using the chlorocarboxylic acid anhydride, a silylamide compound is not generated, and an amide compound represented by General Formula [4] presumed to be a decomposition product thereof is not generated, and thus the cloudiness of the composition can be suppressed.

(ib) In addition, in a case where the silazane compound is not used as the (I) silylating agent, the silylamide compound is

not generated even in a case where the chlorocarboxylic acid anhydride is used, and the amide compound represented by General Formula [4] presumed to be a decomposition product thereof is not generated, so that the cloudiness of the composition can be suppressed.

(ic) The reaction step is preferably carried out in an inert atmosphere such as a nitrogen atmosphere. As a result, even in a case where the composition contains a silylamide compound, the generation of the amide compound represented by General Formula [4] can be suppressed. Therefore, the cloudiness of composition can be suppressed.

In the present specification, the expression "not including a component" includes that the component is equal to or lower than the detection limit.

[0078]

(ii) The composition for film formation contains an aprotic solvent with relatively high solubility in the amide compound represented by General Formula [4].

It is preferable that the (III) aprotic solvent in the composition for film formation includes the aprotic polar solvent.

In addition, all of the aprotic solvents contained in the composition for film formation may be the above-described aprotic polar solvents, or the aprotic polar solvents may be allowed to coexist with other solvents. In a case where the coexisting solvent is present, the content of the aprotic polar solvent is preferably 50% by mass or more, more preferably 70%

by mass or more, and still more preferably 80% by mass or more with respect to 100% by mass of the solvent contained in the composition for film formation. In addition, the solvent to be coexisting with the aprotic polar solvent is not particularly limited as long as it is an aprotic solvent compatible with the aprotic polar solvent. For example, in a case where a derivative of a polyhydric alcohol (however, a derivative having no OH group in the molecule) as described above, and the like are used, it is preferable because they are inexpensive.

[0079]

(iii) The composition for film formation contains an amide compound having a high solubility in a solvent instead of at least a part or all of the amide compound represented by General Formula [4].

In General Formula [4], it is preferable that the composition for film formation contains an amide compound having a structure in which R^{b1} is a hydrocarbon group which does not have a Cl_3C moiety, a Cl_2HC moiety, or a Cl_2FC moiety, instead of the amide compound represented by General Formula [4]. As described above, by adopting the structure in which R^{b1} of General Formula [4] is a hydrocarbon group which does not have a Cl_3C moiety, a Cl_2HC moiety, or a Cl_2FC moiety, the solubility in the (III) aprotic solvent can be increased as compared with the amide compound represented by General Formula [4]. In this manner, the cloudiness of the composition can be suppressed.

In this case, the content of the above-described amide compound having a high solubility in a solvent is, for example,

preferably 3.0% by mass or less, more preferably 1.2% by mass or less, and still more preferably 1.0% by mass or less in 100% by mass of the composition for film formation.

[0080]

(iv) The content of the amide compound represented by General Formula [4] in the composition for film formation is suppressed to be low.

The composition for film formation may not contain the amide compound represented by General Formula [4], or the content of the amide compound may be 0.1% by mass or less in 100% by mass of the composition for film formation even in a case where the composition for film formation contains the amide compound. In this manner, the cloudiness of the composition can be suppressed.

[0081]

In the present specification, turbidity measured using a turbidimeter can be used as an indicator of the degree of cloudiness.

The turbidity of the composition for film formation in which the cloudiness has not occurred is preferably 10 or less, more preferably 6 or less, and still more preferably 1.0 or less.

[0082]

The above-described composition for film formation can contain other components in addition to the above-described components, as long as the above-mentioned object of the present disclosure is not impaired. Examples of other components

include oxidizing agents such as hydrogen peroxide and ozone, surfactants, and antioxidants such as BHT.

[0083]

(Method for Manufacturing Composition for Film Formation)

A method for manufacturing the composition for film formation according to the present embodiment will be described.

[0084]

An example of a method for manufacturing the composition for film formation includes a step of mixing (I) a silylating agent, (II) a silyl ester compound, and (III) an aprotic solvent.

[0085]

In an example of the manufacturing method, the composition for film formation is obtained by mixing the above-described components. The order of addition of different components and the number of times of addition of the same component are not particularly limited. In addition, each component may be added to a solvent, but a solvent may be added to a mixture of components, or other components may be added to a mixed solution containing one or two or more components and a solvent. In addition, the temperature or atmosphere during mixing may be appropriately selected not to impair the performance of the composition for film formation.

[0086]

Another example of the method for manufacturing the composition for film formation includes a reaction step of reacting (I) a silylating agent with (II') a chlorocarboxylic

acid compound including at least one of a chlorocarboxylic acid and a chlorocarboxylic acid anhydride to obtain (II) a silyl ester compound. In this manner, it is possible to obtain a reaction solution including at least (I) the silylating agent and (II) the silyl ester compound.

[0087]

In another example of the manufacturing method, the reaction step may be carried out in (III) an aprotic solvent. In addition, after the reaction step, a step of adding (I) a silylating agent and/or (III) an aprotic solvent to the reaction solution may be included, if necessary. (III) The aprotic solvent is preferably mixed with the (I) silylating agent, the (II') chlorocarboxylic acid compound, or the (II) silyl ester compound after the water content is adjusted to a predetermined amount or less. The water content is not particularly limited as long as the water repellency of the composition for film formation is not impaired, but may be, for example, 0.3% by mass or less in a case where (III) the aprotic solvent is 100% by mass.

[0088]

The above-described chlorocarboxylic acid may include one or more of compounds represented by General Formula [7]. In the present specification, even in a case where chlorocarboxylic acid or chlorocarboxylic acid anhydride contains an atom (for example, a fluorine atom) other than a chlorine atom, it is described as chlorocarboxylic acid and chlorocarboxylic acid anhydride.

R^{C2}-C(=O)OH[7]

In General Formula [7], R^{C2} is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms.

[0089]

In addition, the above-described chlorocarboxylic acid anhydride may include one or more of compounds represented by General Formula [8].

R^{C2}-C(=O)O-C(=O)-R^{C2}[8]

In General Formula [8], R^{C2} is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms.

[0090]

R^{C2} in General Formula [7] and General Formula [8] described above is the same as R^2 in General Formula [2] described above, and the details thereof will not be repeated below as the details of R^2.

[0091]

Examples of the chlorocarboxylic acid include monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, 2-chloropropionic acid, 3-chloropropionic acid, 2,3-dichloropropionic acid, 2,2-dichloropropionic acid, 2,2,3-

trichloropropionic acid, 2,3,3,3-tetrachloropropionic acid, 2,2,3,3,3-pentachloropropionic acid, chlorodifluoroacetic acid, dichlorofluoroacetic acid, chlorofluoroacetic acid, 3-chloro-2,2-difluoropropionic acid, 3-chloro-2,2,3,3-tetrafluoropropionic acid, 2-chloro-2,3,3,3-tetrafluoropropionic acid, 2,3-dichloro-2,3-difluoropropionic acid, 3,3-dichloro-2,2-difluoropropionic acid, 2,2-dichloro-3,3,3-trifluoropropionic acid, 2,3-dichloro-2,3,3-trifluoropropionic acid, 2,2,3-trichloro-3,3-difluoropropionic acid, 2,3,3-trichloro-2,3-difluoropropionic acid, 3,3,3-trichloro-2,2-difluoropropionic acid, 2,3,3,3-tetrachloro-2-fluoropropionic acid, and 2,2,3,3-tetrachloro-3-fluoropropionic acid.

Preferably, the chlorocarboxylic acid may be dichloroacetic acid, trichloroacetic acid, 2,3-dichloropropionic acid, 2,2-dichloropropionic acid, 2,2,3-trichloropropionic acid, 2,3,3,3-tetrachloropropionic acid, chlorodifluoroacetic acid, dichlorofluoroacetic acid, 3-chloro-2,2-difluoropropionic acid, 2,3-dichloro-2,3-difluoropropionic acid, 3,3-dichloro-2,2-difluoropropionic acid, 2,2-dichloro-3,3,3-trifluoropropionic acid, 2,3-dichloro-2,3,3-trifluoropropionic acid, 2,2,3-trichloro-3,3-difluoropropionic acid, 2,3,3-trichloro-2,3-difluoropropionic acid, 3,3,3-trichloro-2,2-difluoropropionic acid, 2,3,3,3-tetrachloro-2-fluoropropionic acid, or 2,2,3,3-tetrachloro-3-fluoropropionic acid, and more preferably, dichloroacetic acid, 2,3-dichloropropionic acid, 2,2-dichloropropionic acid, 2,2,3-trichloropropionic acid, 2,3,3,3-tetrachloropropionic acid, chlorodifluoroacetic acid,

dichlorofluoroacetic acid, 3-chloro-2,2-difluoropropionic acid, 2,3-dichloro-2,3-difluoropropionic acid, 3,3-dichloro-2,2-difluoropropionic acid, 2,2-dichloro-3,3,3-trifluoropropionic acid, 2,3-dichloro-2,3,3-trifluoropropionic acid, 2,2,3-trichloro-3,3-difluoropropionic acid, 2,3,3-trichloro-2,3-difluoropropionic acid, 3,3,3-trichloro-2,2-difluoropropionic acid, 2,3,3,3-tetrachloro-2-fluoropropionic acid, or 2,2,3,3-tetrachloro-3-fluoropropionic acid. Still more preferably, the chlorocarboxylic acid may be dichloroacetic acid, 2,3-dichloropropionic acid, 2,2-dichloropropionic acid, chlorodifluoroacetic acid, or dichlorofluoroacetic acid. In addition, examples of the chlorocarboxylic acid anhydride include the anhydrides of the above-described chlorocarboxylic acids.

[0092]

In addition, the chlorocarboxylic acid compound may include at least one of chlorocarboxylic acid having a pKa of -0.2 or more and 4.5 or less and an anhydride thereof.

The lower limit value of the pKa of the chlorocarboxylic acid may be, for example, -0.2 or more, -0.1 or more, 0 or more, or 0.2 or more. In addition, the upper limit value may be, for example, 4.5 or less, 3.0 or less, 2.0 or less, or 1.5 or less. By setting the pKa to be equal to or lower than the upper limit, it is easy to improve the reactivity of the (II) silyl ester compound to be obtained with the (I) silylating agent.

[0093]

In addition, each step of manufacturing the composition for

film formation may be carried out in the atmosphere or, as necessary, in an inert atmosphere such as a nitrogen atmosphere. For example, in a case where the reactivity of chlorocarboxylic acid or chlorocarboxylic acid anhydride with moisture in the atmosphere is high, each step is performed in an environment where the humidity is adjusted or in an inert atmosphere, so that the occurrence of cloudiness during manufacturing can be suppressed, which is suitable.

[0094]

In addition to the above, the above-described silylamide compound or aminosilane compound may be mixed. In addition, in the process of manufacturing the composition for film formation, a silylamide compound or an aminosilane compound may be generated as a by-product after mixing the raw materials, and these may be used as a component used in combination with the (I) silylating agent.

For example, in a case where a silazane compound is used as a raw material of the (I) silylating agent and a chlorocarboxylic acid anhydride is used as a raw material of the (II') chlorocarboxylic acid compound, the silylamide compound may be obtained as a by-product of the (II) silyl ester compound.

In addition, for example, in a case where a silazane compound is used as a raw material of the (I) silylating agent and a chlorocarboxylic acid is used as a raw material of the (II') chlorocarboxylic acid compound, the aminosilane compound may be obtained as a by-product of the (II) silyl ester

compound, or may be generated by a reaction between a component (for example, water, alcohol, various carboxylic acids, and the like) having an OH group contained in a raw material or a composition and the (I) silylating agent.

[0095]

The mixed solution obtained in the above example and/or the reaction solution obtained in other examples may be purified using an adsorbent, a filter, or the like, as necessary. In addition, each component may be purified in advance by distillation and also purified by using an adsorbent, a filter, or the like.

[0096]

(Method for Manufacturing Substrate)

A method for manufacturing a substrate using the composition for film formation according to the present embodiment will be described.

FIGS. 1 to 3 show an example of a method for manufacturing a substrate. FIG. 1 is a top view of the substrate 10 as viewed from a direction perpendicular to a main surface 12. FIG. 2 is a schematic cross-sectional view of the substrate 10 in a predetermined direction. FIG. 3A to FIG. 3C are schematic views of cross sections of steps in the step of manufacturing the substrate 10.

[0097]

An example of the method for manufacturing a substrate includes a substrate preparation step of preparing a substrate 10 (semiconductor substrate) and a surface treatment step of

supplying a composition 60 for film formation to the substrate 10 and forming a water-repellent film 70 on at least a part of a surface (main surface 12) of the substrate 10.

[0098]

In the preparation step of the substrate 10, as shown in FIGS. 1 and 2, the substrate 10 in which a pattern (concave-convex structure 20) is formed on the main surface 12 is prepared.

[0099]

Here, as an example of forming the concave-convex structure 20 on the surface of the substrate 10, the following method may be used.

First, after applying a resist to the wafer surface, the resist is exposed to light through a resist mask and either the exposed resist or the unexposed resist is removed to produce a resist having a desired uneven pattern. In addition, it is possible to obtain a resist having an uneven pattern by pressing a mold having a pattern against the resist. Next, the wafer is etched. At this time, the substrate surface corresponding to the concave portions of the resist pattern is selectively etched. Finally, in a case of peeling off the resist, a wafer (substrate 10) having the concave-convex structure 20 on the surface is obtained.

[0100]

The wafer on which the concave-convex structure 20 is formed and the material of the concave-convex structure 20 are not particularly limited.

As the material of the wafer, various wafers such as a silicon wafer, a silicon carbide wafer, a wafer composed of a plurality of components including a silicon element, a sapphire wafer, and a semiconductor wafer including various compounds can be used.

[0101]

As the material of the concave-convex structure 20, 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, may be included. For example, as the material of the concave-convex structure 20, silicon-based materials such as silicon oxide, silicon nitride, polycrystalline silicon, single crystalline silicon, and silicon germanium; metal-based materials such as titanium nitride, tungsten, ruthenium, tantalum nitride, and tin; materials obtained by combining these materials; resist (photoresist) materials; and the like can be used.

Among these, silicon-based materials such as silicon oxide, silicon nitride, polycrystalline silicon, single crystalline silicon, and silicon germanium are more preferable.

[0102]

The substrate 10 of FIG. 1 may have a pattern formation region 30 in which a pattern (concave-convex structure 20) is formed on the main surface 12 and a pattern non-formation region 32 in which the pattern is not formed.

In addition, in the substrate 10 of FIG. 1, the notch

portion 14 may be formed in a part of the peripheral edge portion. For the purpose of positioning in an exposure apparatus or the like, the notch portion 14 may be formed with a straight cut called as an orientation flat, which indicates a direction of a crystal axis, or a V-shaped cut called as a notch.

[0103]

The pattern formation region 30 is a region in which one or two or more concave-convex structures 20 are formed in a case of being viewed from a direction perpendicular to the main surface 12, that is, in a top view. The pattern formation region 30 may include an element formation region in which one or two or more semiconductor elements are formed.

[0104]

For example, the concave-convex structure 20 may be constituted of one or two or more structures arranged along a vertical direction of the main surface 12 and/or of a three-dimensional structure having one or two or more structures arranged along a horizontal direction orthogonal to the vertical direction. As an example of such a three-dimensional structure, at least a part of a logic device or a memory device may be formed and examples thereof include a FinFET, a nanowire FET, a nanosheet FET, or another multi-gate type FET, three-dimensional memory cells, and the like.

[0105]

The pattern non-formation region 32 is a region formed on at least a part of an outer circumference of the pattern

formation region 30 or the entire outer circumference thereof in the top view. The pattern non-formation region 32 may be formed continuously with each other or may be divided into a plurality of portions.

The pattern non-formation region 32 has a smooth surface region in which the concave-convex structure 20 is not formed at least in part.

[0106]

In the pattern formation region 30 and/or between the pattern formation region 30 and the pattern non-formation region 32, one or two or more cut regions for dicing may be formed.

[0107]

As shown in FIG. 2, the pattern dimension of the concave-convex structure 20 can be defined as at least one dimension in a width direction in an in-plane direction of the main surface 12 and/or at least one dimension in a height direction perpendicular to the main surface 12.

At least one or more pattern dimensions of the width and the height in the cross-sectional structure (in a thickness direction of the substrate) of the pattern of the concave-convex structure 20, or at least one or more pattern dimensions of the width (length in an X-axis direction), the height (length in a Y-axis direction), and the depth (length in a Z-axis direction) in the three-dimensional structure (three-dimensional coordinates of XYZ) in the pattern of the concave-convex structure 20 may be, for example, 30 nm or less, 20 nm or less, or 10 nm or less. The above may be the interval between

patterns. Even in a case where the substrate 10 having such a fine concave-convex structure 20 used, the composition for film formation according to the present embodiment can be applied.

[0108]

Such a composition for film formation is suitable, for example, for a surface treatment of the substrate 10 having the concave-convex structure 20 having a pattern dimension of 30 nm or less, preferably 20 nm or less.

[0109]

An aspect ratio of a convex portion 22 may be, for example, 3 or more, 5 or more, or 10 or more. Even in the concave-convex structure 20 which has the convex portion 22 having a fragile structure, the pattern collapse can be suppressed.

On the other hand, the aspect ratio of the convex portion 22 is not particularly limited, but may be 100 or less.

The aspect ratio of the convex portion 22 is represented by a value obtained dividing the height of the convex portion 22 by the width of the convex portion 22.

[0110]

As shown in FIG. 2, the substrate 10 may have a bevel region 50 formed in at least a part of the edge portion of the substrate 10. It is sufficient that the substrate 10 in the bevel region 50 includes an inclined surface (bevel) formed on the main surface 12, and for example, the substrate 10 includes a top edge 51, an upper bevel 52, a front shoulder 53, an end face 54, and a lower bevel 55.

[0111]

As necessary, the main surface 12 of the substrate 10 may be cleaned by bringing the main surface 12 into contact with an aqueous cleaning solution (cleaning step).

Examples of the aqueous cleaning solution include 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. These may be used alone, or two or more thereof may be used in combination.

[0112]

The cleaning step may be performed once or more before a surface treatment step or before the first rinsing step.

Other steps may be included between the plurality of cleaning steps or between the cleaning step and the surface treatment step.

[0113]

As necessary, the main surface 12 of the substrate 10 may be brought into contact with a first rinsing solution (first rinsing step). As the first rinsing solution, it is possible to use a cleaning liquid different from the aqueous cleaning solution and examples thereof include water, an organic solvent, a mixture thereof, or cleaning liquids in which at least one of an acid, an alkali, a surfactant, and an oxidizing agent are mixed, or the like.

Examples of the organic solvent used in the first rinsing solution include hydrocarbons, esters, ethers, ketones, halogen

element-containing solvents, sulfoxide-based solvents, alcohols, polyhydric alcohol derivatives, nitrogen element-containing solvents, and the like. Among the above, it is preferable to use, as an organic solvent, at least one selected from alcohols having 3 or less carbon atoms, such as methanol, 1-propanol, and 2-propanol (isopropanol).

[0114]

In addition, a plurality of types may be used as the first rinsing solution. For example, the rinsing can be performed in the order of a solution including an acid aqueous solution or an alkali aqueous solution → an organic solvent. In addition, the rinsing may be performed by adding the aqueous cleaning solution so as to be in the order of a solution including an acid aqueous solution or an alkali aqueous solution → the aqueous cleaning solution → an organic solvent.

[0115]

The first rinsing step may be performed once or twice or more after the cleaning step or before the surface treatment step. Other steps may be included between the plurality of first rinsing steps or between the first rinsing step and the surface treatment step.

[0116]

Subsequently, in the surface treatment step, as shown in FIG. 3A, the composition 60 for film formation according to the present embodiment is supplied to the surface (main surface 12) of the substrate 10.

[0117]

It is preferable to supply the composition 60 for film formation, which is a liquid, to the concave-convex structure 20 formed on the surface of the substrate 10. In this case, the composition for film formation may be supplied so as to fill a part or all of the concave portions 24 of the concave-convex structure 20.

The supply of the composition 60 for film formation may be performed in a state where the first rinsing solution or the aqueous cleaning solution is held on the main surface 12. That is, by substituting the first rinsing solution or the aqueous cleaning solution with the composition 60 for film formation, the surface treatment step can be performed before the surface of the concave-convex structure 20 on the main surface 12 of the substrate 10 is dried.

[0118]

A known method can be used as a method of supplying the composition 60 for film formation, and the composition 60 for film formation may be supplied in a liquid state or in a gas state. For example, a single-wafer method represented by a spin method (spin coating method) in which a liquid composition is supplied to the vicinity of a rotation center while holding one wafer substantially horizontally and rotating the wafer and the cleaning liquid or the like held on the uneven pattern of the wafer is substituted and filled with the composition, and a batch method in which a plurality of wafers are immersed in a composition tank and the cleaning liquid or the like held on the uneven pattern of the wafer is substituted to fill the

composition may be used. In addition, in a case of supplying the composition 60 for film formation with a gas, a method of supplying the vapor of the composition 60 for film formation to the uneven pattern of the wafer and aggregating the vapor on the wafer may be used.

[0119]

Subsequently, as shown in FIG. 3B, the water-repellent film 70 can be formed on at least a part of the main surface 12 by bringing the composition 60 for film formation into contact with the main surface 12 of the substrate 10.

As necessary, the formation of the water-repellent film 70 may be promoted by adopting a known method such as a heating treatment, a decompression treatment, and a drying treatment to the composition 60 for film formation on the main surface 12.

[0120]

The water-repellent film 70 is formed on the main surface 12 of the substrate 10 in at least the pattern formation region 30 and the pattern non-formation region 32. The water-repellent film 70 may be formed on the bevel region 50 on the main surface 12 or may be formed on the entire main surface 12.

[0121]

As necessary, the main surface 12 on which the water-repellent film 70 is formed may be brought into contact with a second rinsing solution (second rinsing step).

As the second rinsing solution, those mentioned for the first rinsing solution can be used.

In addition, a plurality of types may be used as the second

rinsing solution. For example, the rinsing can be performed in the order of water → an organic solvent such as isopropanol or in the order of an organic solvent such as isopropanol → water.

[0122]

The second rinsing step may be performed once or twice or more after the surface treatment step. Other steps may be included between the plurality of second rinsing steps or between the second rinsing step and the surface treatment step.

[0123]

A drying step of drying the main surface 12 of the substrate 10 may be performed as necessary.

By the drying step, the liquid existing on the main surface 12 of the substrate 10 can be removed.

As a drying method, for example, known methods such as a spin drying method, an IPA (2-propanol) steam drying, a Marangoni drying, a heat drying, a warm air drying, and a vacuum drying may be used.

[0124]

The drying step may be performed once or twice or more, for example, after the surface treatment step or after the second rinsing step. The drying step and the second rinsing step may be alternately repeated.

[0125]

If necessary, the water-repellent film 70 on the main surface 12 of the substrate 10 may be removed (removal step) as shown in FIG. 3C after the surface treatment step.

Examples of removal unit include heating, UV irradiation,

ozone exposure, plasma irradiation, corona discharge, and the like. In addition, a treatment using a concentrated fluid such as a supercritical fluid (which may include an acid, a base, and an oxidizing agent) or a vapor treatment may be performed. These may be used alone, or two or more thereof may be used in combination. These treatments may be performed under atmospheric pressure or reduced pressure.

[0126]

As described above, a semiconductor substrate (substrate 10) subjected to a surface treatment with the composition for film formation according to the present embodiment is obtained.

As a result, pattern collapse of the semiconductor substrate can be suppressed.

[0127]

Although a description was given of a manufacturing method in which the supply step described above is carried out after a cleaning step, without being limited thereto, the supply step may be carried out after various treatments carried out on the concave-convex structure 20.

In addition to the steps described above, the method for manufacturing a substrate may use one or a combination of two or more known treatments. For example, after the above-described removal step, a surface treatment such as a plasma treatment may be performed.

[0128]

In addition, the manufacturing method shown in FIGs. 3A to 3C target a wafer pattern, but the present disclosure is not

limited thereto. In the method for manufacturing a substrate according to the present embodiment, it is also possible to suppress a resist pattern from collapsing by using the composition for film formation according to the present disclosure in the cleaning and drying step of the resist pattern.

The composition for film formation according to the present embodiment can be used for suppressing pattern collapse on a substrate surface, but the use thereof is not limited thereto.

As another use, the composition for film formation according to the present embodiment can be used as a selective film. For example, by using the composition for film formation on two or more surfaces having different materials on the substrate surface, a water-repellent film can be formed to selectively impart water repellency to at least a part of the surface.

[0129]

The embodiments of the present disclosure have been described above, but these are only examples of the present disclosure and various configurations other than the above can be adopted. In addition, the present disclosure is not limited to the above-described embodiments, and modifications, improvements, and the like within the range in which the object of the present disclosure can be achieved are included in the present disclosure.

Hereinafter, examples of the reference forms will be added.

1. A composition for film formation, which is used for

forming a water-repellent film, containing: (I) a silylating agent; (II) a silyl ester compound represented by General Formula [2]; and (III) an aprotic solvent.

$(R^2\text{-}C(=O)O)_i\text{-}Si(H)_{4-i-h}(R^3)_h$ [2]

(in General Formula [2], R^2 is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms, R^3's are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, i is an integer of 1 to 3, h is an integer of 1 to 3, and i + h is an integer of 2 to 4)

2. The composition for film formation according to 1., in which 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's are each independently an organic group including a hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, X's are each independently a monovalent group in which an atom bonded to an Si atom is nitrogen, oxygen, carbon, or halogen,

a is an integer of 1 to 3, b is an integer of 0 to 2, and a sum of a and b is 1 to 3)

3. The composition for film formation according to 1. or

2., in which R^2 in General Formula [2] contains the silyl ester compound represented by $-C_qY_{(2q+1-r)}Cl_r$ (where Y's are each independently a hydrogen atom or a fluorine atom bonded to carbon, Cl is a chlorine atom, q is an integer of 1 to 5, and r is 1 to 2q).

4. The composition for film formation according to any one of 1. to 3., in which the aprotic solvent contains one or two or more selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen atom-containing solvents, sulfoxide-based solvents, carbonate-based solvents, a derivative of a polyhydric alcohol that does not have an OH group, a nitrogen atom-containing solvent that does not have an N-H group, and a silicone solvent.

5. The composition for film formation according to any one of 1. to 4., in which a content of the silylating agent is 0.1% by mass or more and 35% by mass or less in 100% by mass of the composition for film formation.

6. The composition for film formation according to any one of 1. to 5., in which a content of the silyl ester compound is 0.01% by mass or more and 10% by mass or less in 100% by mass of the composition for film formation.

7. The composition for film formation according to any one of 1. to 6., in which a water contact angle of a film formed from the composition for film formation, which is measured in accordance with JIS R 3257:1999, is 70° or more.

8. The composition for film formation according to any one of 1. to 7., in which the composition for film formation does

not contain an amide compound represented by General Formula [4] or a content of the amide compound is 1.0% by mass or less in 100% by mass of the composition for film formation.

R^{b1}-C(=O)N(H)Z[4]

(in General Formula [4], R^{b1} is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part of all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms, and Z is a hydrogen atom or a monovalent hydrocarbon group having 1 to 3 carbon atoms, which is bonded to a nitrogen atom)

9. The composition for film formation according to any one of 1. to 8., in which the composition for film formation contains one or two or more selected from the group consisting of a silylamide compound represented by General Formula [5] and an aminosilane compound represented by General Formula [6].

$(R^{b2}$-C(=O)N(H))$_j$-Si(H)$_{4-j-t}(R^{b3})_t$[5]

(in General Formula [5], R^{b2} is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms, R^{b3}'s are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, j is an integer of 1 to 3, t is an integer of 1 to 3, and j + t is an integer of 2 to 4)

$(R^{b4})_uSi(H)_v(NH_2)_{4-u-v}$[6]

(in General Formula [6], R^{b4}'s are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, u is an integer of 1 to 3, v is an integer of 0 to 2, and a sum of u and v is 1 to 3)

10. A method for manufacturing a substrate, including: a step of preparing a substrate; and a step of supplying a composition for film formation to the substrate to form a water-repellent film on at least a part of a surface of the substrate, in which the composition for film formation contains (I) a silylating agent, (II) a silyl ester compound represented by General Formula [2], and (III) an aprotic solvent.

$(R^2\text{-}C(=O)O)_i\text{-}Si(H)_{4-i-h}(R^3)_h$[2]

(in General Formula [2], R^2 is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms, R^3's are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms, i is an integer of 1 to 3, h is an integer of 1 to 3, and i + h is an integer of 2 to 4)

11. The method for manufacturing a substrate according to 10., further including: a step of cleaning the substrate prior

to supplying the composition for film formation.

12. A method for manufacturing a composition for film formation, including: a step of mixing (I) a silylating agent, (II) a silyl ester compound, and (III) an aprotic solvent.

13. A method for manufacturing a composition for film formation, including: a reaction step of reacting (I) a silylating agent with a chlorocarboxylic acid compound containing at least one of a chlorocarboxylic acid and a chlorocarboxylic acid anhydride to obtain (II) a silyl ester compound.

14. The method for manufacturing a composition for film formation according to 13., in which the chlorocarboxylic acid contains one or two or more of compounds represented by General Formula [7], and the chlorocarboxylic acid anhydride contains one or two or more of compounds represented by General Formula [8].

R^{C2}-C(=O)OH[7]

R^{C2}-C(=O)O-C(=O)-R^{C2}[8]

(in General Formulae [7] and [8], R^{C2}'s are each a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms)

15. The method for manufacturing a composition for film formation according to 13. or 14., in which the chlorocarboxylic acid compound contains at least one of the chlorocarboxylic acid

having a pKa of -0.2 or more and 4.5 or less and an anhydride of the chlorocarboxylic acid.

16. The method for manufacturing a composition for film formation according to any one of 13. to 15., in which the reaction step is carried out in (III) an aprotic solvent.

Examples

[0130]

Hereinafter, the present disclosure will be described in detail with reference to Examples, but the present disclosure is not limited to the description of Examples.

[0131]

(Preparation of Composition for Film Formation)

<Examples 1 to 31 and 36 to 41>

The (I) silylating agent, (II') chlorocarboxylic acid compound, and (III) aprotic solvent shown in the raw materials of Table 1 were mixed together at a liquid temperature of 25°C and in the atmosphere at a predetermined mass ratio, and the mixture was stirred for 1 minute to obtain a composition for film formation, containing the (I) silylating agent, (II) silyl ester compound, and (III) aprotic solvent at a mass ratio shown in Table 1. Depending on the composition of Examples, there are those including the amide compound of General Formula [4], the aminosilane compound represented by General Formula [6], and/or the silylamide compound. In a case where the compound is contained, the kind thereof and the content thereof with respect to the total amount of the composition for film formation are shown in Table 1, and in a case where the compound is not

contained, "-" is shown in Table 1. In addition, as the aprotic solvent before mixing, all of the solvents having a water content of 0.01% by mass or less were used. In addition, in Example 31, since the cloudiness was visually observed immediately after all the raw materials were mixed, in a case of performing various measurements and evaluations, the cloudiness (solid matter) was filtered and removed from the measurement target before the measurements and evaluations. In addition, in Table 1, the content of each component other than (III) with respect to the total amount of the composition for film formation was determined by the following gas chromatography measurement.

[0132]

<Examples 32 to 34>

A composition for film formation was obtained by the same method as in Examples 1 to 31, except that the water content of the (III) aprotic solvent was set to 0.1% by mass using the raw materials shown in Table 1. The aminosilane compound estimated to be generated by the reaction of the (I) silylating agent and water in the raw material, which is represented by General Formula [6], was measured in the same manner as described above, and the results are shown in Table 1. In addition, the silylamide compound contained in the composition for film formation was measured in the same manner as described above, and the confirmed compound is listed in Table 1. The amide compound represented by General Formula [4] was also measured in the same manner as described above, and the results are shown in

Table 1.

[0133]

<Examples 35 and 42 to 44>

Using the raw materials shown in Table 1, (I) a silylating agent, (II') a chlorocarboxylic acid compound, and (III) an aprotic solvent were mixed together at a predetermined mass ratio in a glove box at a liquid temperature of 25°C under a nitrogen atmosphere, and the mixture was stirred for 1 minute. As a result, a composition for film formation including (I) a silylating agent, (II) a silyl ester compound, and (III) an aprotic solvent was obtained at a mass ratio shown in Table 1. In Example 35, the amide compound of General Formula [4] was not formed by mixing in an inert atmosphere, and a composition for film formation, in which the cloudiness as in Example 31 was not generated, was obtained.

[0134]

The content (% by mass) of each component in the composition for film formation in Table 1 is determined by quantifying from the GC area of the obtained gas chromatography chart according to the absolute calibration curve method using gas chromatography under the following analysis conditions. The concentration of the aminosilane compound represented by General Formula [6] was expressed in terms of GC area% in a case where the total area of the respective components was set to 100 GC area%. The detected GC area% was rounded off to the number of display digits or less. For example, 0.00% indicates that the value is less than 0.005 GC area%.

(Gas chromatography analysis conditions)

Measurement sample: 1.0 μL

Device: GC-2010 plus (manufactured by Shimadzu Corporation)

Detector: hydrogen flame ionization detector (FID)

Used column: TC-1, length: 30 m × inner diameter: 0.32 mm (manufactured by GL SCIENCES INC.)

Analysis conditions: injection temperature: 270°C, detection temperature: 300°C

Carrier gas: helium

[0135]

<Comparative Example 1>

The (I) silylating agent and the (III) aprotic solvent shown in the raw materials of Table 1 were mixed at a mass ratio of 5% by mass:95% by mass at a liquid temperature of 25°C under the atmosphere, and the mixture was stirred for 1 minute to obtain a composition for film formation. As the aprotic solvent before mixing, an aprotic solvent having a water content of 0.01% by mass or less was used.

[0136]

<Comparative Examples 2 to 4>

The (I) silylating agent, the (II') acid compound, and the (III) aprotic solvent shown in the raw materials of Table 1 were mixed together at a predetermined mass ratio at a liquid temperature of 25°C in the atmosphere, and the mixture was stirred for 1 minute to obtain a composition for film formation, which contained the (I) silylating agent, the (II) silyl ester compound not corresponding to General Formula [2] of the present

disclosure, and the (III) aprotic solvent at a mass ratio shown in Table 1.

[0137]

<Reference Examples 1 to 6>

As a component corresponding to (I) silylating agent shown in the raw materials of Table 1 and (II') of Examples, an acid compound containing no chlorine element and (III) aprotic solvent were mixed together at a predetermined mass ratio at a liquid temperature of 25°C in the atmosphere, and the mixture was stirred for 1 minute. As a result, a composition for film formation including the components shown in Table 1 at a mass ratio shown in Table 1 was obtained. In Reference Examples 1 to 6, none of the components corresponding to (II) of Examples or the amide compound represented by General Formula [4] contain a chlorine element.

[0138]

[Table 1]

Table 1

	Raw material			Composition for film formation						Content in composition					pKa	Water contact angle (°)	Pattern collapse rate evaluation	Pattern collapse rate %	Cloudiness	Turbidity (NTU)
	(I)	(II')	(III)	(I)	Silylamide compound	(II)	(III)	Compound of Formula [4]	Compound of Formula [6]	(I) (wt%)	Silylamide compound (wt%)	(II) (wt%)	Formula [4] (wt%)	Formula [6] (GC area%)						
Example 1	HMDS	MCA	PGMEA	HMDS	-	TMSMCA	PGMEA	-	TMSA	5.3	-	0.3	-	0.12	2.7	76	Good	14	Absent	0.2
Example 2	HMDS	MCA	PGMEA	HMDS	-	TMSMCA	PGMEA	-	TMSA	13.8	-	0.8	-	0.31	2.7	85	Excellent	5	Absent	0.2
Example 3	HMDS	DCA	PGMEA	HMDS	-	TMSDCA	PGMEA	-	TMSA	3.1	-	0.1	-	0.03	1.4	80	Good	12	Absent	0.2
Example 4	HMDS	DCA	PGMEA	HMDS	-	TMSDCA	PGMEA	-	TMSA	5.2	-	0.3	-	0.08	1.4	88	Excellent	2	Absent	0.3
Example 5	HMDS	DCA	PGMEA	HMDS	-	TMSDCA	PGMEA	-	TMSA	12.5	-	0.5	-	0.16	1.4	92	Excellent	2	Absent	0.2
Example 6	HMDS	DCAA	PGMEA	HMDS	TMSDCAAm	TMSDCA	PGMEA	DCAm	TMSA	4.9	0.1	0.1	0.05	0.02	*1.4	72	Good	19	Absent	5.8
Example 7	HMDS	CDFAA	PGMEA	HMDS	TMSCDFAAm	TMSCDFA	PGMEA	CDFAm	TMSA	3.0	0.2	0.2	0.01	0.00	*0.2	80	Good	10	Absent	0.1
Example 8	HMDS	CDFAA	PGMEA	HMDS	TMSCDFAAm	TMSCDFA	PGMEA	CDFAm	TMSA	4.9	0.3	0.3	0.04	0.02	*0.2	87	Excellent	4	Absent	0.2
Example 9	HMDS	CDFAA	PGMEA	HMDS	TMSCDFAAm	TMSCDFA	PGMEA	CDFAm	TMSA	10.9	0.5	0.5	0.07	0.04	*0.2	88	Excellent	2	Absent	0.1
Example 10	HMDS	DCFA	PGMEA	HMDS	-	TMSDCFA	PGMEA	-	TMSA	3.2	-	0.2	-	0.05	0.2	80	Excellent	9	Absent	0.2
Example 11	HMDS	DCFA	PGMEA	HMDS	-	TMSDCFA	PGMEA	-	TMSA	5.2	-	0.3	-	0.09	0.2	89	Excellent	2	Absent	0.3
Example 12	HMDS	DCFA	PGMEA	HMDS	-	TMSDCFA	PGMEA	-	TMSA	11.6	-	0.6	-	0.16	0.2	90	Excellent	2	Absent	0.2
Example 13	HMDS	CFA	PGMEA	HMDS	-	TMSCFA	PGMEA	-	TMSA	11.5	-	0.5	-	0.16	1.5	83	Excellent	7	Absent	0.3
Example 14	HMDS	2CP	PGMEA	HMDS	-	TMS2CP	PGMEA	-	TMSA	3.1	-	0.1	-	0.03	3.0	72	Good	21	Absent	0.2
Example 15	HMDS	2CP	PGMEA	HMDS	-	TMS2CP	PGMEA	-	TMSA	5.2	-	0.2	-	0.09	3.0	78	Good	15	Absent	0.3
Example 16	HMDS	2CP	PGMEA	HMDS	-	TMS2CP	PGMEA	-	TMSA	12.6	-	0.6	-	0.20	3.0	85	Excellent	5	Absent	0.2
Example 17	HMDS	23DCP	PGMEA	HMDS	-	TMS23DCP	PGMEA	-	TMSA	3.1	-	0.1	-	0.01	1.1	77	Good	13	Absent	0.2
Example 18	HMDS	23DCP	PGMEA	HMDS	-	TMS23DCP	PGMEA	-	TMSA	5.3	-	0.3	-	0.08	1.1	86	Excellent	4	Absent	0.2
Example 19	HMDS	23DCP	PGMEA	HMDS	-	TMS23DCP	PGMEA	-	TMSA	12.4	-	0.4	-	0.12	1.1	90	Excellent	3	Absent	0.3
Example 20	HMDS	223TCP	PGMEA	HMDS	-	TMS223TCP	PGMEA	-	TMSA	3.2	-	0.2	-	0.05	0.9	82	Excellent	8	Absent	0.3
Example 21	HMDS	223TCP	PGMEA	HMDS	-	TMS223TCP	PGMEA	-	TMSA	5.4	-	0.4	-	0.09	0.9	87	Excellent	3	Absent	0.2
Example 22	HMDS	22333PCP	PGMEA	HMDS	-	TMS22333PCP	PGMEA	-	TMSA	3.3	-	0.3	-	0.05	-0.1	89	Excellent	3	Absent	0.2
Example 23	HMDS	22333PCP	PGMEA	HMDS	-	TMS22333PCP	PGMEA	-	TMSA	5.5	-	0.5	-	0.10	-0.1	92	Excellent	2	Absent	0.3
Example 24	HMDS	3C2233TFP	PGMEA	HMDS	-	TMS3C2233TFP	PGMEA	-	TMSA	3.2	-	0.2	-	0.04	0.4	81	Excellent	9	Absent	0.2
Example 25	HMDS	3C2233TFP	PGMEA	HMDS	-	TMS3C2233TFP	PGMEA	-	TMSA	5.4	-	0.4	-	0.09	0.4	89	Excellent	2	Absent	0.3
Example 26	HMDS	2C2333TFP	PGMEA	HMDS	-	TMS2C2333TFP	PGMEA	-	TMSA	3.2	-	0.2	-	0.04	-0.1	85	Excellent	5	Absent	0.3
Example 27	HMDS	2C2333TFP	PGMEA	HMDS	-	TMS2C2333TFP	PGMEA	-	TMSA	5.4	-	0.4	-	0.09	-0.1	92	Excellent	2	Absent	0.1
Example 28	HMDS	23DC23DFP	PGMEA	HMDS	-	TMS23DC23DFP	PGMEA	-	TMSA	3.2	-	0.2	-	0.04	0.4	80	Good	13	Absent	0.2
Example 29	HMDS	23DC23DFP	PGMEA	HMDS	-	TMS23DC23DFP	PGMEA	-	TMSA	5.4	-	0.4	-	0.09	0.4	89	Excellent	2	Absent	0.3
Example 30	HMDS	DCAA	γ-butyrolactone	HMDS	TMSDCAAm	TMSDCA	γ-butyrolactone	DCAm	TMSA	5.1	0.2	0.3	0.18	0.02	*1.4	90	Excellent	2	Absent	0.9
Example 31	HMDS	DCAA	PGMEA	HMDS	TMSDCAAm	TMSDCA	PGMEA	DCAm	TMSA	5.1	0.2	0.3	0.18	0.02	*1.4	86	Excellent	4	Present	22.3
Example 32	HMDS	DCA	PGMEA	HMDS	-	TMSDCA	PGMEA	-	TMSA	3.1	-	0.1	-	0.07	1.4	89	Excellent	1	Absent	0.1
Example 33	HMDS	CDFAA	PGMEA	HMDS	TMSCDFAAm	TMSCDFA	PGMEA	CDFAm	TMSA	2.9	0.2	0.2	0.02	0.04	*0.2	88	Excellent	2	Absent	0.2
Example 34	HMDS	DCFAA	PGMEA	HMDS	TMSDCFAAm	TMSDCFA	PGMEA	DCFAm	TMSA	3.0	0.2	0.2	0.09	0.04	*0.2	89	Excellent	1	Absent	4.9
Example 35	HMDS	DCAA	PGMEA	HMDS	TMSDCAAm	TMSDCA	PGMEA	-	-	5.0	0.3	0.3	-	-	*1.4	78	Good	17	Absent	0.1
Example 36	TMSDMA	DCA	PGMEA	TMSDMA	-	TMSDCA	PGMEA	-	-	5.2	-	0.3	-	-	1.4	82	Excellent	8	Absent	0.2
Example 37	TMSDMA	CDFA	PGMEA	TMSDMA	-	TMSCDFA	PGMEA	-	-	5.2	-	0.3	-	-	0.2	90	Excellent	3	Absent	0.2
Example 38	TMSDMA	DCFA	PGMEA	TMSDMA	-	TMSDCFA	PGMEA	-	-	5.2	-	0.3	-	-	0.2	91	Excellent	2	Absent	0.3
Example 39	TMSDMA	CDFAA	PGMEA	TMSDMA	-	TMSCDFA	PGMEA	-	-	5.2	-	0.3	-	-	*0.2	89	Excellent	3	Absent	0.2
Example 40	HMDS	CDFAA	PGMEA	HMDS	TMSCDFAAm	TMSCDFA	PGMEA	CDFAm	TMSA	17.3	1.2	1.2	0.10	0.04	*0.2	89	Excellent	3	Absent	0.2

Example 41	HMDS	CDFAA	PGMEA	HMDS	TMSCDFAAm	TMSCDFA	PGMEA	CDFAm	TMSA	9.4	3.0	3.0	0.14	0.03	*0.2	91	Excellent	1	Absent	0.2
Example 42	HMDS	CDFAA	PGMEA	HMDS	TMSCDFAAm	TMSCDFA	PGMEA	-	-	10.9	0.5	0.5	-	-	*0.2	87	Excellent	4	Absent	0.1
Example 43	HMDS	CDFAA	PGMEA	HMDS	TMSCDFAAm	TMSCDFA	PGMEA	-	-	17.3	1.2	1.2	-	-	*0.2	88	Excellent	3	Absent	0.2
Example 44	HMDS	CDFAA	PGMEA	HMDS	TMSCDFAAm	TMSCDFA	PGMEA	-	-	9.4	3.0	3.0	-	-	*0.2	90	Excellent	2	Absent	0.2
Comparative Example 1	HMDS	None	PGMEA	HMDS	-	None	PGMEA	-	-	5.0	-	0	-	-	-	27	Defective	72		
Comparative Example 2	HMDS	MSA	PGMEA	HMDS	-	TMSMSA	PGMEA	-	TMSA	5.2	-	0.3	-	0.12	1.8	68	Defective	31		
Comparative Example 3	HMDS	CH_3COOH	PGMEA	HMDS	-	TMSCA	PGMEA	-	TMSA	5.2	-	0.3	-	0.13	4.8	64	Defective	45		
Comparative Example 4	HMDS	H_2SO_4	PGMEA	HMDS	-	TMSSA	PGMEA	-	TMSA	5.2	-	0.3	-	0.13	-3.0	64	Defective	46		
Reference Example 1	HMDS	TFAA	PGMEA	HMDS	TMSTFAAm	TMSTFA	PGMEA	TFAm	TMSA	4.9	0.3	0.3	0.01	0.02	*0.1	89	Excellent	5		
Reference Example 2	HMDS	TFAA	PGMEA	HMDS	TMSTFAAm	TMSTFA	PGMEA	TFAm	TMSA	9.4	3.0	3.0	0.10	0.04	*0.1	91	Excellent	3		
Reference Example 3	HMDS	TFMSA	PGMEA	HMDS	-	TMSTFMSA	PGMEA	-	TMSA	5.2	-	0.3	-	0.12	-3.9	84	Excellent	9		
Reference Example 4	HMDS	TFMSA	PGMEA	HMDS	-	TMSTFMSA	PGMEA	-	TMSA	12.4	-	3.0	-	0.17	-3.9	87	Excellent	6		
Reference Example 5	HMDS	TFMSAA	PGMEA	HMDS	TMSTFMSAAm	TMSTFMSA	PGMEA		TMSA	4.9	0.3	0.3		0.02	*-3.9	82	Excellent	9		
Reference Example 6	HMDS	TFMSAA	PGMEA	HMDS	TMSTFMSAAm	TMSTFMSA	PGMEA		TMSA	9.4	3.0	3.0		0.04	*-3.9	84	Excellent	9		

[0139]

The compound names corresponding to the abbreviations in Table 1 are shown below.

· (I) Silylating agent

HMDS: 1,1,1,3,3,3-hexamethyldisilazane

TMSDMA: N-(trimethylsilyl)dimethylamine

· Silylamide compound and silylamide compound according to Reference Example

TMSDCAAm: N-trimethylsilyldichloroacetamide

TMSCDFAAm: N-trimethylsilyl chlorodifluoroacetamide

TMSDCFAAm: N-trimethylsilyldichlorofluoroacetamide

TMSTFAAm: N-trimethylsilyltrifluoroacetamide

TMSTFMSAAm: N-trimethylsilyltrifluoromethanesulfonamide

[0140]

· (II') Chlorocarboxylic acid compound used in Examples and acid compound used in Comparative Examples

MCA: monochloroacetic acid

DCA: dichloroacetic acid

DCAA: dichloroacetic acid anhydride

CDFA: chlorodifluoroacetic acid

CDFAA: chlorodifluoroacetic acid anhydride

DCFA: dichlorofluoroacetic acid

CFA: chlorofluoroacetic acid

2CP: 2-chloropropionic acid

23DCP: 2,3-dichloropropionic acid

22333PCP: 2,2,3,3,3-pentachloropropionic acid

223TCP: 2,2,3-trichloropropionic acid

3C2233TFP: 3-chloro-2,2,3,3-tetrafluoropropionic acid

2C2333TFP: 2-chloro-2,3,3,3-tetrafluoropropionic acid

23DC23DFP: 2,3-dichloro-2,3-difluoropropionic acid

DCFAA: dichlorofluoroacetic acid anhydride

TFAA: trifluoroacetic acid anhydride

TFMSA: trifluoromethanesulfonic acid

TFMSAA: trifluoromethanesulfonic acid anhydride

MSA: methanesulfonic acid

[0141]

· (II) Silyl ester compounds according to Examples and Comparative Examples, and silyl compounds according to Comparative Examples

TMSMCA: trimethylsilyl chloroacetate

TMSDCA: trimethylsilyldichloroacetate

TMSCDFA: trimethylsilyl chlorodifluoroacetate

TMSDCFA: trimethylsilyl dichlorofluoroacetate

TMSCFA: trimethylsilyl chlorofluoroacetate

TMS2CP: trimethylsilyl-2-chloropropionate

TMS23DCP: trimethylsilyl-2,3-dichloropropionate

TMS22333PCP: trimethylsilyl-2,2,3,3,3-pentachloropropionate

TMS223TCP: trimethylsilyl-2,2,3-trichloropropionate

TMS3C2233TFP: trimethylsilyl-3-chloro-2,2,3,3-tetrafluoropropionate

TMS2C2333TFP: trimethylsilyl-2-chloro-2,3,3,3-tetrafluoropropionate

TMS23DC23DFP: trimethylsilyl-2,3-dichloro-2,3-difluoropropionate

TMSMSA: trimethylsilyl methanesulfonate

TMSCA: trimethylsilyl acetate

TMSSA: trimethylsilyl sulfonate

TMSTFA: trimethylsilyl trifluoroacetate

TMSTFMSA: trimethylsilyltrifluoromethanesulfonate

[0142]

· (III) Aprotic solvent

PGMEA: propylene glycol monomethyl ether acetate

[0143]

· (IV) Amide compound

DCAm: 2,2-dichloroacetamide

CDFAm: 2-chloro-2,2-difluoroacetamide

DCFAm: 2,2-dichloro-2-fluoroacetamide

TFAm: trifluoroacetamide

[0144]

· (VI) Aminosilane compound

TMSA: aminotrimethylsilane

[0145]

<Chlorocarboxylic Acid Used in Examples and PKa of Acid Compound Used in Comparative Examples>

In Table 1, the pKa was determined using a calculated value confirmed by the chemical substance search of CAS SciFinder^{n}. Here, a pKa value calculated by Advanced Chemistry Development (ACD/Labs) Software V11.02 (Copyright 1994-2023 ACD/Labs) was adopted.

In addition, the value of pKa marked with * in Table 1 indicates the acid corresponding to the acid anhydride.

[0146]

The obtained composition for film formation was evaluated according to the following items.

[0147]

In Table 1, the turbidity was measured by stirring the composition for film formation for 10 seconds and then using a portable turbidimeter 2100Q (manufactured by HACH) at room temperature. A smaller value for turbidity is an indicator of higher transparency, and it was determined that the cloudiness was not generated when the turbidity was 10 or less.

[0148]

<Water Contact Angle>

For the obtained composition for film formation, a water contact angle (°) was measured according to the following coupon test procedure. The results are listed in Table 1. The coupon test was carried out only in Example 35 under a nitrogen atmosphere, and the coupon test was carried out in the atmosphere in the other Examples.

(Procedure of Coupon Test)

A silicon wafer having no uneven pattern on a surface and having a silicon oxide film with a thickness of 1 μm on the surface was cut to prepare a coupon consisting of a silicon substrate having dimensions of a length of 4 cm, a width of 1 cm, and a thickness of 0.75 mm.

The coupon was immersed in 1% by mass of hydrofluoric acid at room temperature, then immersed in water at room temperature, then immersed in 2-propanol at room temperature, and then

immersed in propylene glycol monomethyl ether acetate at room temperature for cleaning. In addition, at this time, the "room temperature" was 25°C.

An evaluation solution consisting of the composition for film formation was prepared, and the cleaned coupon was immersed in the evaluation solution at room temperature. An immersion time in the evaluation solution is set to 20 seconds.

The coupon taken out from the evaluation solution was cleaned by being immersed in 2-propanol at room temperature, and then the surface of the coupon was dried with nitrogen gas.

In a state in which the dried coupon was placed on a horizontal plane, 2 μl of pure water was placed on the surface of the coupon on which the silicon oxide film had been formed at room temperature of 25°C, and a water contact angle (°) was measured in accordance with JIS R 3257:1999.

In the coupon used as the evaluation solution of Example 31, there was an attachment derived from cloudiness on the surface, but the attachment was removed during subsequent immersion in 2-propanol, and thus the coupon was dried and the water contact angle was measured.

[0149]

<Evaluation of Pattern Collapse Rate>

First, a silicon substrate having a pattern formation region in which a convex structure having a plurality of substantially columnar convex portions having an aspect ratio of 22 and a pattern width of 19 nm in a cross-sectional view at a pitch of 90 nm (a total distance of a width of the convex

portion and an adjacent interval of the convex portions) was formed on a surface was prepared.

The surface of the above-described substrate was dry-cleaned by UV/O_3 irradiation. The surface of the substrate was oxidized to be silicon oxide. Subsequently, the substrate was placed on a spin coater, and while rotating the substrate at a speed of 200 rpm, 2-propanol (IPA), the composition for film formation shown in Table 1, and IPA were discharged in this order at a rate of 200 cc/min. Thereafter, the substrate was dried while discharging N_2 onto the substrate.

Using the substrate subjected to the surface treatment with the composition for film formation, the pattern formation region was observed with an electron microscope (SEM, SU8010 manufactured by Hitachi High-Tech Corporation) at a magnification such that 500 to 600 convex portion were included in the field of view, and the number of convex portion in which pattern collapse occurred was counted. The proportion of the convex portion in which the collapse occurred with respect to all the convex portions is shown in Table 1 as a pattern collapse rate (%). In addition, the calculated values were evaluated as follows, and the results are shown in Table 1.

In a case where Example 31 was used as the composition for film formation, the composition was supplied to the substrate surface after the cloudiness was removed.

<Evaluation standard>

Excellent: pattern collapse rate was less than 10%

Good: pattern collapse rate was 10% or more and less than

30%

Defective: pattern collapse rate was 30% or more

[0150]

The compositions for film formation of Examples 1 to 44 showed results that excellent water repellency was imparted to the substrate surface as compared with Comparative Examples 1 to 4. In addition, since the compositions for film formation of Examples 1 to 44 satisfy the water repellency standard that the water contact angle is 70° or more, it was confirmed that the compositions for film formation of Examples 1 to 44 have the same water repellency as that of Reference Examples 1 to 6 in which the perfluoroalkyl derivative was used as the accelerator.

In addition, in all of Examples 1 to 44, it was found that the pattern collapse rate was less than 30%, and the pattern collapse was able to be satisfactorily suppressed. Further, it was found that in a case where the water contact angle was 81° or more, the pattern collapse rate was less than 10%, and thus the pattern collapse was more easily suppressed.

In addition, in Examples 6 to 9, 30, 31, 33, 34, 40, and 41 in which an anhydride was used as a raw material, a silylamide compound was confirmed. These silylamide compounds are presumed to be by-products generated in a process in which the silylating agent of the silazane compound and the chlorocarboxylic acid anhydride react with each other.

In addition, the aminosilane compound was observed in Examples 1 to 34, 40, and 41.

In addition, in a case of comparing Example 31 prepared in

the atmosphere with Example 35 prepared in the nitrogen atmosphere (the raw materials of both are the same), it was found that Example 31 in which the aminosilane compound was contained in the composition for film formation could impart more excellent water repellency to the substrate surface.

[0151]

This application claims priority based on Japanese Patent Application No. 2023-090176 filed on May 31, 2023, the entire disclosure of which is incorporated herein.

REFERENCE SIGNS LIST

[0152]

10 substrate
12 main surface
14 notch portion
16 back surface
20 concave-convex structure
22 convex portion
24 concave portion
30 pattern formation region
32 pattern non-formation region
50 bevel region
51 top edge
52 upper bevel
53 front shoulder
54 end face
55 lower bevel

60 composition for film formation

70 water-repellent film

CLAIMS

[Claim 1]

A composition for film formation, which is used for forming a water-repellent film, comprising:

(I) a silylating agent;

(II) a silyl ester compound represented by General Formula [2]; and

(III) an aprotic solvent,

$(R^2\text{-}C(=O)O)_i\text{-}Si(H)_{4-i-h}(R^3)_h$ [2]

(in General Formula [2],

R^2 is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms,

R^3's are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms,

i is an integer of 1 to 3, h is an integer of 1 to 3, and i + h is an integer of 2 to 4).

[Claim 2]

The composition for film formation according to Claim 1,

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's are each independently an organic group including a hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms,

X's are each independently a monovalent group in which an atom bonded to an Si atom is nitrogen, oxygen, carbon, or halogen,

a is an integer of 1 to 3, b is an integer of 0 to 2, and a sum of a and b is 1 to 3).

[Claim 3]

The composition for film formation according to Claim 1 or 2,

contains the silyl ester compound wherein R^2 in General Formula [2] is represented by $-C_qY_{(2q+1-r)}Cl_r$ (where Y's are each independently a hydrogen atom or a fluorine atom bonded to carbon, Cl is a chlorine atom, q is an integer of 1 to 5, and r is 1 to 2q).

[Claim 4]

The composition for film formation according to Claim 1 or 2,

wherein the aprotic solvent contains one or two or more selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen atom-containing solvents, sulfoxide-

based solvents, carbonate-based solvents, a derivative of a polyhydric alcohol that does not have an OH group, a nitrogen atom-containing solvent that does not have an N-H group, and a silicone solvent.

[Claim 5]

The composition for film formation according to Claim 1 or 2,

wherein a content of the silylating agent is 0.1% by mass or more and 35% by mass or less in 100% by mass of the composition for film formation.

[Claim 6]

The composition for film formation according to Claim 1 or 2,

wherein a content of the silyl ester compound is 0.01% by mass or more and 10% by mass or less in 100% by mass of the composition for film formation.

[Claim 7]

The composition for film formation according to Claim 1 or 2,

wherein a water contact angle of a film formed from the composition for film formation, which is measured in accordance with JIS R 3257:1999, is 70° or more.

[Claim 8]

The composition for film formation according to Claim 1 or 2,

wherein the composition for film formation contains (III) the aprotic solvent having a polarity.

[Claim 9]

The composition for film formation according to Claim 1 or 2,

wherein the composition for film formation does not contain an amide compound represented by General Formula [4] or a content of the amide compound is 0.1% by mass or less in 100% by mass of the composition for film formation,

R^{b1}-C(=O)N(H)Z[4]

(in General Formula [4],

R^{b1} is a hydrocarbon group having a Cl_3C moiety, a Cl_2HC moiety, or a Cl_2FC moiety, and

Z is a hydrogen atom or a monovalent hydrocarbon group having 1 to 3 carbon atoms, which is bonded to a nitrogen atom).

[Claim 10]

The composition for film formation according to Claim 9,

wherein the composition for film formation contains an amide compound having a structure in which R^{b1} is a hydrocarbon group that does not have a Cl_3C moiety, a Cl_2HC moiety, or a Cl_2FC moiety in General Formula [4].

[Claim 11]

The composition for film formation according to Claim 1 or 2,

wherein the composition for film formation contains one or two or more selected from the group consisting of a silylamide compound represented by General Formula [5] and an aminosilane compound represented by General Formula [6],

$(R^{b2}-C(=O)N(H))_j-Si(H)_{4-j-t}(R^{b3})_t$ [5],

(in General Formula [5],

R^{b2} is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms,

R^{b3}'s are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms,

j is an integer of 1 to 3, t is an integer of 1 to 3, and j + t is an integer of 2 to 4), and

$(R^{b4})_uSi(H)_v(NH_2)_{4-u-v}$ [6]

(in General Formula [6],

R^{b4}'s are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms,

u is an integer of 1 to 3, v is an integer of 0 to 2, and a sum of u and v is 1 to 3).

[Claim 12]

A method for manufacturing a substrate, comprising:

a step of preparing a substrate; and

a step of supplying a composition for film formation to the substrate to form a water-repellent film on at least a part of a surface of the substrate,

wherein the composition for film formation contains

(I) a silylating agent,

(II) a silyl ester compound represented by General Formula [2], and

(III) an aprotic solvent,

$(R^2\text{-}C(=O)O)_i\text{-}Si(H)_{4-i-h}(R^3)_h$ [2]

(in General Formula [2],

R^2 is a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms,

R^3's are each independently an organic group including a monovalent hydrocarbon group having 1 to 18 carbon atoms, in which a part or all of hydrogen atoms may be substituted with fluorine atoms or chlorine atoms,

i is an integer of 1 to 3, h is an integer of 1 to 3, and i + h is an integer of 2 to 4).

[Claim 13]

The method for manufacturing a substrate according to Claim 12, further comprising:

a step of cleaning the substrate prior to supplying the composition for film formation.

[Claim 14]

A method for manufacturing a composition for film formation, comprising:

a step of mixing (I) a silylating agent, (II) a silyl ester compound, and (III) an aprotic solvent.

[Claim 15]

A method for manufacturing a composition for film formation, comprising:

a reaction step of reacting (I) a silylating agent with a chlorocarboxylic acid compound containing at least one of a chlorocarboxylic acid and a chlorocarboxylic acid anhydride to obtain (II) a silyl ester compound.

[Claim 16]

The method for manufacturing a composition for film formation according to Claim 15,

wherein the chlorocarboxylic acid contains one or two or more of compounds represented by General Formula [7], and

the chlorocarboxylic acid anhydride contains one or two or more of compounds represented by General Formula [8],

R^{C2}-C(=O)OH[7]

R^{C2}-C(=O)O-C(=O)-R^{C2} [8]

(in General Formulae [7] and [8],

R^{C2}'s are each a monovalent hydrocarbon group having 1 to 5 carbon atoms, in which a part or all of hydrogen atoms are substituted with chlorine atoms, and the other hydrogen atoms which are not substituted may be partially or wholly substituted with fluorine atoms).

[Claim 17]

The method for manufacturing a composition for film formation according to Claim 15 or 16,

wherein the chlorocarboxylic acid compound contains at least one of the chlorocarboxylic acid having a pKa of -0.2 or more and 4.5 or less and an anhydride of the chlorocarboxylic acid.

[Claim 18]

The method for manufacturing a composition for film formation according to Claim 15 or 16,

wherein the reaction step is carried out in (III) an aprotic solvent.

[Claim 19]

The method for manufacturing a composition for film formation according to Claim 15 or 16,

wherein in the reaction step, the chlorocarboxylic acid compound contains the chlorocarboxylic acid and does not contain

the chlorocarboxylic acid anhydride.

[Claim 20]

The method for manufacturing a composition for film formation according to Claim 15 or 16,

wherein (I) the silylating agent is not a silazane compound.

[Claim 21]

The method for manufacturing a composition for film formation according to Claim 15 or 16,

wherein the reaction step is carried out in an inert atmosphere.