

CLAIMS

~~[Claim 1] — A liquid chemical for forming a water-repellent protective film, characterized by comprising:~~

~~———— a water-repellent protective film forming agent for forming a~~
~~water-repellent protective film on a wafer having at its surface an uneven~~
~~pattern and containing at least one kind of element selected from the group~~
~~consisting of titanium, tungsten, aluminum, copper, tin, tantalum and~~
~~ruthenium at surfaces of recessed portions of the uneven pattern, the water-~~
~~repellent protective film being formed at least on the surfaces of the recessed~~
~~portions by retaining the liquid chemical at least on the recessed portions of the~~
~~wafer before a rinsing treatment step of rinsing the wafer surface with a rinsing~~
~~liquid consisting only of a protic polar solvent or a rinsing liquid containing a~~
~~protic polar solvent as the principal component; and~~
~~———— a solvent,~~

~~———— wherein the water-repellent protective film forming agent is at~~
~~least one kind of compound represented by the following general formulas [1] to~~
~~[3].~~



~~(In the formula [1], R¹ represents a C₆-C₁₈ monovalent~~
~~hydrocarbon group the hydrogen elements of which may partially or entirely be~~
~~replaced with a fluorine element(s), R² mutually independently represents a~~
~~monovalent organic group having a C₁-C₁₈ hydrocarbon group the hydrogen~~
~~elements of which may partially or entirely be replaced with a fluorine~~
~~element(s), and “a” is an integer of from 0 to 2.)~~

~~(R³)_b(R⁴)_cNH_{3-b-c} [2]~~

~~(In the formula [2], R³ mutually independently represents a~~
~~C₆-C₁₈ monovalent hydrocarbon group the hydrogen elements of which may~~
~~partially or entirely be replaced with a fluorine element(s), R⁴ mutually~~

~~independently represents a C₁-C₃ monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), “b” is an integer of from 1 to 3, “c” is an integer of from 0 to 2, and the total of “b” and “c” is an integer of from 1 to 3.)~~

5 ~~————— R⁵(X)_d — [3]~~

~~————— (The formula [3] represents a compound obtained by mutually independently substituting “d” hydrogen element(s) or fluorine element(s) of R⁵ which represents a C₄-C₁₈ hydrocarbon the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s) with at least one group indicated by X and selected from the group consisting of an isocyanate group, mercapto group, CONHOH group and a cyclic structure containing a nitrogen element, wherein “d” is an integer of from 1 to 6.)~~

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~~[Claim 2] — A liquid chemical for forming a water-repellent protective film, as claimed in claim 1, characterized in that “a” in the general formula [1] is 2.~~

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~~[Claim 3] — A liquid chemical for forming a water-repellent protective film, as claimed in claim 1 or 2, characterized in that R¹ in the general formula [1] is a C₈-C₁₈ monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s).~~

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~~[Claim 4] — A liquid chemical for forming a water-repellent protective film, as claimed in claim 1, characterized in that “b” in the general formula [2] is 1.~~

~~[Claim 5] — A liquid chemical for forming a water-repellent protective film, as claimed in claim 1 or 4, characterized in that R³ in the general formula [2] is a C₈-C₁₈ monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s).~~

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~~[Claim 6] — A liquid chemical for forming a water-repellent protective film, as claimed in claim 1, characterized in that R⁵ in the general formula [3] has a~~

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carbon number of 6 to 18.

[Claim 7] — ~~A water-repellent protective film formed on a wafer having at its surface an uneven pattern and containing at least one kind of element selected from the group consisting of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern, the water-repellent protective film being formed at least on the surfaces of the recessed portions by retaining the liquid chemical for forming water-repellent protective film as claimed in any of claims 1 to 6 at least on the recessed portions before a rinsing treatment step of rinsing the wafer surface with a rinsing liquid consisting only of a protic polar solvent or a rinsing liquid containing a protic polar solvent as the principal component, characterized in that the water-repellent protective film is formed of at least one kind of compounds that serve as the water-repellent protective film forming agent and represented by the general formulas [1] to [3].~~

[Claim 8] A method of cleaning a wafer having at its surface an uneven pattern and containing at least one kind of element selected from the group consisting of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern, ~~characterized by comprising wherein the method comprises~~ at least the steps of:

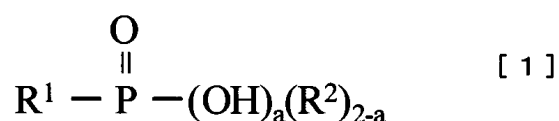
a water-repellent protective film forming step for retaining a liquid chemical for forming a water-repellent protective film at least in the recessed portions of the uneven pattern;

a rinsing treatment step of retaining ~~a rinsing liquid consisting only of a protic polar solvent or a rinsing liquid containing a protic polar solvent as the principal component~~ a rinsing liquid containing 50-100 mass% protic polar solvent, on the wafer surface that had undergone the water-repellent protective film forming step;

a rinsing liquid removal step for removing the rinsing liquid; and

a water-repellent protective film removal step for removing a water-repellent protective film;

wherein the liquid chemical for forming a water-repellent protective film is a liquid chemical comprising a water-repellent protective film forming agent for forming a water-repellent protective film at least on the surfaces of the recessed portions, and the water-repellent protective film forming agent is at least one kind of compound represented by the following general formulas [1] to [3]:



(in the formula [1], R¹ represents a C₆-C₁₈ monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), R² mutually independently represents a monovalent organic group having a C₁-C₁₈ hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), and "a" is an integer of from 0 to 2),



(in the formula [2], R³ mutually independently represents a C₆-C₁₈ monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), R⁴ mutually independently represents a C₁-C₃ monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), "b" is an integer of from 1 to 3, "c" is an integer of from 0 to 2, and the total of "b" and "c" is an integer of from 1 to 3),



(the formula [3] represents a compound obtained by mutually independently substituting "d" hydrogen element(s) or fluorine element(s) of R⁵ which represents a C₄-C₁₈ hydrocarbon the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s) with at least one group indicated by X and selected from the group consisting of an isocyanate group, mercapto group, -CONHOH group and a cyclic structure containing a

nitrogen element, wherein “d” is an integer of from 1 to 6).

[Claim ~~92~~] A method of cleaning a wafer, as claimed in claim ~~81~~,
~~characterized in that wherein~~ the protic polar solvent is an alcohol.

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[Claim ~~103~~] A method of cleaning a wafer, as claimed in claim ~~81~~ or ~~92~~,
~~characterized in that wherein~~ the water-repellent protective film removal step
is performed by at least one treatment selected from the group consisting of:
irradiating the wafer surface with light; heating the wafer; exposing the wafer
10 to ozone; irradiating the wafer surface with plasma; and subjecting the wafer
surface to corona discharge, thereby removing the water-repellent protective
film.

[Claim 4] A method of cleaning a wafer having at its surface an uneven
15 pattern and containing at least one kind of element selected from the group
consisting of titanium, tungsten, aluminum, copper, tin, tantalum and
 ruthenium at surfaces of recessed portions of the uneven pattern, wherein the
method comprises at least the steps of:

a water-repellent protective film forming step for retaining a
20 liquid chemical for forming a water-repellent protective film at least in the
recessed portions of the uneven pattern;

a rinsing treatment step of retaining a rinsing liquid consisting
only of a protic polar solvent or a rinsing liquid containing a protic polar solvent
as the principal component, on the wafer surface that had undergone the water-
25 repellent protective film forming step;

a rinsing liquid removal step for removing the rinsing liquid; and
a water-repellent protective film removal step for removing a
water-repellent protective film;

wherein the liquid chemical for forming a water-repellent
30 protective film is a liquid chemical comprising a water-repellent protective film
forming agent for forming a water-repellent protective film at least on the

surfaces of the recessed portions, and the water-repellent protective film forming agent is at least one kind of compound represented by the following general formulas [2] and [3]:



5 (in the formula [2], R³ mutually independently represents one of a C₁₂-C₁₄ monovalent hydrocarbon group having no substituent and a C₆-C₁₈ monovalent hydrocarbon group the hydrogen elements of which is partially or entirely replaced with a fluorine element(s), R⁴ mutually independently represents a C₁-C₃ monovalent hydrocarbon group the hydrogen elements of
 10 which may partially or entirely be replaced with a fluorine element(s), “b” is an integer of from 1 to 3, “c” is an integer of from 0 to 2, and the total of “b” and “c” is an integer of from 1 to 3),



15 (the formula [3] represents a compound obtained by mutually independently substituting “d” hydrogen element(s) or fluorine element(s) of R⁵ which represents a C₄-C₁₈ hydrocarbon the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s) with at least one group indicated by X and selected from the group consisting of –CONHOH group and a cyclic structure containing a nitrogen element, wherein “d” is an
 20 integer of from 1 to 6).

[Claim 5] A method of cleaning a wafer, as claimed in claim 4, wherein the protic polar solvent is an alcohol.

25 [Claim 6] A method of cleaning a wafer, as claimed in claim 4 or 5, wherein the water-repellent protective film removal step is performed by at least one treatment selected from the group consisting of: irradiating the wafer surface with light; heating the wafer; exposing the wafer to ozone; irradiating the wafer surface with plasma; and subjecting the wafer surface to corona discharge,
 30 thereby removing the water-repellent protective film.