SPECIFICATION

TITLE OF THE INVENTION:

METHOD FOR PREPARING LIQUID CHEMICAL FOR FORMING WATER-REPELLENT PROTECTIVE FILM

TECHNICAL FIELD

[0001] The present invention relates to a technique for cleaning a substrate (a wafer) in semiconductor device manufacturing and the like, the objective of which is to improve the production yield of devices having a circuit pattern. The present invention particularly relates to: a liquid chemical for forming a water-repellent protective film and to a method for preparing the same, the objective of which is to improve a cleaning step which tends to induce a wafer having an uneven pattern at its surface to cause a collapse of the uneven pattern.

BACKGROUND OF THE INVENTION

[0002] Semiconductor devices for use in networks or digital household electric appliances are being further desired to be sophisticated, multifunctional, and low in power consumption. Accordingly, the trend toward micro-patterning for circuits has been developed, with which micro-sizing of particles has so advanced as to cause reduction of production yield. As a result of this, a cleaning step for the purpose of removing contaminants such as the micro-sized particles and the like has frequently been used. As a result, 30-40% of the whole of the semiconductor fabrication process is occupied with the cleaning step.

[0003] On the other hand, at the time of cleaning as conventionally performed with an ammonia-mixed cleaning agent, damages to a wafer due to its basicity has been getting serious together with the trend toward micro-patterning for circuits. Therefore, alternation with a less damaging one e.g. a dilute hydrofluoric acid-based cleaning agent has been proposed.

[0004] With this, problems about the damages to the wafer due to cleaning

have been solved; however, problems due to an aspect ratio increased with the trend toward micro-processing in the semiconductor devices have become obvious. In other words, a phenomenon where the pattern causes a collapse when a gas-liquid interface passes through the pattern is brought about after cleaning or rinsing so as to largely reduce the yield, which has become a significant problem.

[0005] The pattern collapse occurs at the time of removing cleaning liquid or rinsing liquid from the wafer. The reason thereof is said that a difference in height of residual liquid between a part having a high aspect ratio and a part having a low aspect ratio makes a difference in capillary force which acts on the pattern.

[0006] Accordingly, the pattern collapse is excepted to be solved by reducing the capillary force to decrease the difference in capillary force due to the difference in height of the residual liquid. The degree of the capillary force is the absolute value of P obtained by the equation as shown below. From this equation, it is expected that the capillary force can be reduced by decreasing γ or $\cos\theta$.

$$P = 2 \times \gamma \times \cos\theta / S$$

(γ: Surface tension, θ: Contact angle, S: Pattern width (the widths of the recessed portions))

[0007] In Patent Publication 1, there is disclosed a cleaning process in which a wafer surface provided to have an uneven pattern with a film containing silicon is surface-reformed by oxidation or the like and a water-repellent protective film is formed on the surface by using a water-soluble surfactant or a silane coupling agent thereby reducing the capillary force to prevent the pattern collapse. Additionally, in Patent Publications 2 to 6, it is disclosed that a cleaning step which tends to cause a collapse can be improved by using a water-repellent cleaning liquid for imparting water repellency at least to recessed portions of an uneven pattern of a silicon wafer.

[0008] As the above-mentioned wafer, a wafer that contains a silicon

element at its surface has generally been employed; however, a wafer that contains elements such as titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at its surface is getting employed together with the diversification of the pattern. In Patent Document 7, there is disclosed a wafer having a finely uneven pattern at its surface and containing at least one kind of element selected from the group consisting of titanium, titanium nitride, tungsten, aluminum, copper, tin, tantalum nitride, ruthenium and silicon at surfaces of recessed portions of the uneven pattern, and it is disclosed that a cleaning step which tends to cause a collapse in such a wafer can be improved by using a liquid chemical that contains a water-repellent protective film-forming agent for forming a water-repellent protective film at least on the surfaces of the recessed portions at the time of cleaning the wafer.

REFERENCES ABOUT PRIOR ART

Patent Documents

[0009] Patent Document 1: Japanese Patent No. 4403202

Patent Document 2: Japanese Patent Application Publication No. 2010-192878

Patent Document 3: Japanese Patent Application Publication No. 2010-192879

Patent Document 4: Japanese Patent Application Publication No. 2010-272852

Patent Document 5: Japanese Patent Application Publication No. 2012-033873

Patent Document 6: Japanese Patent Application Publication No. 2012-015335

Patent Document 7: Japanese Patent No. 4743340

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0010] A liquid chemical for forming a water-repellant protective film which liquid chemical is for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the

uneven pattern at its surface (the liquid chemical may hereinafter be referred to as "a liquid chemical for forming a protective film" or merely as "a liquid chemical") is required to be low in content of metal impurities which can bring about a fear of increasing a junction leak current in the device and to be clean, like a cleaning liquid for cleaning a wafer. However, of the above-mentioned liquid chemical, some are subject to degeneration by heat and some are liable to exhibit hydrolizability; hence such liquid chemicals may not be refined by distillation. The present invention is directed to a liquid chemical for forming a water-repellant protective film which liquid chemical is for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the uneven pattern at its surface (the wafer may hereinafter be referred to merely as "a wafer"), in which an object of the present invention is to provide: a liquid chemical reduced in concentration of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag (the concentration may hereinafter be referred to as "metal impurity concentration") and in amount of particles contained in the liquid chemical; and a method for preparing the same. Another object of the present invention is to provide: a liquid chemical kit for forming a water-repellant protective film, the liquid chemical kit allowing producing the liquid chemical by being mixed; and a method for preparing the liquid chemical kit.

Means for Solving the Problems

[0011] In the present invention, "a water-repellent protective film" means a film formed on a wafer surface so as to reduce the wettability of the wafer surface, i.e., a film that imparts water repellency to the surface. In the present invention, "water repellency" means to decrease a surface energy of a surface of an article thereby weakening the interaction between water or another liquid and the surface of the article (i.e., at the interface) such as a hydrogen bond, intermolecular forces and the like. The effect of reducing the interaction is particularly exhibited against water, but it is also exhibited against a mixture liquid of water and a liquid other than water or against a liquid other than water. With the reduction of the interaction, the contact

angle of the liquid to the article surface can be increased. Hereinafter, the water-repellent protective film may be referred to merely as "a protective film". Incidentally, the water-repellent protective film may be formed from an agent for forming a water-repellent protective film as will be discussed below, and may be formed to contain a reactant of which primary component is the agent for forming a water-repellent protective film.

[0012] If a treatment is conducted on the wafer by using the liquid chemical or a liquid chemical obtained from a liquid chemical kit of the present invention, the protective film has been formed on the surfaces of the recessed portions of the wafer at the time of removing or drying the cleaning liquid out of the recessed portions of the uneven pattern of the wafer, so that the capillary force of the surfaces of the recessed portions is lowered to make a pattern collapse difficult to occur. "A treatment on the wafer by using a liquid chemical" means to form a protective film at least on the surfaces of the recessed portions while retaining the liquid chemical or a liquid chemical obtained from a liquid chemical kit at least in the recessed portions of the uneven pattern of the wafer. A system of treating the wafer is not particularly limited so long as the liquid chemical can be retained at least in the recessed portions of the uneven pattern of the wafer. Examples of the system of treating the wafer are: a single treatment system represented by spin treatment where a generally horizontally held wafer is rotated and treated one by one while supplying a liquid chemical to the vicinity of the center of the rotation; and a batch system where a plurality of wafer sheets are immersed in a treatment bath to be treated. Incidentally, the form of the liquid chemical at the time of supplying the liquid chemical at least to the recessed portions of the uneven pattern of the wafer is not particularly limited as far as it is in a condition of liquid at the time of being retained in the recessed portions, and is exemplified by liquid, vapor or the like.

[0013] The liquid chemical preferably has a metal impurity concentration of not higher than 0.1 mass ppb per each element, relative to the total amount of the liquid chemical. A concentration of higher than 0.1 mass ppb brings about

a fear of increasing a junction leak current in the device so as to result in the occurrence of the reduction of the yield of the device and the reduction of the reliability, which is therefore not preferable. On the other hand, a concentration of not higher than 0.1 mass ppb is preferable because a step of cleaning the wafer surface (or the surface of the protective film) with use of a solvent or water after the protective film is formed on the wafer surface can be omitted or downscaled. Thus a lower metal impurity concentration is preferable. However, a concentration of not lower than 0.001 mass ppb per each element relative to the total amount of the liquid chemical is acceptable insofar as it falls within the above-mentioned concentration range. In the case of a liquid chemical kit, the metal impurity concentration in a liquid chemical obtained from the liquid chemical kit is preferably of not higher than 0.1 mass ppb per each element, relative to the total amount of the liquid chemical. Incidentally, the liquid chemical kit according to the present invention is provided to contain a treatment liquid (A) and a treatment liquid (B) as will be mentioned below, wherein the metal impurity concentration in the treatment liquid (A) is not higher than 0.1 mass ppb per each element relative to the total amount of the treatment liquid (A) while the metal impurity concentration in the treatment liquid (B) is not higher than 0.1 mass ppb per each element relative to the total amount of the treatment liquid (B). The reason for preparing the treatment liquids (A) and (B) to fall within the above-mentioned metal impurity concentration range is that the metal impurity concentration in the liquid chemical obtained from the liquid chemical kit becomes readily adjusted to not higher than 0.1 mass ppb per each element relative to the total amount of the liquid chemical. Measurement of the metal impurity concentration in the present invention can be performed by a measurement using an inductively coupled plasma mass spectroscope, for example.

[0014] The above-mentioned metal impurities include the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag in the form of metal particle, ion, colloid, complex, oxide and nitride, and correspond to all that exists in the

liquid chemical irrespective of whether it is dissolved or not.

[0015] Additionally, concerning a particle measurement in a liquid phase of the liquid chemical conducted by a laser light-scattering type detector, it is preferable that the number of particles of larger than 0.2 μm is not more than 100 per 1 mL of the liquid chemical. If the number of particles of larger than 0.2 μm exceeds 100 per 1 mL of the liquid chemical, there arises a fear of inducing a pattern damage due to particles so as to result in reducing the device in yield and reliability and therefore not preferable. Additionally, if the number of particles of larger than 0.2 μm is not more than 100 per 1 mL of the liquid chemical, a cleaning operation to be conducted with a solvent or water after the formation of the protective film can be omitted or downscaled and therefore preferable. Incidentally, a lower number of particles of larger than 0.2 μm is more preferable but one or more per 1 mL of the liquid chemical is acceptable. Incidentally, the liquid chemical kit according to the present invention is provided to contain a treatment liquid (A) and a treatment liquid (B) as will be mentioned below, wherein the number of particles of larger than 0.2 μm measured by a particle measurement in a liquid phase of the treatment liquid (A) conducted by a laser light-scattering type detector is preferably not more than 100 per 1 mL of the treatment liquid (A) while the number of such particles in a liquid phase of the treatment liquid (B) is preferably not more than 100 per 1 mL of the treatment liquid (B). The reason for preparing the treatment liquids (A) and (B) to fall within the above-mentioned particle number range is that the particle number in the liquid chemical obtained from the liquid chemical kit becomes readily adjusted to not more than 100per 1 mL. Additionally, the particle measurement in the liquid phase of the liquid chemical or the treatment liquid according to the present invention is conducted by using a commercially available measurement device to which a light-scattering type measuring method for particles in liquid is applied, where a particle diameter means a light-scattering equivalent diameter based on a PSL (a latex formed of polystyrene) standard particle.

[0016] By the way, "particle" as discussed above means particle of dust,

organic solid matters, inorganic solid matters and the like contained in the raw material as impurities, particle of dust, organic solid matters, inorganic solid matters and the like brought about as impurities during preparation of the liquid chemical or the treatment liquid, etc., and correspond to all that is not dissolved and finally exists in the liquid chemical or the treatment liquid as particles.

[0017] Among the liquid chemicals, some have corrosivity against metals. In this case, it is necessary for the material of a portion brought into contact with the liquid to adopt a resinous material not causing metal elution into the liquid chemical, in order to reduce metal impurities in the liquid chemical and keep the liquid chemical clear. The resinous material is low in electric conductivity and insulative; therefore, when the liquid chemical is led through a resinous pipe or when the liquid chemical is refined by filtration using a particle-eliminating resinous membrane or resinous ion exchange resin membrane having a large contacting area between a filter medium and a liquid, the charged electric potential in the liquid chemical is so increased as to raise a fear of causing an electric shock at the time of human body being contacted with the exterior or the like of the pipe or a fear of causing fire or damage (e.g. cracks and pinpole) to the pipe or facilities due to spark (spark discharge), which sometimes increases the risk of bringing about static electricity disaster. A measure of management of the liquid chemical for forming a water-repellent protective film, the liquid chemical kit for forming a water-repellent protective film and the solvent used as raw material in terms of the charged electric potential is as discussed in page 88 of "Static Electricity Safety Guideline 2007" edited by National Institute of Occupational Safety and Health, Japan. More specifically, the charged electric potential of a liquid is preferably managed to be not higher than 1 kV when the minimum ignition energy of a liquid is less than 0.1 mJ, and not higher than 5 kV when the minimum ignition energy of a liquid is not less than 0.1 mJ and less than 1 mJ, and not higher than 10 kV when the minimum ignition energy of a liquid exceeds 1 mJ. Furthermore, a charged electric potential which is held smaller makes the

obtained liquid chemical or liquid chemical kit more difficult to ignite, which is therefore preferable in view of safety. In the present invention, incidentally, the measurement of the charged electric potential can be conducted by a static meter, for example.

[0018] The present invention is a method for preparing a liquid chemical for forming a water-repellant protective film, the liquid chemical having a solvent and an agent for forming a water-repellant protective film, the liquid chemical being for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the uneven pattern at its surface, the method being characterized by comprising:

a first refinement step for eliminating the elements (metal impurities) Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag in a solvent by distilling the solvent or by using a particle-eliminating membrane and an ion exchange resin membrane;

a mixing step for mixing the solvent of after the first refinement step and an agent for forming a water-repellant protective film; and

a second refinement step for eliminating particles in a liquid chemical of after the mixing step by using a particle-eliminating membrane. Hereinafter, the above-mentioned preparation method will be referred to as "a first preparation method of the present invention". A flowchart of the first preparation method is shown in Fig. 1.

[0019] The solvent to be mixed with the agent for forming a water-repellent protective film in the mixing step of the first preparation method of the present invention may be formed of the solvent of after the first refinement step only. Incidentally, the solvent to be mixed with the agent for forming a water-repellent protective film in the mixing step may be a mixed solvent formed of two or more kinds of solvents and all of them may be the solvent refined by the first refinement step.

[0020] Moreover, the solvent to be mixed with the agent for forming a water-repellent protective film in the mixing step of the first preparation method may be two or more kind. Of these, a solvent component of less than

35 mass % relative to the total amount of the mixed solvent may not undergo the first refinement step. More specifically, among the solvents to be mixed with the agent for forming a water-repellent protective film in the mixing step, a solvent component of not less than 35 mass % relative to the total amount of the solvents undergoes the first refinement step but a solvent component of less than 35 mass % relative to the total amount of the solvents may not undergo the first refinement step. If a solvent component of less than 35 mass % is two or more kinds and the total of these amounts to not less than 35 mass %, any of the solvent components of less than 35 mass % is required to undergo the first refinement step thereby adjusting the total amount of solvent components that have undergone the first refinement step to 65 mass % or more relative to the total amount of solvents to be mixed with the agent for forming a water-repellent protective film.

[0021] Additionally, it is preferable that the first preparation method of the present invention further involves a discharge step where at least one selected from the solvent of after the first refinement step and the liquid chemical for forming a water-repellent protective film which liquid chemical is obtained after the second refinement step is brought into contact with an electrically conductive material. By virtue of the discharge step, the charged electric potential of a solvent or liquid chemical which is under a charged condition can be reduced to the range as discussed above in the measure of management of the charged electric potential. With this, it becomes possible to safely prepare the liquid chemical while obtaining a liquid chemical which is under a safer condition, i.e., a condition lower in risk of ignition.

[0022] Moreover, the present invention is a method for preparing a liquid chemical for forming a water-repellant protective film, the liquid chemical having a solvent and an agent for forming a water-repellant protective film, the liquid chemical being for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the uneven pattern at its surface, the method being characterized by comprising:

a mixing step for mixing a solvent and an agent for forming a

water-repellant protective film; and

a third refinement step for eliminating the elements (metal impurities) Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag and particles in a liquid chemical of after the mixing step, by using a particle-eliminating membrane and an ion exchange resin membrane. Hereinafter, the above-mentioned preparation method will be referred to as "a second preparation method of the present invention". A flowchart of the second preparation method is shown in Fig. 2.

[0023] Additionally, it is preferable that the second preparation method of the present invention further involves a discharge step where the liquid chemical for forming a water-repellent protective film obtained after the third refinement step is brought into contact with an electrically conductive material. By virtue of the discharge step, the charged electric potential of a liquid chemical which is under a charged condition can be reduced to the range as discussed above in the measure of management of the charged electric potential. With this, it becomes possible to safely prepare the liquid chemical while obtaining a liquid chemical which is under a safer condition, i.e., a condition lower in risk of ignition.

[0024] In the first and second preparation methods, it is preferable that the agent for forming a water-repellant protective film comprises at least one selected from the group consisting of silylation reagents represented by the following general formula [1] and an acid or base. Hereinafter, the method for preparing a liquid chemical for forming a water-repellant protective film, to which the above-mentioned agent for forming a water-repellant protective film is used may be referred to as "a first embodiment".

$$(R^1)_aSi(H)_bX^1_{4-a-b} \qquad [1]$$

[In the formula [1], R^1 mutually independently represents a monovalent organic group having a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^1 mutually independently represents at least one selected from the group consisting of a monovalent functional group of which element to

be bonded to a silicon element is nitrogen, a monovalent functional group of which element to be bonded to a silicon element is oxygen, a halogen group, a nitrile group and –CO–NH–$Si(CH_3)_3$ group; "a" is an integer of from 1 to 3; "b" is an integer of from 0 to 2; and the total of "a" and "b" is 1 to 3.]

[0025] Hereinafter, a first embodiment will be discussed.

[0026] The acid preferably comprises at least one selected from the group consisting of hydrogen chloride, sulfuric acid, perchloric acid, phosphoric acid, sulfonic acid represented by the following general formula [2] and anhydride thereof, carboxylic acid represented by the following general formula [3] and anhydride thereof, alkyl borate ester, aryl borate ester, boron tris(trifluoroacetate), trialkoxyboroxin, boron trifluoride and a silane compound represented by the following general formula [4].

$R^2S(O)_2OH$ [2]

[In the formula [2], R^2 represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s).]

R^3COOH [3]

[In the formula [3], R^3 represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s).]

$(R^4)_cSi(H)_dX^2_{4-c-d}$ [4]

[In the formula [4], R^4 mutually independently represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^2 mutually independently represents at least one selected from the group consisting of chloro group, –OCO–R^5 (where R^5 is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)) and –$OS(O)_2$–R^6 (where R^6 is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)); "c" is an integer of from 1 to 3; "d" is an integer of from 0 to 2; and the total of "c" and "d" is 1 to 3.]

[0027] The base preferably comprises at least one selected from the group consisting of ammonia, N,N,N',N'-tetramethylethylenediamine, triethylenediamine, dimethylaniline, alkylamine, dialkylamine, trialkylamine, pyridine, piperazine, N-alkylmorpholine and a silane compound represented by the following general formula [5].

$(R^7)_eSi(H)_fX^3_{4-e-f}$ [5]

[In the formula [5], R^7 mutually independently represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^3 mutually independently represents a monovalent functional group of which element to be bonded to a silicon element is nitrogen, the monovalent functional group possibly containing a fluorine element or a silicon element; "e" is an integer of from 1 to 3; "f" is an integer of from 0 to 2; and the total of "e" and "f" is 1 to 3.]

[0028] The solvent preferably comprises at least one selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen-containing solvents, sulfoxide-based solvents, lactone-based solvents, carbonate-based solvents, polyalcohol derivatives having no OH group, and nitrogen element-containing solvents having no N–H group.

[0029] Additionally, in the first and second preparation methods, it is preferable that the agent for forming a water-repellant protective film comprises at least one kind selected from the group consisting of compounds represented by the following general formulas [6] to [13] and their salts. Hereinafter, a method for preparing a liquid chemical for forming a water-repellent protective film where the above-mentioned agent for forming a water-repellant protective film is used will sometimes be referred to as "a second embodiment".

R^8–$P(=O)(OH)_g(R^9)_{2-g}$ [6]

[In the formula [6], R^8 represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); R^9 mutually independently represents a monovalent organic group having a C_1-C_3 hydrocarbon group the hydrogen

elements of which may partially or entirely be replaced with a fluorine element(s); and "g" is an integer of from 0 to 2.]

R^{10}–C(=O)–X^4 [7]

[In the formula [7], R^{10} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; X^4 represents a group selected from the group consisting of fluoro group, chloro group, bromo group and iodo group.]

$R^{11}R^{12}R^{13}N$ [8]

[In the formula [8], R^{11} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; R^{12} represents a hydrogen element, a monovalent organic group having a C_1-C_{18} hydrocarbon group, or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; R^{13} represents a hydrogen element, a monovalent organic group having a C_1-C_{18} hydrocarbon group, or a monovalent organic group having a C_1-C_8 fluoroalkyl chain.]

R^{14}–C(=O)–X^5–X^6 [9]

[In the formula [9], R^{14} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; X^5 represents an oxygen element or sulfur element; X^6 represents a group selected from the group consisting of a hydrogen element, alkyl group, aromatic group, pyridyl group, quinolyl group, succinimide group, maleimide group, benzoxazole group, benzothiazole group and benzotriazole group; and a hydrogen element(s) of these groups may be substituted with an organic group.]

$R^{15}(X^7)_h$ [10]

[The formula [10] represents a compound where "h" hydrogen element(s) or fluorine element(s) of R^{15} representing a C_1-C_{18} hydrocarbon the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s) is mutually independently substituted with a group represented by X^7, the group X^7 being at least one selected from the group consisting of an isocyanate group, mercapto group, aldehyde group, –CONHOH

group and a cyclic structure containing a nitrogen element, wherein "h" is an integer of from 1 to 6.]

R^{16}–X^8 [11]

[In the formula [11], X^8 represents a cyclic structure containing a sulfur element; R^{16} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain.]

R^{17}–C(=O)–X^9–C(=O)–R^{18} [12]

[In the formula [12], R^{17} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; R^{18} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; and X^9 represents an oxygen element or a sulfur element.]

$(R^{24}–O–(R^{25}O)_t–)_uP(=O)(OH)_{3-u}$ [13]

[In the formula [13], R^{24} mutually independently represents a C_4-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); R^{25} mutually independently represents a C_2-C_6 divalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); "t" mutually independently represents an integer of from 0 to 10; and "u" is 1 or 2.]

[0030] Hereinafter, the second embodiment will be discussed.

[0031] The solvent preferably comprises at least one selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen-containing solvents, sulfoxide-based solvents, lactone-based solvents, carbonate-based solvents, alcohols, polyalcohol derivatives, nitrogen element-containing solvents and water.

[0032] Furthermore, the present invention is a liquid chemical for forming a water-repellant protective film, prepared through the steps of the method for preparing a liquid chemical for forming a water-repellant protective film, as discussed in any of the above.

[0033] Additionally, the present invention is a method for preparing a liquid

chemical kit for forming a water-repellant protective film, the liquid chemical kit being for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the uneven pattern at its surface, the liquid chemical kit having a treatment liquid (A) that contains a nonaqueous organic solvent and a silylation reagent and a treatment liquid (B) that contains a nonaqueous organic solvent and an acid or base, the method being characterized by comprising:

a fourth refinement step for eliminating the elements (metal impurities) Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag in a nonaqueous organic solvent by distilling the nonaqueous organic solvent or by using a particle-eliminating membrane and an ion exchange resin membrane;

a step of preparing a treatment liquid (A) by mixing the nonaqueous organic solvent of after the fourth refinement step and a silylation reagent;

a step of preparing a treatment liquid (B) by mixing the nonaqueous organic solvent of after the fourth refinement step and an acid or base; and

a fifth refinement step for eliminating particles in the treatment liquid (A) of after the step of preparing the treatment liquid (A) and /or the treatment liquid (B) of after the step of preparing the treatment liquid (B), by using a particle-eliminating membrane. Hereinafter, the above-mentioned preparation method will be referred to as "a third preparation method of the present invention". A flowchart of the third preparation method is shown in Fig. 3.

[0034] Hereinafter, the third preparation method will be discussed.

[0035] The nonaqueous organic solvent to be mixed with the silylation reagent and the acid or base in the step of preparing a treatment liquid (A) and in the step of preparing a treatment liquid (B) of the third preparation method of the present invention may be formed of the nonaqueous organic solvent of after the fourth refinement step only. Incidentally, the nonaqueous organic solvent to be mixed with the silylation agent and the acid or base in each of the step of preparing a treatment liquid (A) and the step of preparing a treatment liquid (B) may be a mixed solvent formed of two or more kinds of nonaqueous

organic solvents and all of them may be the nonaqueous organic solvent refined by the fourth refinement step.

[0036] Moreover, the nonaqueous organic solvent to be mixed with the silylation reagent and the acid or base in the step of preparing a treatment liquid (A) and in the step of preparing a treatment liquid (B) of the third preparation method may be two or more kind. Of these, a nonaqueous organic solvent component of less than 35 mass % relative to the total amount of the mixed nonaqueous organic solvent may not undergo the fourth refinement step. More specifically, among the nonaqueous organic solvents to be mixed with silylation reagent and the acid or base in the step of preparing a treatment liquid (A) and in the step of preparing a treatment liquid (B), a nonaqueous organic solvent component of not less than 35 mass % relative to the total amount of the nonaqueous organic solvents undergoes the fourth refinement step but a nonaqueous organic solvent component of less than 35 mass % may not undergo the fourth refinement step. If a nonaqueous organic solvent component of less than 35 mass % is two or more kinds and the total of these amounts to not less than 35 mass %, any of the nonaqueous organic solvent components of less than 35 mass % is required to undergo the fourth refinement step thereby adjusting the total amount of solvent components that have undergone the fourth refinement step to 65 mass % or more relative to the total amount of nonaqueous organic solvents to be mixed with the silylation reagent and the acid or base.

[0037] Additionally, it is preferable that a discharge step where at least one selected from the nonaqueous organic solvent of after the fourth refinement step and a treatment liquid obtained after the fifth refinement step is brought into contact with an electrically conductive material is involved. By virtue of the discharge step, the charged electric potential of the nonaqueous organic solvent, the treatment liquid (A) or the treatment liquid (B) which is under a charged condition can be reduced to the range as discussed above in the measure of management of the charged electric potential. With this, it becomes possible to safely prepare the treatment liquid (A) and the treatment

liquid (B) while obtaining a treatment liquid (A) and a treatment liquid (B) which are under a safer condition, i.e., a condition lower in risk of ignition.

[0038] Additionally, the present invention is a method for preparing a liquid chemical kit for forming a water-repellant protective film, the liquid chemical kit being for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the uneven pattern at its surface, the liquid chemical kit having a treatment liquid (A) that contains a nonaqueous organic solvent and a silylation reagent and a treatment liquid (B) that contains a nonaqueous organic solvent and an acid or base, the method being characterized by comprising:

a step of preparing a treatment liquid (A) by mixing a nonaqueous organic solvent and a silylation reagent;

a step of preparing a treatment liquid (B) by mixing a nonaqueous organic solvent and an acid or base; and

a sixth refinement step for eliminating the elements (metal impurities) Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag and particles in the treatment liquid (A) of after the step of preparing the treatment liquid (A) and /or the treatment liquid (B) of after the step of preparing the treatment liquid (B), by using a particle-eliminating membrane and an ion exchange resin membrane. Hereinafter, the above-mentioned preparation method will be referred to as "a fourth preparation method of the present invention". A flowchart of the fourth preparation method is shown in Fig. 4.

[0039] Hereinafter, the fourth preparation method will be discussed.

[0040] In the fourth preparation method, it is preferable that a discharge step where the treatment liquid (A) and/or the treatment liquid (B) obtained after the sixth refinement step is brought into contact with an electrically conductive material. By virtue of the discharge step, the charged electric potential of the treatment liquid (A) or the treatment liquid (B) which is under a charged condition can be reduced to the range as discussed above in the measure of management of the charged electric potential. With this, it becomes possible to safely prepare the treatment liquid (A) and the treatment

liquid (B) while obtaining a treatment liquid (A) and a treatment liquid (B) which are under a safer condition, i.e., a condition lower in risk of ignition.

[0041] In the third and fourth preparation methods, the nonaqueous organic solvent preferably comprises at least one selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen-containing solvents, sulfoxide-based solvents, lactone-based solvents, carbonate-based solvents, polyalcohol derivatives having no OH group, and nitrogen element-containing solvents having no N–H group.

[0042] In the third and fourth preparation methods, the silylation reagent preferably comprises at least one selected from the group consisting of silicon compounds represented by the following general formula [1].

$$(R^1)_aSi(H)_bX^1_{4-a-b} \qquad [1]$$

[In the formula [1], R^1 mutually independently represents a monovalent organic group having a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^1 mutually independently represents at least one selected from the group consisting of a monovalent functional group of which element to be bonded to a silicon element is nitrogen, a monovalent functional group of which element to be bonded to a silicon element is oxygen, a halogen group, a nitrile group and –CO–NH–$Si(CH_3)_3$ group; "a" is an integer of from 1 to 3; "b" is an integer of from 0 to 2; and the total of "a" and "b" is 1 to 3.]

[0043] Moreover, the silylation reagent preferably comprises a silicon compound represented by the following general formula [14].

$$R^{19}_iSiX^{10}_{4-i} \qquad [14]$$

[In the formula [14], R^{19} mutually independently represents at least one group selected from a hydrogen group and a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), wherein the total number of carbons contained in all of the hydrocarbon groups bonded to a silicon element is not smaller than 6; X^{10} mutually independently represents at least one group selected from a monovalent functional group of which element to be bonded to

a silicon element is nitrogen, a monovalent functional group of which element to be bonded to a silicon element is oxygen, a halogen group, a nitrile group and –CO–NH–$Si(CH_3)_3$ group; "i" is an integer of from 1 to 3.]

[0044] The acid preferably comprises at least one selected from the group consisting of hydrogen chloride, sulfuric acid, perchloric acid, phosphoric acid, sulfonic acid represented by the following general formula [2] and anhydride thereof, carboxylic acid represented by the following general formula [3] and anhydride thereof, alkyl borate ester, aryl borate ester, boron tris(trifluoroacetate), trialkoxyboroxin, boron trifluoride and a silane compound represented by the following general formula [4].

$R^2S(O)_2OH$ [2]

[In the formula [2], R^2 represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s).]

R^3COOH [3]

[In the formula [3], R^3 represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s).]

$(R^4)_cSi(H)_dX^2_{4-c-d}$ [4]

[In the formula [4], R^4 mutually independently represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^2 mutually independently represents at least one selected from the group consisting of chloro group, –OCO–R^5 (where R^5 is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)) and –$OS(O)_2$–R^6 (where R^6 is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)); "c" is an integer of from 1 to 3; "d" is an integer of from 0 to 2; and the total of "c" and "d" is 1 to 3.]

[0045] The base preferably comprises at least one selected from the group consisting of ammonia, N,N,N',N'-tetramethylethylenediamine,

triethylenediamine, dimethylaniline, alkylamine, dialkylamine, trialkylamine, pyridine, piperazine, N-alkylmorpholine and a silane compound represented by the following general formula [5].

$$(R^7)_eSi(H)_fX^3_{4-e-f} \qquad [5]$$

[In the formula [5], R^7 mutually independently represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^3 mutually independently represents a monovalent functional group of which element to be bonded to a silicon element is nitrogen, the monovalent functional group possibly containing a fluorine element or a silicon element; "e" is an integer of from 1 to 3; "f" is an integer of from 0 to 2; and the total of "e" and "f" is 1 to 3.]

[0046] Furthermore, the present invention is a liquid chemical kit for forming a water-repellant protective film, prepared through the steps of the method for preparing a liquid chemical kit for forming a water-repellant protective film, as discussed in any of the above.

EFFECTS OF THE INVENTION

[0047] By the method for preparing a liquid chemical for forming a water-repellant protective film according to the present invention, it becomes possible to obtain a liquid chemical for forming a water-repellant protective film which liquid chemical is for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the uneven pattern at its surface, in such a condition that the concentration of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag and the amount of particles contained in the liquid chemical are reduced. Moreover, by the method for preparing a liquid chemical kit for forming a water-repellant protective film according to the present invention, it becomes possible to obtain a liquid chemical kit for forming a water-repellant protective film which liquid chemical kit can provide the above-mentioned liquid chemical by mixture, in such a condition that the concentration of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag and the amount of particles contained in the liquid chemical kit are reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

[0048] [Fig. 1] A flowchart of a first preparation method.

[Fig. 2] A flowchart of a second preparation method.

[Fig. 3] A flowchart of a third preparation method.

[Fig. 4] A flowchart of a fourth preparation method.

MODE(S) FOR CARRYING OUT THE INVENTION

[0049] In a first refinement step of a first preparation method or a forth refinement step of a third preparation method according to the present invention, distillation of a solvent or nonaqueous organic solvent is sometimes carried out in order to eliminate metal impurities contained in the solvent or nonaqueous organic solvent. For example, it is possible to cite a distillation of a solvent or nonaqueous organic solvent not having hydrolizability and not subject to degeneration by heat, under reduced pressure or atmospheric pressure. If a liquid chemical for forming a water-repellent protective film is prepared by using a solvent obtained by distilling a solvent or nonaqueous organic solvent having hydrolizability or a solvent or nonaqueous organic solvent subject to degeneration by heat, the liquid chemical sometimes cannot impart sufficient water repellency to a wafer surface, which is not favorable for the formation of a protective film.

[0050] In the first refinement step of the first preparation method or the forth refinement step of the third preparation method according to the present invention, elimination of metal impurities by using a particle-eliminating membrane and an ion exchange resin membrane is sometimes carried out in order to eliminate metal impurities contained in the solvent or nonaqueous organic solvent. For example, elimination of metal impurities is performed by: permeating the solvent or nonaqueous organic solvent through a particle-eliminating membrane formed of a membrane material such as a high-density polyethylene membrane, a high-density polypropylene membrane, a tetrafluoroethylene membrane, a membrane of copolymer of tetrafluoroethylene and perfluoroalkylvinylether and a membrane of nylon-6,6 and having a particle-eliminating diameter of 0.005-10 μm or through an ion

exchange resin membrane such as a strongly acidic cation exchange resin obtained by chemically modifying a high-density polyethylene membrane by a cation exchange group e.g. a sulfo group; or permeating the solvent or nonaqueous organic solvent through an ion exchange resin membrane with particle-eliminating membrane in which an ion exchange resin membrane and a particle-eliminating membrane are integrally formed by chemically introducing a strongly acidic cation exchange resin onto surfaces of pores of a porous high-density polyethylene media. Concrete examples of the particle-eliminating membrane include Optimizer produced by Nihon Entegris K.K., NanoSHIELD produced by Sumitomo 3M Limited, Fluoroline produced by Nihon Entegris K.K., Ultipleat P-Nylon produced by Pall Corporation, etc. Concrete examples of the ion exchange resin membrane include IonKleen SL produced by Pall Corporation, IonKleen AQ produced by Pall Corporation, etc. Concrete examples of the ion exchange resin membrane with particle-eliminating membrane include Protego Plus produced by Nihon Entegris K.K., etc. A system of permeation may be the so-called one-pass system where the solvent or nonaqueous organic solvent is permeated through the membrane one time, or may be a system of circulating the solvent or nonaqueous organic solvent to be permeated through the membrane two or more times. Additionally, each of the above-mentioned membranes may be of only one stage type or of a multistage type.

[0051] In a third refinement step of a second preparation method or a sixth refinement step of a fourth preparation method according to the present invention, a method for eliminating metal impurities and particles contained in a liquid chemical or in a treatment liquid is exemplified by permeation of the liquid chemical or the treatment liquid through the particle-eliminating membrane and the ion exchange resin membrane as discussed above. For permeation, a system of circulating the solvent or nonaqueous organic solvent to be permeated through the membrane two or more times is preferable. Additionally, each of the above-mentioned membranes may be of only one stage type or of a multistage type. In a second refinement step of the first

preparation method or a fifth refinement step of the third preparation method according to the present invention, it is possible to use the particle-eliminating membrane alone or to use the particle-eliminating membrane and the ion exchange resin membrane.

[0052] It is preferable that the particle-eliminating membrane and the ion exchange resin membrane used in the present invention have a larger surface area. Since metal impurities and particles not dissolved in the liquid chemical are adsorbed and trapped on the particle-eliminating membrane, a particle-eliminating membrane having a larger surface area tends to more lower the load applied on the membrane at the time of refinement. Moreover, since metal impurities dissolved in the liquid chemical are adsorbed and trapped on the ion exchange resin membrane by being brought into contact with ion exchange groups that exist in the ion exchange resin membrane, the metal impurities becomes more readily adsorbed if a time for intercepting the liquid to be permeated in the membrane becomes longer. Furthermore, an ion exchange resin membrane having a larger surface area can intercept the liquid in the membrane for a longer time and therefore tends to have a better effect on the elimination of metal impurities. In the first preparation method of the present invention, it is preferable that the surface area of the particle-eliminating membrane and the ion exchange resin membrane used in the second refinement step is larger than the surface area of the particle-eliminating membrane and the ion exchange resin membrane used in the first refinement step because the metal impurity concentration in the obtained liquid chemical can be readily adjusted to be smaller. Likewise, it is preferable in the third preparation method that the surface area of the particle-eliminating membrane and the ion exchange resin membrane used in the fifth refinement step is larger than the surface area of the particle-eliminating membrane and the ion exchange resin membrane used in the fourth refinement step.

[0053] In the first refinement step of the first preparation method, metal impurities are previously removed from a neutral solvent. In this refinement

step, the target for refinement is a neutral solvent only; therefore, the degree of dissociation of metal impurities is so high as to be able to reduce the metal impurity concentration in the solvent sufficiently only by one-pass filtration. Additionally, the solvent is formed containing a neutral solvent only and therefore the metal impurity concentration in the solvent may sufficiently be reduced by distillation. In a subsequent refinement step (the second refinement step), metal impurities have previously been removed from the solvent because of having already undergone the first refinement step, so that the content of metal impurities and particles in the liquid chemical may sufficiently be reduced only by one-pass filtration. On the contrary, in the third refinement step of the second preparation method, if the obtained liquid chemical is acidic or basic, the degree of dissociation of metal impurities is so low. Since the metal impurities and particles are eliminated from a liquid chemical of after the mixing step, the metal impurity concentration in the liquid chemical may not be sufficiently reduced by one-pass filtration. In this case, it is necessary to carry out refinement by a system of conducting one-pass filtration at multistage to permeate the liquid chemical through the membrane two or more times or by a system of circulating the liquid chemical to permeate it through the membrane two or more times. In order to shorten the refinement time, therefore, it is required to increase the membrane area of the particle-eliminating membrane and the ion exchange resin membrane to increase the permeation amount of the liquid chemical. In view of facilities and efficiency thus required, the first preparation method is preferable to the second preparation method.

[0054] In the fourth refinement step of the third preparation method, metal impurities are previously removed from a neutral nonaqueous organic solvent. In this refinement step, the target for refinement is a neutral nonaqueous organic solvent only; therefore, the degree of dissociation of metal impurities is so high as to be able to reduce the metal impurity concentration in the nonaqueous organic solvent sufficiently only by one-pass filtration. Additionally, the nonaqueous organic solvent is formed containing a neutral

nonaqueous organic solvent only and therefore the metal impurity concentration in the nonaqueous organic solvent may sufficiently be reduced by distillation. In a subsequent refinement step (the fifth refinement step), metal impurities have previously been removed from the nonaqueous organic solvent because of having already undergone the fourth refinement step, so that refinement is efficiently performed and the content of metal impurities and particles in the treatment liquid may sufficiently be reduced only by one-pass filtration. On the contrary, in the sixth refinement step of the fourth preparation method, if the obtained treatment liquid is acidic or basic, the degree of dissociation of metal impurities is so low. Since the metal impurities and particles are eliminated from a treatment liquid of after the step of preparing the treatment liquid, the metal impurity concentration in the treatment liquid may not be sufficiently reduced by one-pass filtration. In this case, it is necessary to carry out refinement by a system of conducting one-pass filtration at multistage to permeate the treatment liquid through the membrane two or more times or by a system of circulating the treatment liquid to permeate it through the membrane two or more times. In order to shorten the refinement time, therefore, it is required to increase the membrane area of the particle-eliminating membrane and the ion exchange resin membrane to increase the permeation amount of the treatment liquid. In view of facilities and efficiency thus required, the third preparation method is preferable to the fourth preparation method.

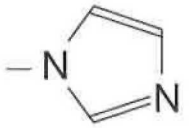
[0055] A liquid chemical for forming a water-repellent protective film, obtained according to a first embodiment of the present invention can form a water-repellent protective film on surfaces of recessed portions of a wafer having the uneven pattern at its surface and containing silicon element at least at the surfaces of the recessed portions (hereinafter, such a wafer may be referred to as "a silicon element-containing wafer"). Examples of the above-mentioned wafer include: a wafer the surface of which is formed with a film containing a silicon element such as silicon, silicon oxide and silicon nitride; and a wafer formed with an uneven pattern and contains a silicon

element such as silicon, silicon oxide and silicon nitride at least at a part of the surface of the uneven pattern. Additionally, the liquid chemical can form a protective film also against a wafer consisting of two or more components including at least a silicon element, on the surface of the component including a silicon element. Examples of the above-mentioned wafer that consists of two or more components include: a wafer the surface of which is formed of a component containing a silicon element such as silicon, silicon oxide and silicon nitride; and a wafer formed with an uneven pattern and wherein at least a part of the uneven pattern is formed of a component containing a silicon element such as silicon, silicon oxide and silicon nitride. Incidentally, where the protective film can be formed by the liquid chemical is on the unevenly patterned surface that corresponds to a part containing a silicon element.

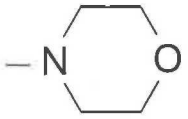
[0056] The formation of the protective film on the surfaces of the recessed portions of the silicon element-containing wafer is achieved such that a reactive moiety of a silylation reagent contained in the liquid chemical prepared according to the first embodiment causes reaction with a silanol group that serves as a reaction site of the silicon element-containing wafer, i.e., such that the silylation reagent is chemically bonded to a silicon element of the silicon element-containing wafer through a siloxane bond. The reaction moiety is a group represented by X^1 in general formula [1].

[0057] The monovalent functional group of which element to be bonded to silicon element is nitrogen, which is one example of X^1 of the general formula [1], may include not only hydrogen element, carbon element, nitrogen element and oxygen element but also silicon element, sulfur element and halogen element and the like. Examples of the functional group are an isocyanate group, amino group, dialkylamino group, isothiocyanate group, azide group, acetamide group, $-N(CH_3)C(O)CH_3$, $-N(CH_3)C(O)CF_3$, $-N=C(CH_3)OSi(CH_3)_3$, $-N=C(CF_3)OSi(CH_3)_3$, $-NHC(O)-OSi(CH_3)_3$, $-NHC(O)-NH-Si(CH_3)_3$, imidazole ring (the following formula [15]), oxazolidinone ring (the following formula [16]), morpholine ring (the following formula [17]), $-NH-C(O)-Si(CH_3)_3$, $-N(H)_{2-j}(Si(H)_kR^{20}{}_{3-k})_j$ (where R^{20} is a C_1-C_{18} monovalent

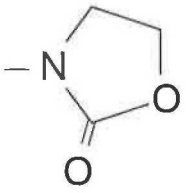
hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), "j" is an integer of 1 or 2, and "k" is an integer of from 0 to 2) and the like.



[15]



[16]



[17]

[0058] The monovalent functional group of which element to be bonded to silicon element is oxygen, which is one example of X^1 of the general formula [1], may include not only hydrogen element, carbon element, nitrogen element and oxygen element but also silicon element, sulfur element and halogen element and the like. Examples of the organic group are an alkoxy group, $-OC(CH_3)=CHCOCH_3$, $-OC(CH_3)=N-Si(CH_3)_3$, $-OC(CF_3)=N-Si(CH_3)_3$, $-O-CO-R^{21}$ (where R^{21} is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)) and an alkyl sulfonate group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s) and the like.

[0059] Additionally, a halogen group, which is one example of X^1 of the general formula [1], is exemplified by a chloro group, bromo group, iodo group and the like.

[0060] In addition, R^1 of the general formula [1] serves as a hydrophobic moiety which decreases a surface energy of an article to reduce the interaction caused between water or another liquid and the article surface (i.e., at the interface), such as hydrogen bond, intermolecular forces and the like. The effect of reducing the interaction is particularly exhibited with water, but the effect of reducing the interaction is exhibited also with a mixture liquid of water and a liquid other than water or with a liquid other than water. With this, the contact angle of the liquid to the article surface can be increased.

[0061] Examples of the silylation reagent represented by the general

formula [1] are: alkylmethoxysilanes such as $CH_3Si(OCH_3)_3$, $C_2H_5Si(OCH_3)_3$, $C_3H_7Si(OCH_3)_3$, $C_4H_9Si(OCH_3)_3$, $C_5H_{11}Si(OCH_3)_3$, $C_6H_{13}Si(OCH_3)_3$, $C_7H_{15}Si(OCH_3)_3$, $C_8H_{17}Si(OCH_3)_3$, $C_9H_{19}Si(OCH_3)_3$, $C_{10}H_{21}Si(OCH_3)_3$, $C_{11}H_{23}Si(OCH_3)_3$, $C_{12}H_{25}Si(OCH_3)_3$, $C_{13}H_{27}Si(OCH_3)_3$, $C_{14}H_{29}Si(OCH_3)_3$, $C_{15}H_{31}Si(OCH_3)_3$, $C_{16}H_{33}Si(OCH_3)_3$, $C_{17}H_{35}Si(OCH_3)_3$, $C_{18}H_{37}Si(OCH_3)_3$, $(CH_3)_2Si(OCH_3)_2$, $C_2H_5Si(CH_3)(OCH_3)_2$, $(C_2H_5)_2Si(OCH_3)_2$, $C_3H_7Si(CH_3)(OCH_3)_2$, $(C_3H_7)_2Si(OCH_3)_2$, $C_4H_9Si(CH_3)(OCH_3)_2$, $(C_4H_9)_2Si(OCH_3)_2$, $C_5H_{11}Si(CH_3)(OCH_3)_2$, $C_6H_{13}Si(CH_3)(OCH_3)_2$, $C_7H_{15}Si(CH_3)(OCH_3)_2$, $C_8H_{17}Si(CH_3)(OCH_3)_2$, $C_9H_{19}Si(CH_3)(OCH_3)_2$, $C_{10}H_{21}Si(CH_3)(OCH_3)_2$, $C_{11}H_{23}Si(CH_3)(OCH_3)_2$, $C_{12}H_{25}Si(CH_3)(OCH_3)_2$, $C_{13}H_{27}Si(CH_3)(OCH_3)_2$, $C_{14}H_{29}Si(CH_3)(OCH_3)_2$, $C_{15}H_{31}Si(CH_3)(OCH_3)_2$, $C_{16}H_{33}Si(CH_3)(OCH_3)_2$, $C_{17}H_{35}Si(CH_3)(OCH_3)_2$, $C_{18}H_{37}Si(CH_3)(OCH_3)_2$, $(CH_3)_3SiOCH_3$, $C_2H_5Si(CH_3)_2OCH_3$, $(C_2H_5)_2Si(CH_3)OCH_3$, $(C_2H_5)_3SiOCH_3$, $C_3H_7Si(CH_3)_2OCH_3$, $(C_3H_7)_2Si(CH_3)OCH_3$, $(C_3H_7)_3SiOCH_3$, $C_4H_9Si(CH_3)_2OCH_3$, $(C_4H_9)_3SiOCH_3$, $C_5H_{11}Si(CH_3)_2OCH_3$, $C_6H_{13}Si(CH_3)_2OCH_3$, $C_7H_{15}Si(CH_3)_2OCH_3$, $C_8H_{17}Si(CH_3)_2OCH_3$, $C_9H_{19}Si(CH_3)_2OCH_3$, $C_{10}H_{21}Si(CH_3)_2OCH_3$, $C_{11}H_{23}Si(CH_3)_2OCH_3$, $C_{12}H_{25}Si(CH_3)_2OCH_3$, $C_{13}H_{27}Si(CH_3)_2OCH_3$, $C_{14}H_{29}Si(CH_3)_2OCH_3$, $C_{15}H_{31}Si(CH_3)_2OCH_3$, $C_{16}H_{33}Si(CH_3)_2OCH_3$, $C_{17}H_{35}Si(CH_3)_2OCH_3$, $C_{18}H_{37}Si(CH_3)_2OCH_3$, $(CH_3)_2Si(H)OCH_3$, $CH_3Si(H)_2OCH_3$, $(C_2H_5)_2Si(H)OCH_3$, $C_2H_5Si(H)_2OCH_3$, $C_2H_5Si(CH_3)(H)OCH_3$, $(C_3H_7)_2Si(H)OCH_3$ and the like; fluoroalkylmethoxysilanes such as $CF_3CH_2CH_2Si(OCH_3)_3$, $C_2F_5CH_2CH_2Si(OCH_3)_3$, $C_3F_7CH_2CH_2Si(OCH_3)_3$, $C_4F_9CH_2CH_2Si(OCH_3)_3$, $C_5F_{11}CH_2CH_2Si(OCH_3)_3$, $C_6F_{13}CH_2CH_2Si(OCH_3)_3$, $C_7F_{15}CH_2CH_2Si(OCH_3)_3$, $C_8F_{17}CH_2CH_2Si(OCH_3)_3$, $CF_3CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_2F_5CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_3F_7CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_4F_9CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_5F_{11}CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_6F_{13}CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_7F_{15}CH_2CH_2Si(CH_3)(OCH_3)_2$, $C_8F_{17}CH_2CH_2Si(CH_3)(OCH_3)_2$, $CF_3CH_2CH_2Si(CH_3)_2OCH_3$, $C_2F_5CH_2CH_2Si(CH_3)_2OCH_3$, $C_3F_7CH_2CH_2Si(CH_3)_2OCH_3$, $C_4F_9CH_2CH_2Si(CH_3)_2OCH_3$, $C_5F_{11}CH_2CH_2Si(CH_3)_2OCH_3$,

$C_6F_{13}CH_2CH_2Si(CH_3)_2OCH_3$, $C_7F_{15}CH_2CH_2Si(CH_3)_2OCH_3$, $C_8F_{17}CH_2CH_2Si(CH_3)_2OCH_3$, $CF_3CH_2CH_2Si(CH_3)(H)OCH_3$ and the like; alkoxysilane compounds obtained by substituting a methyl group moiety of methoxy group of the above-mentioned alkylmethoxysilanes or fluoroalkylmethoxysilanes with a C_2-C_{18} monovalent hydrocarbon group; and compounds obtained by substituting the methoxy group with $-OC(CH_3)=CHCOCH_3$, $-OC(CH_3)=N-Si(CH_3)_3$, $-OC(CF_3)=N-Si(CH_3)_3$, $-O-CO-R^{21}$ (where R^{21} is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)), an alkyl sulfonate group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), isocyanate group, amino group, dialkylamino group, isothiocyanate group, azide group, acetamide group, $-N(CH_3)C(O)CH_3$, $-N(CH_3)C(O)CF_3$, $-N=C(CH_3)OSi(CH_3)_3$, $-N=C(CF_3)OSi(CH_3)_3$, $-NHC(O)-OSi(CH_3)_3$, $-NHC(O)-NH-Si(CH_3)_3$, imidazole ring, oxazolidinone ring, morpholine ring, $-NH-C(O)-Si(CH_3)_3$, $-N(H)_{2-j}(Si(H)_kR^{20}{}_{3-k})_j$ (where R^{20} is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), "j" is an integer of 1 or 2, and "k" is an integer of from 0 to 2), chloro group, bromo group, iodo group, nitrile group or $-CO-NH-Si(CH_3)_3$.

[0062] The number of X^1 of the silylation reagent, which is represented by "4 −a−b" in the general formula [1], is preferably 1 because the protective film can uniformly be formed thereby.

[0063] It is preferable that R^1 in the general formula [1] mutually independently represents at least one group selected from C_1-C_{18} monovalent hydrocarbon groups the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s) and more preferably at least one group selected from C_mH_{2m+1} ("m"=1-18) and $C_nF_{2n+1}CH_2CH_2$ ("n"=1-8) because the wettability of the surface of the silicon element-containing wafer can be more reduced when the protective film is formed thereon, i.e., because a more excellent water repellency can be imparted to the surface. Additionally, it is preferable that "m" is 1 to 12 and "n" is 1 to 8 because the protective film can be

formed on the surface of the silicon element-containing wafer in a short time.

[0064] Furthermore, it is preferable that the acid is at least one selected from the group consisting of hydrogen chloride, sulfuric acid, perchloric acid, phosphoric acid, sulfonic acid represented by the general formula [2] and anhydride thereof, carboxylic acid represented by the general formula [3] and anhydride thereof, alkyl borate ester, aryl borate ester, boron tris(trifluoroacetate), trialkoxyboroxin, boron trifluoride and a silicon compound represented by the general formula [4].

[0065] Sulfonic acid represented by the general formula [2] and anhydride thereof are exemplified by methansulfonic acid, benzenesulfonic acid, *p*-toluenesulfonic acid, trifluoromethanesulfonic acid, trifluoromethanesulfonic anhydride and the like. Carboxylic acid represented by the general formula [3] and anhydride thereof are exemplified by acetic acid, trifluoroacetic acid, pentafluoropropionic acid, acetic anhydride, trifluoroacetic anhydride, pentafluoropropionic anhydride and the like. The silicon compound represented by the general formula [4] is preferably a chlorosilane, alkyl silyl alkyl sulfonate or alkyl silyl ester, and exemplified by trimethylsilyl trifluoroacetate, trimethylsilyl trifluoromethanesulfonate, dimethylsilyl trifluoroacetate, dimethylsilyl trifluoromethanesulfonate, butyldimethylsilyl trifluoroacetate, butyldimethylsilyl trifluoromethanesulfonate, hexyldimethylsilyl trifluoroacetate, hexyldimethylsilyl trifluoromethanesulfonate, octyldimethylsilyl trifluoroacetate, octyldimethylsilyl trifluoromethanesulfonate, decyldimethylsilyl trifluoroacetate, decyldimethylsilyl trifluoromethanesulfonate, dodecyldimethylsilyl trifluoroacetate, dodecyldimethylsilyl trifluoromethanesulfonate and the like.

[0066] Furthermore, it is preferable that the base is at least one selected from the group consisting of ammonia, N,N,N',N'-tetramethylethylenediamine, triethylenediamine, dimethylaniline, alkylamine, dialkylamine, trialkylamine, pyridine, piperazine, N-alkylmorpholine and a silane compound represented by the general formula [5].

[0067] By virtue of the acid or base contained in the liquid chemical, the reaction between the silylation reagent and a silanol group serving as a reaction site of the surface of the silicon element-containing wafer is accelerated, so that it becomes possible to impart an excellent water repellency to the surface of the silicon element-containing wafer by conducting a surface treatment in the use of the liquid chemical. Incidentally, the acid or base may constitute a part of the protective film.

[0068] With consideration given to a reaction-accelerating effect, it is preferable that the liquid chemical contains acid. Particularly, the acid is preferably: a strong acid (Brönsted acid) such as hydrogen chloride, sulfuric acid, perchloric acid and the like; an alkane sulfonic acid the hydrogen elements of which are partially or entirely replaced with a fluorine element(s) or acid anhydride thereof, such as trifluoromethanesulfonic acid, trifluoromethanesulfonic anhydride and the like; carboxylic acid the hydrogen elements of which are partially or entirely replaced with a fluorine element(s) or acid anhydride thereof, such as trifluoroacetic acid, trifluoroacetic anhydride, pentafluoropropionic acid and the like; chlorosilane; alkyl silyl alkyl sulfonate the hydrogen elements of which are partially or entirely replaced with a fluorine element(s); or alkyl silyl ester the hydrogen elements of which are partially or entirely replaced with a fluorine element(s). Incidentally, alkyl silyl ester is formed such that an alkyl group and –O–CO–R' group (where R' is an alkyl group) are bonded to a silicon element. Moreover, the acid contained in the liquid chemical may be formed by a reaction; for example, it is acceptable to cause a reaction between an alkylchlorosilane and an alcohol to produce a liquid chemical containing the formed alkylalkoxysilane as a silylation reagent, the formed hydrochloric acid as the acid, and an alcohol not consumed by the reaction as a solvent. In this case, a step that ranges from mixing of alkylchlorosilane and alcohol to the acquirement of the liquid chemical is referred to as "a mixing step".

[0069] As the solvent used in the first embodiment, there are preferably cited: hydrocarbons such as toluene, benzene, xylene, hexane, heptane, octane

and the like; esters such as ethyl acetate, propyl acetate, butyl acetate, ethyl acetoacetate and the like; ethers such as diethyl ether, dipropyl ether, dibutyl ether, tetrahydrofuran, dioxane and the like; ketones such as acetone, acetylacetone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, cyclohexanone, isophorone and the like; halogen-containing solvents including perfluorocarbons such as perfluorooctane, perfluorononane, perfluorocyclopentane, perfluorocyclohexane, hexafluorobenzene and the like, hydrofluorocarbons such as 1,1,1,3,3-pentafluorobutane, octafluorocyclopentane, 2,3-dihydrodecafluoropentane, ZEORORA-H (produced by ZEON CORPORATION) and the like, hydrofluoroethers such as methyl perfluoroisobutyl ether, methyl perfluorobutyl ether, ethyl perfluorobutyl ether, ethyl perfluoroisobutyl ether, ASAHIKLIN AE-3000 (produced by Asahi Glass Co., Ltd.), Novec 7100, Novec 7200, Novec 7300, Novec 7600 (any of these are produced by 3M Limited) and the like, chlorocarbons such as tetrachloromethane and the like, hydrochlorocarbons such as chloroform and the like, chlorofluorocarbons such as dichlorodifluoromethane and the like, 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, 1,2-dichloro-3,3,3-trifuoropropene and the like, perfluoroethers, perfluoropolyethers and the like; sulfoxide-based solvents such as dimethyl sulfoxide and the like; lactone-based solvents such as 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, ε-hexanolactone and the like; carbonate-based solvents such as dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, propylene carbonate and the like; polyalcohol derivatives having no OH group, such as 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, glycerine triacetate and the like; and nitrogen element-containing solvents having no N–H group, such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, diethylamine, triethylamine, pyridine and the like.

[0070] Additionally, it is preferable to use a nonflammable solvent as a part

or the entire of the solvent since the liquid chemical for forming a protective film becomes nonflammable or increases in flash point thereby reducing the risk of the liquid chemical. Most of the halogen-containing solvents are nonflammable, and such a halogen-containing nonflammable solvent can preferably be used as a nonflammable solvent.

[0071] Additionally, it is preferable, in view of safety under the fire protection law, to use a solvent having a flash point exceeding 70°C as the solvent.

[0072] According to "Globally Harmonized System of Classification and Labelling of Chemicals; GHS", a solvent having a flash point of not higher than 93 °C is defined as "a flammable liquid". Therefore, when a solvent having a flash point exceeding 93 °C is used as the solvent, the liquid chemical for forming a protective film tends to have a flash point exceeding 93 °C even if the solvent is not nonflammable one. Hence the liquid chemical hardly corresponds to "a flammable liquid" and therefore further preferable in view of safety.

[0073] Most of the lactone-based solvents, the carbonate-based solvents and the polyalcohol derivatives having no OH group have high flash point so as to be preferably used because the risk of the liquid chemical for forming a protective film can be lowered. In view of the safety, a solvent having a flash point exceeding 70 °C is more preferably used as the solvent, which is concretely exemplified by 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, ε-hexanolactone, propylene carbonate, ethylene glycol dibutyl ether, ethylene glycol monobutyl ether acetate, ethylene glycol diacetate, 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 diacetate, dipropylene glycol methyl propyl 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 diacetate, glycerine triacetate and the like. It is further preferable to use a solvent having a flash point exceeding 93 °C as the solvent, which is concretely exemplified by γ-butyrolactone, 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, ε-hexanolactone, propylene carbonate, ethylene glycol diacetate, diethylene glycol butyl methyl ether, diethylene glycol dibutyl ether, diethylene glycol diacetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, 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 diacetate, dipropylene glycol diacetate, dipropylene glycol monomethyl ether acetate, dipropylene glycol monoethyl ether acetate, dipropylene glycol monobutyl ether acetate, 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 diacetate, glycerine triacetate and the like.

[0074] Among the liquid chemicals prepared according to the first embodiment, it is preferable to use: one containing a mixture of 76 to 99.8999 mass% of at least one kind of solvent selected from the group consisting of hydrofluoroethers, hydrochlorofluorocarbons, polyalcohol derivatives having no OH group and lactone-based solvents, 0.1 to 20 mass% of at least one kind of silylation reagent selected from the group consisting of alkoxysilanes having C_xH_{2x+1} group (x=1-12) or $C_yF_{2y+1}CH_2CH_2$ group (y=1-8), trimethyldimethylaminosilane, trimethyldiethylaminosilane, butyldimethyl(dimethylamino)silane, butyldimethyl(diethylamino)silane, hexyldimethyl(dimethylamino)silane, hexyldimethyl(diethylamino)silane, octyldimethyl(dimethylamino)silane, octyldimethyl(diethylamino)silane, decyldimethyl(dimethylamino)silane, decyldimethyl(diethylamino)silane, dodecyldimethyl(dimethylamino)silane and dodecyldimethyl(diethylamino)silane and 0.0001 to 4 mass% of at least one kind of acid selected from the group consisting of trifluoroacetic acid, trifluoroacetic anhydride, trifluoromethanesulfonic acid, trifluoromethanesulfonic anhydride, trimethylsilyl trifluoroacetate, trimethylsilyl trifluoromethanesulfonate, dimethylsilyl trifluoroacetate, dimethylsilyl trifluoromethanesulfonate, butyldimethylsilyl trifluoroacetate,

butyldimethylsilyl trifluoromethanesulfonate, hexyldimethylsilyl trifluoroacetate, hexyldimethylsilyl trifluoromethanesulfonate, octyldimethylsilyl trifluoroacetate, octyldimethylsilyl trifluoromethanesulfonate, decyldimethylsilyl trifluoroacetate, decyldimethylsilyl trifluoromethanesulfonate, dodecyldimethylsilyl trifluoroacetate and dodecyldimethylsilyl trifluoromethanesulfonate; or one consisting only of the mixture.

[0075] It is also preferable to use: one containing a mixture of 76 to 99.8999 mass% of at least one kind of solvent selected from the group consisting of hydrofluoroethers, hydrochlorofluorocarbons and polyalcohol derivatives having no OH group, 0.1 to 20 mass% of at least one kind of silylation reagent selected from the group consisting of hexamethyldisilazane, tetramethyldisilazane, 1,3-dibutyltetramethyldisilazane, 1,3-dihexyltetramethyldisilazane, 1,3-dioctyltetramethyldisilazane, 1,3-didecyltetramethyldisilazane and 1,3-didodecyltetramethyldisilazane, and 0.0001 to 4 mass% of at least one kind of acid selected from the group consisting of trifluoroacetic acid, trifluoroacetic anhydride, trifluoromethanesulfonic acid, trifluoromethanesulfonic anhydride, trimethylsilyl trifluoroacetate, trimethylsilyl trifluoromethanesulfonate, dimethylsilyl trifluoroacetate, dimethylsilyl trifluoromethanesulfonate, butyldimethylsilyl trifluoroacetate, butyldimethylsilyl trifluoromethanesulfonate, hexyldimethylsilyl trifluoroacetate, hexyldimethylsilyl trifluoromethanesulfonate, octyldimethylsilyl trifluoroacetate, octyldimethylsilyl trifluoromethanesulfonate, decyldimethylsilyl trifluoroacetate, decyldimethylsilyl trifluoromethanesulfonate, dodecyldimethylsilyl trifluoroacetate and dodecyldimethylsilyl trifluoromethanesulfonate; or one consisting only of the mixture.

[0076] A liquid chemical for forming a water-repellent protective film, obtained according to a second embodiment of the present invention can form a water-repellent protective film on surfaces of recessed portions of an uneven

pattern of a wafer having the uneven pattern at its surface and containing at least one kind of element among titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at least at the surfaces of the recessed portions (hereinafter, such a wafer may be referred to as "a metallic element-containing wafer"). Hereinafter, the elements of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium may generically be referred to as "metallic element(s)". Examples of the above-mentioned metallic element-containing wafer include a silicon wafer, a wafer formed of a plurality of components including silicon and/or silicon oxide (SiO_2), a silicon carbide wafer, a sapphire wafer, semiconductor wafers formed of various kinds of compounds, a plastic wafer or the like coated at these surfaces with a layer formed of a matter containing titanium element such as titanium, titanium nitride, titanium oxide and the like, a matter containing tungsten element such as tungsten, tungsten oxide and the like, a matter containing aluminum element such as aluminum and aluminum oxide and the like, a matter containing copper element such as copper and copper oxide and the like, a matter containing tin element such as tin and tin oxide and the like, a matter containing tantalum element such as tantalum nitride and tantalum oxide and the like or a matter containing ruthenium element such as ruthenium and ruthenium oxide and the like, and a wafer formed having a multilayer film at least one layer of which is a film formed of a matter containing the above-mentioned metallic element. The step of forming the uneven pattern is conducted on a layer including a layer formed of a matter containing the above-mentioned metallic element. Additionally, those in which at least a part of the surface of the uneven pattern serves as a matter containing at least one kind element of the above-mentioned metallic elements at the time of being formed with the uneven pattern are also included.

[0077] Also concerning a wafer formed of a plurality of components that include a matter containing at least one kind of the above-mentioned metallic elements, it is possible to form the protective film on the surface of the matter containing at least one kind of the above-mentioned metallic elements. The

wafer formed of a plurality of components is exemplified by those in which the matter containing at least one kind of metallic element is formed at least at a part of the surfaces of the recessed portions and those in which at least a part of the surfaces of the recessed portions serves as the matter containing at least one kind of element of the above-mentioned metallic elements at the time of being formed with the uneven pattern. In the uneven pattern, where the liquid chemical obtained according to the second embodiment can form the protective film is on a surface of a moiety of the matter containing at least one kind of metallic element. Hence the protective film may be formed at least on a part of the surfaces of the recessed portions of the metallic element-containing wafer.

[0078] The formation of the water-repellent protective film on the surfaces of the recessed portions of the metallic element-containing wafer is accomplished in such a manner that a functional moiety (having compatibility with the matter containing the metallic element) of an agent for forming a protective film (which agent is contained in the liquid chemical obtained according to the second embodiment, and selected from compounds represented by the general formulas [6] to [13]) is physically adsorbed onto a surface of the matter containing the metallic element, and/or in such a manner that the functional moiety is reacted with the surface of the matter to form a chemical bond thereby causing chemical adsorption. Hereinafter, the above-mentioned "physical adsorption" and "chemical adsorption" may generically be referred to merely as "adsorption". The above-mentioned functional moiety is: in the general formula [6], a group represented by P–OH and/or P=O; in the general formula [7], a group represented by $-C(=O)-X^4$; in the general formula [8], a nitrogen element; in the general formula [9], a group represented by $-C(=O)-X^5-X^6$; in the general formula [10], a group represented by $(X^7)_h$; in the general formula [11], a group represented by $-X^8$; in the general formula [12], a group represented by $-C(=O)-X^9-C(=O)-$; and in the general formula [13], a group represented by P–OH and/or P=O. By the way, "having compatibility" means that Van der Waals force, an electrostatic interaction and

the like act between the surface of the matter containing the metallic element and the functional moiety of the agent for forming a protective film.

[0079] Additionally, R^8 of the general formula [6], R^{10} of the general formula [7], R^{11} of the general formula [8], R^{14} of the general formula [9], R^{15} of the general formula [10], R^{16} of the general formula [11], R^{17} and R^{18} of the general formula [12] and R^{24} of the general formula [13] are hydrophobic moieties that can reduce the surface energy of an article thereby decreasing the interaction between water or another liquid and the surface of the article (i.e., at the interface) such as hydrogen bond, intermolecular forces and the like. The effect of reducing the interaction is particularly exhibited against water, but it is also exhibited against a mixture liquid of water and a liquid other than water or against a liquid other than water. With this, the contact angle of the liquid to the article surface can be increased.

[0080] A hydrocarbon group contained in R^9 of the general formula [6] is exemplified by an alkyl group, alkylene group, and those the hydrogen elements of which are partially or entirely replaced with a fluorine element(s). Additionally, R^9 is preferably $-OR^{22}$ (where R^{22} is a C_1-C_3 hydrocarbon group). Moreover, it is preferable that R^{22} has a carbon number of 1, since a more excellent water repellency is obtained thereby. It is further preferable that R^{22} is a straight-chained alkyl group.

[0081] A compound represented by the general formula [6] is exemplified by $CH_3P(O)(OH)_2$, $C_2H_5P(O)(OH)_2$, $C_3H_7P(O)(OH)_2$, $C_4H_9P(O)(OH)_2$, $C_5H_{11}P(O)(OH)_2$, $C_6H_{13}P(O)(OH)_2$, $C_7H_{15}P(O)(OH)_2$, $C_8H_{17}P(O)(OH)_2$, $C_9H_{19}P(O)(OH)_2$, $C_{10}H_{21}P(O)(OH)_2$, $C_{11}H_{23}P(O)(OH)_2$, $C_{12}H_{25}P(O)(OH)_2$, $C_{13}H_{27}P(O)(OH)_2$, $C_{14}H_{29}P(O)(OH)_2$, $C_{15}H_{31}P(O)(OH)_2$, $C_{16}H_{33}P(O)(OH)_2$, $C_{17}H_{35}P(O)(OH)_2$, $C_{18}H_{37}P(O)(OH)_2$, $C_6H_5P(O)(OH)_2$, $CF_3P(O)(OH)_2$, $C_2F_5P(O)(OH)_2$, $C_3F_7P(O)(OH)_2$, $C_4F_9P(O)(OH)_2$, $C_5F_{11}P(O)(OH)_2$, $C_6F_{13}P(O)(OH)_2$, $C_7F_{15}P(O)(OH)_2$, $C_8F_{17}P(O)(OH)_2$, $CF_3C_2H_4P(O)(OH)_2$, $C_2F_5C_2H_4P(O)(OH)_2$, $C_3F_7C_2H_4P(O)(OH)_2$, $C_4F_9C_2H_4P(O)(OH)_2$, $C_5F_{11}C_2H_4P(O)(OH)_2$, $C_6F_{13}C_2H_4P(O)(OH)_2$, $C_7F_{15}C_2H_4P(O)(OH)_2$, $C_8F_{17}C_2H_4P(O)(OH)_2$, those obtained by substituting $-P(O)(OH)_2$ group of these

compounds with $-P(O)(OH)OCH_3$ group, $-P(O)(OH)OC_2H_5$ group, $-P(O)(OCH_3)_2$ group or $-P(O)(OC_2H_5)_2$ group, and the like.

[0082] In order that the compound represented by the general formula [6] provides more excellent water repellency, it is preferable that "g" of the general formula [6] is 1 or 2, and it is more preferable that "g" is 2. Moreover, R^8 of the general formula [6] is exemplified by an alkyl group, a phenyl group, a phenyl group the hydrogen elements of which are replaced with alkyl groups, a naphthyl group, these hydrocarbon groups the hydrogen elements of which are partially or entirely replaced with a fluorine element(s), and the like.

[0083] Additionally, R^8 of the general formula [6] having a carbon number of from 2 to 16, particularly from 4 to 14 and more particularly from 6 to 14 are preferable because the water repellency is more excellently obtained thereby. In addition, it is preferable that the hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s) is an alkyl group, more preferably a straight-chained alkyl group. If a straight-chained alkyl group is used as the hydrocarbon group, hydrophobic moieties of the agent for forming a protective film tend to be arranged perpendicularly to the surface of the protective film at the time of forming the protective film thereby more excellently exhibiting a water-repellency-imparting effect, which is therefore further preferable. Moreover, R^8 of the general formula [6] is preferably hydrocarbon groups whose hydrogen elements are partially or entirely substituted with a fluorine element(s), in order to impart a far better water repellency.

[0084] Additionally, the agent for forming a protective film may exist in the form of a salt represented by the general formula [6]. The salt can be cited by ammonium salt, amine salt and the like.

[0085] Additionally, it is preferable that R^{10} of the general formula [7], R^{11} of the general formula [8], R^{14} of the general formula [9], R^{15} of the general formula [10], R^{16} of the general formula [11], and R^{17} and R^{18} of the general formula [12] are C_1-C_{18} monovalent hydrocarbon groups each of which hydrogen elements may partially or entirely be replaced with a fluorine

element(s), and more preferably, C_mH_{2m+1} (m=1-18), $C_nF_{2n+1}CH_2CH_2$ (n=1-8), $C_pF_{2p+1}CH_2$ (p=1-8) and C_qF_{2q+1} (q=1-8). Furthermore, R^{24} of the general formula [13] is preferably C_vH_{2v+1} (v=4-18) or C_rF_{2r+1}–$(CH_2)_s$– group (r=4-8, s=0-2).

[0086] A compound represented by the general formula [7] is exemplified by CH_3COCl, C_2H_5COCl, C_3H_7COCl, C_4H_9COCl, $C_5H_{11}COCl$, $C_6H_{13}COCl$, $C_7H_{15}COCl$, $C_8H_{17}COCl$, $C_9H_{19}COCl$, $C_{10}H_{21}COCl$, $C_{11}H_{23}COCl$, $C_{12}H_{25}COCl$, $C_{13}H_{27}COCl$, $C_{14}H_{29}COCl$, $C_{15}H_{31}COCl$, $C_{16}H_{33}COCl$, $C_{17}H_{35}COCl$, $C_{18}H_{37}COCl$, C_6H_5COCl, CF_3COCl, C_2F_5COCl, C_3F_7COCl, C_4F_9COCl, $C_5F_{11}COCl$, $C_6F_{13}COCl$, $C_7F_{15}COCl$, $C_8F_{17}COCl$, compounds obtained by substituting –Cl group of the above compounds with –F group, –Br group or –I group, and the like.

[0087] In view of the compatibility with a matter containing metallic element and the water-repellency-imparting effect onto the surface of the metallic element-containing wafer, the particularly preferable examples of the above compounds are $C_8H_{17}COCl$, $C_9H_{19}COCl$, $C_{10}H_{21}COCl$, $C_{11}H_{23}COCl$, $C_{12}H_{25}COCl$, $C_{13}H_{27}COCl$, $C_{14}H_{29}COCl$, $C_{15}H_{31}COCl$, $C_{16}H_{33}COCl$, $C_{17}H_{35}COCl$, $C_{18}H_{37}COCl$, C_4F_9COCl, $C_5F_{11}COCl$, $C_6F_{13}COCl$, $C_7F_{15}COCl$, $C_8F_{17}COCl$, compounds obtained by substituting –Cl group of the above compounds with –F group, –Br group or –I group, and the like.

[0088] A compound represented by the general formula [8] is exemplified by compounds such as $C_5H_{11}NH_2$, $C_6H_{13}NH_2$, $C_7H_{15}NH_2$, $C_8H_{17}NH_2$, $C_9H_{19}NH_2$, $C_{10}H_{21}NH_2$, $C_{11}H_{23}NH_2$, $C_{12}H_{25}NH_2$, $C_{13}H_{27}NH_2$, $C_{14}H_{29}NH_2$, $C_{15}H_{31}NH_2$, $C_{16}H_{33}NH_2$, $C_{17}H_{35}NH_2$, $C_{18}H_{37}NH_2$, CF_3NH_2, $CF_3C_2H_4NH_2$, $C_2F_5NH_2$, $C_2F_5C_2H_4NH_2$, $C_3F_7NH_2$, $C_3F_7C_2H_4NH_2$, $C_4F_9NH_2$, $C_4F_9C_2H_4NH_2$, $C_4F_9CH_2NH_2$, $C_5F_{11}NH_2$, $C_5F_{11}C_2H_4NH_2$, $C_5F_{11}CH_2NH_2$, $C_6F_{13}NH_2$, $C_6F_{13}C_2H_4NH_2$, $C_6F_{13}CH_2NH_2$, $C_7F_{15}NH_2$, $C_7F_{15}C_2H_4NH_2$, $C_7F_{15}CH_2NH_2$, $C_8F_{17}NH_2$, $C_8F_{17}C_2H_4NH_2$, $C_8F_{17}CH_2NH_2$, $C_4F_7H_2NH_2$, $C_6F_{11}H_2NH_2$, $C_8F_{15}H_2NH_2$, $(C_3H_7)_2NH$, $(C_4H_9)_2NH$, $(C_5H_{11})_2NH$, $(C_6H_{13})_2NH$, $(C_7H_{15})_2NH$, $(C_8H_{17})_2NH$, $(C_9H_{19})_2NH$, $(C_{10}H_{21})_2NH$, $(C_{11}H_{23})_2NH$, $(C_{12}H_{25})_2NH$, $(C_{13}H_{27})_2NH$, $(C_{14}H_{29})_2NH$, $(C_{15}H_{31})_2NH$, $(C_{16}H_{33})_2NH$, $(C_{17}H_{35})_2NH$, $(C_{18}H_{37})_2NH$, $(CF_3)_2NH$, $(C_2F_5)_2NH$, $(C_3F_7)_2NH$, $(C_4F_9)_2NH$, $(C_5F_{11})_2NH$, $(C_6F_{13})_2NH$, $(C_7F_{15})_2NH$,

$(C_8F_{17})_2NH$, $(C_4F_7H_2)_2NH$, $(C_6F_{11}H_2)_2NH$, $(C_8F_{15}H_2)_2NH$, $(C_2H_5)_3N$, $(C_3H_7)_3N$, $(C_4H_9)_3N$, $(C_5H_{11})_3N$, $(C_6H_{13})_3N$, $(C_7H_{15})_3N$, $(C_8H_{17})_3N$, $(C_9H_{19})_3N$, $(C_{10}H_{21})_3N$, $(C_{11}H_{23})_3N$, $(C_{12}H_{25})_3N$, $(C_{13}H_{27})_3N$, $(C_{14}H_{29})_3N$, $(C_{15}H_{31})_3N$, $(C_{16}H_{33})_3N$, $(C_{17}H_{35})_3N$, $(C_{18}H_{37})_3N$, $(CF_3)_3N$, $(C_2F_5)_3N$, $(C_3F_7)_3N$, $(C_4F_9)_3N$, $(C_5F_{11})_3N$, $(C_6F_{13})_3N$, $(C_7F_{15})_3N$, $(C_8F_{17})_3N$, $(C_4F_7H_2)_3N$, $(C_6F_{11}H_2)_3N$, $(C_8F_{15}H_2)_3N$, $(C_5H_{11})(CH_3)NH$, $(C_6H_{13})(CH_3)NH$, $(C_7H_{15})(CH_3)NH$, $(C_8H_{17})(CH_3)NH$, $(C_9H_{19})(CH_3)NH$, $(C_{10}H_{21})(CH_3)NH$, $(C_{11}H_{23})(CH_3)NH$, $(C_{12}H_{25})(CH_3)NH$, $(C_{13}H_{27})(CH_3)NH$, $(C_{14}H_{29})(CH_3)NH$, $(C_{15}H_{31})(CH_3)NH$, $(C_{16}H_{33})(CH_3)NH$, $(C_{17}H_{35})(CH_3)NH$, $(C_{18}H_{37})(CH_3)NH$, $(CF_3)(CH_3)NH$, $(C_2F_5)(CH_3)NH$, $(C_3F_7)(CH_3)NH$, $(C_4F_9)(CH_3)NH$, $(C_5F_{11})(CH_3)NH$, $(C_6F_{13})(CH_3)NH$, $(C_7F_{15})(CH_3)NH$, $(C_8F_{17})(CH_3)NH$, $(C_3H_7)(CH_3)_2N$, $(C_4H_9)(CH_3)_2N$, $(C_5H_{11})(CH_3)_2N$, $(C_6H_{13})(CH_3)_2N$, $(C_7H_{15})(CH_3)_2N$, $(C_8H_{17})(CH_3)_2N$, $(C_9H_{19})(CH_3)_2N$, $(C_{10}H_{21})(CH_3)_2N$, $(C_{11}H_{23})(CH_3)_2N$, $(C_{12}H_{25})(CH_3)_2N$, $(C_{13}H_{27})(CH_3)_2N$, $(C_{14}H_{29})(CH_3)_2N$, $(C_{15}H_{31})(CH_3)_2N$, $(C_{16}H_{33})(CH_3)_2N$, $(C_{17}H_{35})(CH_3)_2N$, $(C_{18}H_{37})(CH_3)_2N$, $(CF_3)(CH_3)_2N$, $(C_2F_5)(CH_3)_2N$, $(C_3F_7)(CH_3)_2N$, $(C_4F_9)(CH_3)_2N$, $(C_5F_{11})(CH_3)_2N$, $(C_6F_{13})(CH_3)_2N$, $(C_7F_{15})(CH_3)_2N$, $(C_8F_{17})(CH_3)_2N$ and the like. In addition, the agent for forming a protective film may exist in the form of a salt of the general formula [8]. It is possible to exemplify the salt by inorganic acid salts such as carbonate, hydrochloride, sulfate, nitrate and the like, and organic acid salts such as acetate, propionate, butyrate, phthalate and the like.

[0089] In consideration of the compatibility with a matter containing metallic element and the water-repellency-imparting effect onto the surface of the metallic element-containing wafer, the particularly preferable examples of the above compounds are compounds such as $C_6H_{13}NH_2$, $C_7H_{15}NH_2$, $C_8H_{17}NH_2$, $C_9H_{19}NH_2$, $C_{10}H_{21}NH_2$, $C_{11}H_{23}NH_2$, $C_{12}H_{25}NH_2$, $C_{13}H_{27}NH_2$, $C_{14}H_{29}NH_2$, $C_{15}H_{31}NH_2$, $C_{16}H_{33}NH_2$, $C_{17}H_{35}NH_2$, $C_{18}H_{37}NH_2$, $(C_4H_9)_2NH$, $(C_5H_{11})_2NH$, $(C_6H_{13})_2NH$, $(C_7H_{15})_2NH$, $(C_8H_{17})_2NH$, $(C_9H_{19})_2NH$, $(C_{10}H_{21})_2NH$, $(C_{11}H_{23})_2NH$, $(C_{12}H_{25})_2NH$, $(C_{13}H_{27})_2NH$, $(C_{14}H_{29})_2NH$, $(C_{15}H_{31})_2NH$, $(C_{16}H_{33})_2NH$, $(C_{17}H_{35})_2NH$, $(C_{18}H_{37})_2NH$, $(C_4H_9)_3N$, $(C_5H_{11})_3N$, $(C_6H_{13})_3N$, $(C_7H_{15})_3N$, $(C_8H_{17})_3N$, $(C_9H_{19})_3N$, $(C_{10}H_{21})_3N$, $(C_{11}H_{23})_3N$, $(C_{12}H_{25})_3N$, $(C_{13}H_{27})_3N$,

$(C_{14}H_{29})_3N$, $(C_{15}H_{31})_3N$, $(C_{16}H_{33})_3N$, $(C_{17}H_{35})_3N$, $(C_{18}H_{37})_3N$, $(C_5H_{11})(CH_3)NH$, $(C_6H_{13})(CH_3)NH$, $(C_7H_{15})(CH_3)NH$, $(C_8H_{17})(CH_3)NH$, $(C_9H_{19})(CH_3)NH$, $(C_{10}H_{21})(CH_3)NH$, $(C_{11}H_{23})(CH_3)NH$, $(C_{12}H_{25})(CH_3)NH$, $(C_{13}H_{27})(CH_3)NH$, $(C_{14}H_{29})(CH_3)NH$, $(C_{15}H_{31})(CH_3)NH$, $(C_{16}H_{33})(CH_3)NH$, $(C_{17}H_{35})(CH_3)NH$, $(C_{18}H_{37})(CH_3)NH$, $(C_4H_9)(CH_3)_2N$, $(C_5H_{11})(CH_3)_2N$, $(C_6H_{13})(CH_3)_2N$, $(C_7H_{15})(CH_3)_2N$, $(C_8H_{17})(CH_3)_2N$, $(C_9H_{19})(CH_3)_2N$, $(C_{10}H_{21})(CH_3)_2N$, $(C_{11}H_{23})(CH_3)_2N$, $(C_{12}H_{25})(CH_3)_2N$, $(C_{13}H_{27})(CH_3)_2N$, $(C_{14}H_{29})(CH_3)_2N$, $(C_{15}H_{31})(CH_3)_2N$, $(C_{16}H_{33})(CH_3)_2N$, $(C_{17}H_{35})(CH_3)_2N$, $(C_{18}H_{37})(CH_3)_2N$, $C_4F_9NH_2$, $C_4F_9C_2H_4NH_2$, $C_4F_9CH_2NH_2$, $C_5F_{11}NH_2$, $C_5F_{11}C_2H_4NH_2$, $C_5F_{11}CH_2NH_2$, $C_6F_{13}NH_2$, $C_6F_{13}C_2H_4NH_2$, $C_6F_{13}CH_2NH_2$, $C_7F_{15}NH_2$, $C_7F_{15}C_2H_4NH_2$, $C_7F_{15}CH_2NH_2$, $C_8F_{17}NH_2$, $C_8F_{17}C_2H_4NH_2$, $C_8F_{17}CH_2NH_2$ and the like, inorganic acid salts thereof such as carbonate, hydrochloride, sulfate, nitrate and the like, and organic acid salts thereof such as acetate, propionate, butyrate, phthalate and the like.

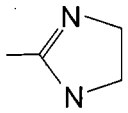
[0090] A compound represented by the general formula [9] is exemplified by compounds such as $C_5H_{11}COOH$, $C_6H_{13}COOH$, $C_7H_{15}COOH$, $C_8H_{17}COOH$, $C_9H_{19}COOH$, $C_{10}H_{21}COOH$, $C_{11}H_{23}COOH$, $C_{12}H_{25}COOH$, $C_{13}H_{27}COOH$, $C_{14}H_{29}COOH$, $C_{15}H_{31}COOH$, $C_{16}H_{33}COOH$, $C_{17}H_{35}COOH$, $C_{18}H_{37}COOH$, C_6H_5COOH, $C_5F_{11}COOH$, $C_6F_{13}COOH$, $C_7F_{15}COOH$, $C_8F_{17}COOH$ and the like, compounds obtained by substituting –COOH group of the above compounds with $–COOCH_3$ group, $–COOC_2H_5$ group, $–COOC_6H_5$ group, –COSH group or $–COSCH_3$ group, and the like.

[0091] In consideration of the compatibility with a matter containing metallic element and the water-repellency-imparting effect onto the surface of the metallic element-containing wafer, the particularly preferable examples of the above compounds are compounds such as $C_5H_{11}COOH$, $C_6H_{13}COOH$, $C_7H_{15}COOH$, $C_8H_{17}COOH$, $C_9H_{19}COOH$, $C_{10}H_{21}COOH$, $C_{11}H_{23}COOH$, $C_{12}H_{25}COOH$, $C_{13}H_{27}COOH$, $C_{14}H_{29}COOH$, $C_{15}H_{31}COOH$, $C_{16}H_{33}COOH$, $C_{17}H_{35}COOH$, $C_{18}H_{37}COOH$, $C_4H_9COOCH_3$, $C_5H_{11}COOCH_3$, $C_6H_{13}COOCH_3$, $C_7H_{15}COOCH_3$, $C_8H_{17}COOCH_3$, $C_9H_{19}COOCH_3$, $C_{10}H_{21}COOCH_3$, $C_{11}H_{23}COOCH_3$, $C_{12}H_{25}COOCH_3$, $C_{13}H_{27}COOCH_3$, $C_{14}H_{29}COOCH_3$,

$C_{15}H_{31}COOCH_3$, $C_{16}H_{33}COOCH_3$, $C_{17}H_{35}COOCH_3$, $C_{18}H_{37}COOCH_3$, $C_4H_9COOC_2H_5$, $C_5H_{11}COOC_2H_5$, $C_6H_{13}COOC_2H_5$, $C_7H_{15}COOC_2H_5$, $C_8H_{17}COOC_2H_5$, $C_9H_{19}COOC_2H_5$, $C_{10}H_{21}COOC_2H_5$, $C_{11}H_{23}COOC_2H_5$, $C_{12}H_{25}COOC_2H_5$, $C_{13}H_{27}COOC_2H_5$, $C_{14}H_{29}COOC_2H_5$, $C_{15}H_{31}COOC_2H_5$, $C_{16}H_{33}COOC_2H_5$, $C_{17}H_{35}COOC_2H_5$, $C_{18}H_{37}COOC_2H_5$, $C_4H_9COOC_6H_5$, $C_5H_{11}COOC_6H_5$, $C_6H_{13}COOC_6H_5$, $C_7H_{15}COOC_6H_5$, $C_8H_{17}COOC_6H_5$, $C_9H_{19}COOC_6H_5$, $C_{10}H_{21}COOC_6H_5$, $C_{11}H_{23}COOC_6H_5$, $C_{12}H_{25}COOC_6H_5$, $C_{13}H_{27}COOC_6H_5$, $C_{14}H_{29}COOC_6H_5$, $C_{15}H_{31}COOC_6H_5$, $C_{16}H_{33}COOC_6H_5$, $C_{17}H_{35}COOC_6H_5$, $C_{18}H_{37}COOC_6H_5$, $C_5H_{11}COSH$, $C_6H_{13}COSH$, $C_7H_{15}COSH$, $C_8H_{17}COSH$, $C_9H_{19}COSH$, $C_{10}H_{21}COSH$, $C_{11}H_{23}COSH$, $C_{12}H_{25}COSH$, $C_{13}H_{27}COSH$, $C_{14}H_{29}COSH$, $C_{15}H_{31}COSH$, $C_{16}H_{33}COSH$, $C_{17}H_{35}COSH$, $C_{18}H_{37}COSH$, $C_4H_9COSCH_3$, $C_5H_{11}COSCH_3$, $C_6H_{13}COSCH_3$, $C_7H_{15}COSCH_3$, $C_8H_{17}COSCH_3$, $C_9H_{19}COSCH_3$, $C_{10}H_{21}COSCH_3$, $C_{11}H_{23}COSCH_3$, $C_{12}H_{25}COSCH_3$, $C_{13}H_{27}COSCH_3$, $C_{14}H_{29}COSCH_3$, $C_{15}H_{31}COSCH_3$, $C_{16}H_{33}COSCH_3$, $C_{17}H_{35}COSCH_3$, $C_{18}H_{37}COSCH_3$ and the like.

[0092] A compound represented by the general formula [10] is exemplified by: isocyanate compounds such as C_2H_5NCO, C_3H_7NCO, C_4H_9NCO, $C_5H_{11}NCO$, $C_6H_{13}NCO$, $C_7H_{15}NCO$, $C_8H_{17}NCO$, $C_9H_{19}NCO$, $C_{10}H_{21}NCO$, $C_{11}H_{23}NCO$, $C_{12}H_{25}NCO$, $C_{13}H_{27}NCO$, $C_{14}H_{29}NCO$, $C_{15}H_{31}NCO$, $C_{16}H_{33}NCO$, $C_{17}H_{35}NCO$, $C_{18}H_{37}NCO$, CF_3NCO, CF_3CH_2NCO, $CF_3C_2H_4NCO$, C_2F_5NCO, $C_2F_5CH_2NCO$, $C_2F_5C_2H_4NCO$, C_3F_7NCO, $C_3F_7CH_2NCO$, $C_3F_7C_2H_4NCO$, C_4F_9NCO, $C_4F_9CH_2NCO$, $C_4F_9C_2H_4NCO$, $C_5F_{11}NCO$, $C_5F_{11}CH_2NCO$, $C_5F_{11}C_2H_4NCO$, $C_6F_{13}NCO$, $C_6F_{13}CH_2NCO$, $C_6F_{13}C_2H_4NCO$, $C_7F_{15}NCO$, $C_7F_{15}CH_2NCO$, $C_7F_{15}C_2H_4NCO$, $C_8F_{17}NCO$, $C_8F_{17}CH_2NCO$, $C_8F_{17}C_2H_4NCO$, $C_2H_4(NCO)_2$, $C_3H_6(NCO)_2$, $C_4H_8(NCO)_2$, $C_5H_{10}(NCO)_2$, $C_6H_{12}(NCO)_2$, $C_7H_{14}(NCO)_2$, $C_8H_{16}(NCO)_2$, $C_9H_{18}(NCO)_2$, $C_{10}H_{20}(NCO)_2$, $C_{11}H_{22}(NCO)_2$, $C_{12}H_{24}(NCO)_2$, $C_{13}H_{26}(NCO)_2$, $C_{14}H_{28}(NCO)_2$, $C_{15}H_{30}(NCO)_2$, $C_{16}H_{32}(NCO)_2$, $C_{17}H_{34}(NCO)_2$, $C_{18}H_{36}(NCO)_2$, $(NCO)C_2H_4NCO$, $(NCO)C_3H_6NCO$, $(NCO)C_4H_8NCO$, $(NCO)C_5H_{10}NCO$, $(NCO)C_6H_{12}NCO$, $(NCO)C_7H_{14}NCO$, $(NCO)C_8H_{16}NCO$, $(NCO)C_9H_{18}NCO$, $(NCO)C_{10}H_{20}NCO$, $(NCO)C_{11}H_{22}NCO$, $(NCO)C_{12}H_{24}NCO$, $(NCO)C_{13}H_{26}NCO$, $(NCO)C_{14}H_{28}NCO$, $(NCO)C_{15}H_{30}NCO$, $(NCO)C_{16}H_{32}NCO$,

$(NCO)C_{17}H_{34}NCO$, $(NCO)C_{18}H_{36}NCO$, $C_2H_3(NCO)_3$, $C_3H_5(NCO)_3$, $C_4H_7(NCO)_3$, $C_5H_9(NCO)_3$, $C_6H_{11}(NCO)_3$, $C_7H_{13}(NCO)_3$, $C_8H_{15}(NCO)_3$, $C_9H_{17}(NCO)_3$, $C_{10}H_{19}(NCO)_3$, $C_{11}H_{21}(NCO)_3$, $C_{12}H_{23}(NCO)_3$, $C_{13}H_{25}(NCO)_3$, $C_{14}H_{27}(NCO)_3$, $C_{15}H_{29}(NCO)_3$, $C_{16}H_{31}(NCO)_3$, $C_{17}H_{33}(NCO)_3$, $C_{18}H_{35}(NCO)_3$, $C(NCO)_4$, $(NCO)_2C_2H_2(NCO)_2$, $(NCO)_2C_3H_4(NCO)_2$, $(NCO)_2C_4H_6(NCO)_2$, $(NCO)_2C_5H_8(NCO)_2$, $(NCO)_2C_6H_{10}(NCO)_2$, $(NCO)_2C_7H_{12}(NCO)_2$, $(NCO)_2C_8H_{14}(NCO)_2$, $(NCO)_2C_9H_{16}(NCO)_2$, $(NCO)_2C_{10}H_{18}(NCO)_2$, $(NCO)_2C_{11}H_{20}(NCO)_2$, $(NCO)_2C_{12}H_{22}(NCO)_2$, $(NCO)_2C_{13}H_{24}(NCO)_2$, $(NCO)_2C_{14}H_{26}(NCO)_2$, $(NCO)_2C_{15}H_{28}(NCO)_2$, $(NCO)_2C_{16}H_{30}(NCO)_2$, $(NCO)_2C_{17}H_{32}(NCO)_2$, $(NCO)_2C_{18}H_{34}(NCO)_2$ and the like; compounds obtained by substituting an isocyanate group (–NCO group) of the above isocyanate compounds with –SH group, –CHO group, –CONHOH group or a nitrogen element-containing cyclic structure such as an imidazoline ring (the following formula [18]); and the like.



[18]

[0093] In consideration of the compatibility with a matter containing metallic element and the water-repellency-imparting effect onto the surface of the metallic element-containing wafer, the particularly preferable examples of the above compounds are isocyanate compounds such as C_4H_9NCO, $C_5H_{11}NCO$, $C_6H_{13}NCO$, $C_7H_{15}NCO$, $C_8H_{17}NCO$, $C_9H_{19}NCO$, $C_{10}H_{21}NCO$, $C_{11}H_{23}NCO$, $C_{12}H_{25}NCO$, $C_{13}H_{27}NCO$, $C_{14}H_{29}NCO$, $C_{15}H_{31}NCO$, $C_{16}H_{33}NCO$, $C_{17}H_{35}NCO$, $C_{18}H_{37}NCO$, $C_3F_7CH_2NCO$, $C_3F_7C_2H_4NCO$, C_4F_9NCO, $C_4F_9CH_2NCO$, $C_4F_9C_2H_4NCO$, $C_5F_{11}NCO$, $C_5F_{11}CH_2NCO$, $C_5F_{11}C_2H_4NCO$, $C_6F_{13}NCO$, $C_6F_{13}CH_2NCO$, $C_6F_{13}C_2H_4NCO$, $C_7F_{15}NCO$, $C_7F_{15}CH_2NCO$, $C_7F_{15}C_2H_4NCO$, $C_8F_{17}NCO$, $C_8F_{17}CH_2NCO$, $C_8F_{17}C_2H_4NCO$ and the like; compounds obtained by substituting an isocyanate group (–NCO group) of the above isocyanate compounds with –SH group, –CHO group, –CONHOH group or a nitrogen element-containing cyclic structure such as an imidazoline ring; and the like.

[0094] A compound represented by the general formula [11] is exemplified by compounds such as $CH_3C_4H_3S$, $C_2H_5C_4H_3S$, $C_3H_7C_4H_3S$, $C_4H_9C_4H_3S$, $C_5H_{11}C_4H_3S$, $C_6H_{13}C_4H_3S$, $C_7H_{15}C_4H_3S$, $C_8H_{17}C_4H_3S$, $C_9H_{19}C_4H_3S$, $C_{10}H_{21}C_4H_3S$, $C_{11}H_{23}C_4H_3S$, $C_{12}H_{25}C_4H_3S$, $C_{13}H_{27}C_4H_3S$, $C_{14}H_{29}C_4H_3S$, $C_{15}H_{31}C_4H_3S$, $C_{16}H_{33}C_4H_3S$, $C_{17}H_{35}C_4H_3S$, $C_{18}H_{37}C_4H_3S$, C_3H_3NS, $CH_3C_3H_2NS$, $C_2H_5C_3H_2NS$, $C_3H_7C_3H_2NS$, $C_4H_9C_3H_2NS$, $C_5H_{11}C_3H_2NS$, $C_6H_{13}C_3H_2NS$, $C_7H_{15}C_3H_2NS$, $C_8H_{17}C_3H_2NS$, $C_9H_{19}C_3H_2NS$, $C_{10}H_{21}C_3H_2NS$, $C_{11}H_{23}C_3H_2NS$, $C_{12}H_{25}C_3H_2NS$, $C_{13}H_{27}C_3H_2NS$, $C_{14}H_{29}C_3H_2NS$, $C_{15}H_{31}C_3H_2NS$, $C_{16}H_{33}C_3H_2NS$, $C_{17}H_{35}C_3H_2NS$, and $C_{18}H_{37}C_3H_2NS$. Incidentally, C_4H_3S represents a thiophene ring, C_3H_3NS represents thiazole, and C_3H_2NS represents a thiazole ring.

[0095] A compound represented by the general formula [12] is exemplified by compounds such as $CH_3COOCOCH_3$, $C_2H_5COOCOC_2H_5$, $C_3H_7COOCOC_3H_7$, $C_4H_9COOCOC_4H_9$, $C_5H_{11}COOCOC_5H_{11}$, $C_6H_{13}COOCOC_6H_{13}$, $C_7H_{15}COOCOC_7H_{15}$, $C_8H_{17}COOCOC_8H_{17}$, $C_9H_{19}COOCOC_9H_{19}$, $C_{10}H_{21}COOCOC_{10}H_{21}$, $C_{11}H_{23}COOCOC_{11}H_{23}$, $C_{12}H_{25}COOCOC_{12}H_{25}$, $C_{13}H_{27}COOCOC_{13}H_{27}$, $C_{14}H_{29}COOCOC_{14}H_{29}$, $C_{15}H_{31}COOCOC_{15}H_{31}$, $C_{16}H_{33}COOCOC_{16}H_{33}$, $C_{17}H_{35}COOCOC_{17}H_{35}$, $C_{18}H_{37}COOCOC_{18}H_{37}$, $C_6H_5COOCOC_6H_5$, $CF_3COOCOCF_3$, $C_2F_5COOCOC_2F_5$, $C_3F_7COOCOC_3F_7$, $C_4F_9COOCOC_4F_9$, $C_5F_{11}COOCOC_5F_{11}$, $C_6F_{13}COOCOC_6F_{13}$, $C_7F_{15}COOCOC_7F_{15}$, and $C_8F_{17}COOCOC_8F_{17}$.

[0096] A compound represented by the general formula [13] is exemplified by: compounds such as $C_4H_9O(C_2H_4O)P(O)(OH)_2$, $C_5H_{11}O(C_2H_4O)P(O)(OH)_2$, $C_6H_{13}O(C_2H_4O)P(O)(OH)_2$, $C_7H_{15}O(C_2H_4O)P(O)(OH)_2$, $C_8H_{17}O(C_2H_4O)P(O)(OH)_2$, $C_9H_{19}O(C_2H_4O)P(O)(OH)_2$, $C_{10}H_{21}O(C_2H_4O)P(O)(OH)_2$, $C_{12}H_{25}O(C_2H_4O)P(O)(OH)_2$, $C_{14}H_{29}O(C_2H_4O)P(O)(OH)_2$, $C_{16}H_{33}O(C_2H_4O)P(O)(OH)_2$, $C_{18}H_{37}O(C_2H_4O)P(O)(OH)_2$, $C_6H_5O(C_2H_4O)P(O)(OH)_2$, $C_4F_9O(C_2H_4O)P(O)(OH)_2$, $C_5F_{11}O(C_2H_4O)P(O)(OH)_2$, $C_6F_{13}O(C_2H_4O)P(O)(OH)_2$, $C_7F_{15}O(C_2H_4O)P(O)(OH)_2$, $C_8F_{17}O(C_2H_4O)P(O)(OH)_2$, $C_3F_7C_2H_4O(C_2H_4O)P(O)(OH)_2$, $C_4F_9C_2H_4O(C_2H_4O)P(O)(OH)_2$,

$C_5F_{11}C_2H_4O(C_2H_4O)P(O)(OH)_2$, $C_6F_{13}C_2H_4O(C_2H_4O)P(O)(OH)_2$,
$C_7F_{15}C_2H_4O(C_2H_4O)P(O)(OH)_2$, $C_8F_{17}C_2H_4O(C_2H_4O)P(O)(OH)_2$,
$\{C_4H_9O(C_2H_4O)\}_2P(O)OH$, $\{C_5H_{11}O(C_2H_4O)\}_2P(O)OH$,
$\{C_6H_{13}O(C_2H_4O)\}_2P(O)OH$, $\{C_7H_{15}O(C_2H_4O)\}_2P(O)OH$,
$\{C_8H_{17}O(C_2H_4O)\}_2P(O)OH$, $\{C_9H_{19}O(C_2H_4O)\}_2P(O)OH$,
$\{C_{10}H_{21}O(C_2H_4O)\}_2P(O)OH$, $\{C_{12}H_{25}O(C_2H_4O)\}_2P(O)OH$,
$\{C_{14}H_{29}O(C_2H_4O)\}_2P(O)OH$, $\{C_{16}H_{33}O(C_2H_4O)\}_2P(O)OH$,
$\{C_{18}H_{37}O(C_2H_4O)\}_2P(O)OH$, $\{C_6H_5O(C_2H_4O)\}_2P(O)OH$, $\{C_4F_9O(C_2H_4O)\}_2P(O)OH$,
$\{C_5F_{11}O(C_2H_4O)\}_2P(O)OH$, $\{C_6F_{13}O(C_2H_4O)\}_2P(O)OH$,
$\{C_7F_{15}O(C_2H_4O)\}_2P(O)OH$, $\{C_8F_{17}O(C_2H_4O)\}_2P(O)OH$,
$\{C_4F_9C_2H_4O(C_2H_4O)\}_2P(O)OH$, $\{C_5F_{11}C_2H_4O(C_2H_4O)\}_2P(O)OH$,
$\{C_6F_{13}C_2H_4O(C_2H_4O)\}_2P(O)OH$, $\{C_7F_{15}C_2H_4O(C_2H_4O)\}_2P(O)OH$,
$\{C_8F_{17}C_2H_4O(C_2H_4O)\}_2P(O)OH$ and the like; compounds obtained by substituting $-O(C_2H_4O)-$ group of the above compounds with $-O-$ group, $-O(C_2H_4O)_w-$ group (w=2-10) or $-O(C_3H_6O)_z-$ group (z=1-10); and the like. In addition, the agent for forming a protective film may exist in the form of a salt represented by the general formula [13]. The salt can be cited by ammonium salt, amine salt and the like.

[0097] Moreover, it is preferable that the agent for forming a protective film which agent is selected from compounds represented by the general formulas [6] to [13] and salt compounds thereof has an HLB value (according to Griffin's method) of from 0.001 to 10, because such a compound can impart better water repellency to the surface of the metallic element-containing wafer.

[0098] Additionally, it is preferable that the agent for forming a protective film which agent is selected from compounds represented by the general formulas [6] to [13] and salt compounds thereof is a compound represented by the following general formula [19] or a salt compound thereof, because such a compound can impart better water repellency to the surface of the metallic element-containing wafer.

$$R^{23}–X^{11} \quad [19]$$

[In the formula [19], X^{11} represents at least one selected from the

group consisting of $-P(O)(OH)_2$, $-NH_2$ group, -N=C=O group, -SH group, -CONHOH group and an imidazoline ring. R^{23} represents a C_4-C_{18} hydrocarbon group or $C_rF_{2r+1}-(CH_2)_s-$ group (r=4-8, s=0-2).]

[0099] The solvent used in the second embodiment is concretely exemplified by the solvent as discussed in the first embodiment, such as hydrocarbons, esters, ethers, ketones, halogen element-containing solvents, sulfoxide-based solvents, lactone-based solvents, carbonate-based solvents, polyalcohol derivatives having no OH group and nitrogen element-containing solvents having no N–H group. Additionally, it is also possible to cite: water; alcohols such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, ethylene glycol, diethylene glycol, 1,3–propanediol, 1,2–propanediol, dipropylene glycol, 1,2–butanediol, 1,3–butanediol, 1,4–butanediol, triethylene glycol, tripropylene glycol, tetraethylene glycol, tetrapropylene glycol, glycerine and the like; polyalcohol derivatives having OH group, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monopropyl ether, triethylene glycol monobutyl ether, tetraethylene glycol monomethyl ether, tetraethylene glycol monoethyl ether, tetraethylene glycol monopropyl ether, tetraethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, tripropylene glycol monoethyl ether, tripropylene glycol monopropyl ether, tripropylene glycol monobutyl ether, tetrapropylene glycol monomethyl ether, butylene glycol monomethyl ether and the like; and nitrogen element-containing solvents having N–H group, such as formamide.

[0100] Additionally, it is preferable to use a nonflammable solvent as a part

or the entire of the solvent, since the liquid chemical for forming a protective film becomes nonflammable or increases in flash point thereby reducing the risk of the liquid chemical. Most of the halogen-containing solvents are nonflammable, and such a halogen-containing nonflammable solvent can preferably be used as a nonflammable solvent. Furthermore, water can also be used as the nonflammable solvent.

[0101] Additionally, it is preferable, in view of safety under the fire protection law, to use a solvent having a flash point exceeding 70°C as the solvent.

[0102] According to "Globally Harmonized System of Classification and Labelling of Chemicals; GHS", a solvent having a flash point of not higher than 93 °C is defined as "a flammable liquid". Therefore, when a solvent having a flash point exceeding 93 °C is used as the solvent, the liquid chemical for forming a protective film tends to have a flash point exceeding 93 °C even if the solvent is not nonflammable one. Hence the liquid chemical hardly corresponds to "a flammable liquid" and therefore further preferable in view of safety.

[0103] Additionally, most of the lactone-based solvents, carbonate-based solvents and the polyalcohol derivatives have a high flash point; therefore, it is preferable to use these solvents because the risk of the liquid chemical for forming a protective film can be reduced. In view of the safety, it is preferable to use: the solvents as discussed in the first embodiment to have a flash point exceeding 70 °C; or solvents having a flash point exceeding 70 °C and concretely exemplified by ethylene glycol, diethylene glycol, 1,2–propanediol, 1,3–propanediol, dipropylene glycol, 1,2–butanediol, 1,3–butanediol, 1,4–butanediol, triethylene glycol, tripropylene glycol, tetraethylene glycol, tetrapropylene glycol, glycerine, diethylene glycol monometnyl ether, diethylene glycol monoetnyl ether, diethylene glycol monopropyl ether, diethylene glycol monobutyl ether, triethylene glycol monometnyl ether, triethylene glycol monoetnyl ether, triethylene glycol monopropyl ether, triethylene glycol monobutyl ether, tetraethylene glycol monometnyl ether,

tetraethylene glycol monoetnyl ether, tetraethylene glycol monopropyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol monometnyl ether, dipropylene glycol monoetnyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monometnyl ether, tripropylene glycol monoetnyl ether, tripropylene glycol monopropyl ether, tripropylene glycol monobutyl ether, tetrapropylene glycol monometnyl ether and the like. It is much more preferable to use: the solvents as discussed in the first embodiment to have a flash point exceeding 93 °C; or a solvent having a flash point exceeding 93 °C and concretely exemplified by ethylene glycol, diethylene glycol, 1,2–propanediol, 1,3–propanediol, dipropylene glycol, 1,2–butanediol, 1,3–butanediol, 1,4–butanediol, triethylene glycol, tripropylene glycol, tetraethylene glycol, tetrapropylene glycol, glycerine, diethylene glycol monomethyl ether, diethylene glycol monopropyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monopropyl ether, triethylene glycol monobutyl ether, tetraethylene glycol monomethyl ether, tetraethylene glycol monoethyl ether, tetraethylene glycol monopropyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, tripropylene glycol monoethyl ether, tripropylene glycol monopropyl ether, tripropylene glycol monobutyl ether, tetrapropylene glycol monomethyl ether and the like.

[0104] Among the liquid chemicals prepared according to the second embodiment, it is preferable to use: one containing a mixture of 85 to 99.9995 mass% of at least one kind of solvent selected from the group consisting of ketones, polyalcohol derivatives, water and alcohols and 15 to 0.0005 mass% of a compound represented by the following general formula [19]; or one consisting only of the mixture.

$$R^{23}–X^{11} \quad [19]$$

[In the formula [19], X^{11} represents at least one selected from the group consisting of $–P(O)(OH)_2$, $–NH_2$ group, –N=C=O group, –SH group,

–CONHOH group and an imidazoline ring. R^{23} represents a C_4-C_{18} hydrocarbon group or C_rF_{2r+1}–$(CH_2)_s$– group (r=4-8, s=0-2).]

[0105] A liquid chemical kit (a treatment liquid (A) and a treatment liquid (B)) for forming a water-repellent protective film, obtained according to a third and a fourth embodiment of the present invention can provide a liquid chemical for forming a water-repellent protective film by mixing the treatment liquids (A) and (B) thereby allowing the formation of a water-repellent protective film on the surfaces of the recessed portions of a silicon element-containing wafer.

[0106] The formation of the water-repellent protective film on the surfaces of the recessed portions of the silicon element-containing wafer is achieved: by causing a reaction between a reactive moiety of a silylation reagent contained in the treatment liquid (A) and a silanol group that serves as a reaction site of the silicon element-containing wafer thereby chemically bonding the silylation reagent to a silicon element of the silicon element-containing wafer through a siloxane bond; or by causing a reaction between a reaction product (obtained between a silylation reagent contained in the treatment liquid (A) and an acid or base contained in the treatment liquid (B)) and a silanol group that serves as a reaction site of the silicon element-containing wafer thereby chemically bonding the reaction product to a silicon element of the silicon element-containing wafer through a siloxane bond. The reaction moiety is a group represented by X^1 in general formula [1].

[0107] In addition, R^1 of the general formula [1] serves as a hydrophobic moiety which decreases a surface energy of an article to reduce the interaction caused between water or another liquid and the article surface (i.e., at the interface), such as hydrogen bond, intermolecular forces and the like. The effect of reducing the interaction is particularly exhibited with water, but the effect of reducing the interaction is exhibited also with a mixture liquid of water and a liquid other than water or with a liquid other than water. With this, the contact angle of the liquid to the article surface can be increased.

[0108] A silylation agent represented by the general formula [1] can be

concretely exemplified by the same as discussed in the first embodiment.

[0109] As the above-mentioned silylation reagent, it is preferable to use a silicon compound represented by the general formula [14], since water repellency can sufficiently and easily be provided even onto a wafer the surface of which is low in number of silanol groups that serve as a reaction site in the silicon element-containing wafer, e.g. silicon nitride. Incidentally, X^{10} in the general formula [14] represents the reactive moiety and R^{19} represents the hydrophobic moiety.

[0110] Examples of the silicon compound represented by the general formula [14] are: chlorosilane-based compounds such as $C_4H_9(CH_3)_2SiCl$, $C_5H_{11}(CH_3)_2SiCl$, $C_6H_{13}(CH_3)_2SiCl$, $C_7H_{15}(CH_3)_2SiCl$, $C_8H_{17}(CH_3)_2SiCl$, $C_9H_{19}(CH_3)_2SiCl$, $C_{10}H_{21}(CH_3)_2SiCl$, $C_{11}H_{23}(CH_3)_2SiCl$, $C_{12}H_{25}(CH_3)_2SiCl$, $C_{13}H_{27}(CH_3)_2SiCl$, $C_{14}H_{29}(CH_3)_2SiCl$, $C_{15}H_{31}(CH_3)_2SiCl$, $C_{16}H_{33}(CH_3)_2SiCl$, $C_{17}H_{35}(CH_3)_2SiCl$, $C_{18}H_{37}(CH_3)_2SiCl$, $C_5H_{11}(CH_3)HSiCl$, $C_6H_{13}(CH_3)HSiCl$, $C_7H_{15}(CH_3)HSiCl$, $C_8H_{17}(CH_3)HSiCl$, $C_9H_{19}(CH_3)HSiCl$, $C_{10}H_{21}(CH_3)HSiCl$, $C_{11}H_{23}(CH_3)HSiCl$, $C_{12}H_{25}(CH_3)HSiCl$, $C_{13}H_{27}(CH_3)HSiCl$, $C_{14}H_{29}(CH_3)HSiCl$, $C_{15}H_{31}(CH_3)HSiCl$, $C_{16}H_{33}(CH_3)HSiCl$, $C_{17}H_{35}(CH_3)HSiCl$, $C_{18}H_{37}(CH_3)HSiCl$, $C_2F_5C_2H_4(CH_3)_2SiCl$, $C_3F_7C_2H_4(CH_3)_2SiCl$, $C_4F_9C_2H_4(CH_3)_2SiCl$, $C_5F_{11}C_2H_4(CH_3)_2SiCl$, $C_6F_{13}C_2H_4(CH_3)_2SiCl$, $C_7F_{15}C_2H_4(CH_3)_2SiCl$, $C_8F_{17}C_2H_4(CH_3)_2SiCl$, $(C_2H_5)_3SiCl$, $C_3H_7(C_2H_5)_2SiCl$, $C_4H_9(C_2H_5)_2SiCl$, $C_5H_{11}(C_2H_5)_2SiCl$, $C_6H_{13}(C_2H_5)_2SiCl$, $C_7H_{15}(C_2H_5)_2SiCl$, $C_8H_{17}(C_2H_5)_2SiCl$, $C_9H_{19}(C_2H_5)_2SiCl$, $C_{10}H_{21}(C_2H_5)_2SiCl$, $C_{11}H_{23}(C_2H_5)_2SiCl$, $C_{12}H_{25}(C_2H_5)_2SiCl$, $C_{13}H_{27}(C_2H_5)_2SiCl$, $C_{14}H_{29}(C_2H_5)_2SiCl$, $C_{15}H_{31}(C_2H_5)_2SiCl$, $C_{16}H_{33}(C_2H_5)_2SiCl$, $C_{17}H_{35}(C_2H_5)_2SiCl$, $C_{18}H_{37}(C_2H_5)_2SiCl$, $(C_4H_9)_3SiCl$, $C_5H_{11}(C_4H_9)_2SiCl$, $C_6H_{13}(C_4H_9)_2SiCl$, $C_7H_{15}(C_4H_9)_2SiCl$, $C_8H_{17}(C_4H_9)_2SiCl$, $C_9H_{19}(C_4H_9)_2SiCl$, $C_{10}H_{21}(C_4H_9)_2SiCl$, $C_{11}H_{23}(C_4H_9)_2SiCl$, $C_{12}H_{25}(C_4H_9)_2SiCl$, $C_{13}H_{27}(C_4H_9)_2SiCl$, $C_{14}H_{29}(C_4H_9)_2SiCl$, $C_{15}H_{31}(C_4H_9)_2SiCl$, $C_{16}H_{33}(C_4H_9)_2SiCl$, $C_{17}H_{35}(C_4H_9)_2SiCl$, $C_{18}H_{37}(C_4H_9)_2SiCl$, $CF_3C_2H_4(C_4H_9)_2SiCl$, $C_2F_5C_2H_4(C_4H_9)_2SiCl$, $C_3F_7C_2H_4(C_4H_9)_2SiCl$, $C_4F_9C_2H_4(C_4H_9)_2SiCl$, $C_5F_{11}C_2H_4(C_4H_9)_2SiCl$, $C_6F_{13}C_2H_4(C_4H_9)_2SiCl$, $C_7F_{15}C_2H_4(C_4H_9)_2SiCl$, $C_8F_{17}C_2H_4(C_4H_9)_2SiCl$, $C_5H_{11}(CH_3)SiCl_2$, $C_6H_{13}(CH_3)SiCl_2$, $C_7H_{15}(CH_3)SiCl_2$, $C_8H_{17}(CH_3)SiCl_2$,

$C_9H_{19}(CH_3)SiCl_2$, $C_{10}H_{21}(CH_3)SiCl_2$, $C_{11}H_{23}(CH_3)SiCl_2$, $C_{12}H_{25}(CH_3)SiCl_2$, $C_{13}H_{27}(CH_3)SiCl_2$, $C_{14}H_{29}(CH_3)SiCl_2$, $C_{15}H_{31}(CH_3)SiCl_2$, $C_{16}H_{33}(CH_3)SiCl_2$, $C_{17}H_{35}(CH_3)SiCl_2$, $C_{18}H_{37}(CH_3)SiCl_2$, $C_3F_7C_2H_4(CH_3)SiCl_2$, $C_4F_9C_2H_4(CH_3)SiCl_2$, $C_5F_{11}C_2H_4(CH_3)SiCl_2$, $C_6F_{13}C_2H_4(CH_3)SiCl_2$, $C_7F_{15}C_2H_4(CH_3)SiCl_2$, $C_8F_{17}C_2H_4(CH_3)SiCl_2$, $C_6H_{13}SiCl_3$, $C_7H_{15}SiCl_3$, $C_8H_{17}SiCl_3$, $C_9H_{19}SiCl_3$, $C_{10}H_{21}SiCl_3$, $C_{11}H_{23}SiCl_3$, $C_{12}H_{25}SiCl_3$, $C_{13}H_{27}SiCl_3$, $C_{14}H_{29}SiCl_3$, $C_{15}H_{31}SiCl_3$, $C_{16}H_{33}SiCl_3$, $C_{17}H_{35}SiCl_3$, $C_{18}H_{37}SiCl_3$, $C_4F_9C_2H_4SiCl_3$, $C_5F_{11}C_2H_4SiCl_3$, $C_6F_{13}C_2H_4SiCl_3$, $C_7F_{15}C_2H_4SiCl_3$, $C_8F_{17}C_2H_4SiCl_3$ and the like; a compound obtained by substituting the chloro (Cl) group of the above-mentioned chlorosilanes with alkoxy group, $-OC(CH_3)=CHCOCH_3$, $-OC(CH_3)=N-Si(CH_3)_3$, $-OC(CF_3)=N-Si(CH_3)_3$, $-O-CO-R^{21}$ (where R^{21} is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)), an alkyl sulfonate group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), isocyanate group, amino group, dialkylamino group, isothiocyanate group, azide group, acetamide group, $-N(CH_3)C(O)CH_3$, $-N(CH_3)C(O)CF_3$, $-N=C(CH_3)OSi(CH_3)_3$, $-N=C(CF_3)OSi(CH_3)_3$, $-NHC(O)-OSi(CH_3)_3$, $-NHC(O)-NH-Si(CH_3)_3$, imidazole ring, oxazolidinone ring, morpholine ring, $-NH-C(O)-Si(CH_3)_3$, $-N(H)_{2-j}(Si(H)_kR^{20}{}_{3-k})_j$ (where R^{20} is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), "j" is an integer of 1 or 2, and "k" is an integer of from 0 to 2), bromo group, iodo group, nitrile group or $-CO-NH-Si(CH_3)_3$; and the like.

[0111] Additionally, "i" in the general formula [14] is required only to be an integer of from 1 to 3; however, when "i" is 1 or 2 and when a liquid chemical obtained from the liquid chemical kit is preserved for a long period of time, there is a possibility of causing polymerization of silicon compound due to the contamination of water content and the like to shorten a possible preservation period. In view of this, it is preferable that "i" in the general formula [14] is 3.

[0112] Moreover, among the silicon compounds represented by the general formula [14], those in which one R^{19} is a C_4-C_{18} monovalent hydrocarbon group

the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s) and the other R^{19} consist of two methyl groups are preferable since the rate of reaction against OH groups resident on the surface of the silicon element-containing wafer is accelerated thereby. This is because steric hindrance due to hydrophobic group has a great influence upon the reaction rate and because it is preferable that an alkyl chain to be bonded to silicon element has the longest chain and two other shorter chains, in a reaction between OH group resident on the surface of the silicon element-containing wafer and the silicon compound.

[0113] An acid which may be contained in the treatment liquid (B) can be exemplified by the same acids as those discussed in the first embodiment. Moreover, a base which may be contained in the treatment liquid (B) can be exemplified by the same as those discussed in the first embodiment. Furthermore, a nonaqueous organic solvent used in the third and fourth preparation method of the present invention can concretely be exemplified by the same solvents as discussed in the first embodiment.

[0114] Additionally, the present invention is a liquid chemical kit for forming a water-repellent protective film, prepared according to the method for preparing a liquid chemical kit for forming a water-repellent protective film as discussed in any of the above. As the treatment liquid (A) of the liquid chemical kit, it is preferable to use: one containing a mixture of 60 to 99.8 mass% of at least one kind of nonaqueous organic solvent selected from the group consisting of hydrofluoroethers, hydrochlorofluorocarbons, polyalcohol derivatives having no OH group and lactone-based solvents, and 0.2 to 40 mass% of at least one kind of silylation reagent selected from the group consisting of alkoxysilanes having C_xH_{2x+1} group (x=1-12) or $C_yF_{2y+1}CH_2CH_2$ group (y=1-8), trimethyldimethylaminosilane, trimethyldimethylaminosilane, trimethyldiethylaminosilane, dimethyldimethylaminosilane, dimethyldiethylaminosilane, butyldimethyl(dimethylamino)silane, butyldimethyl(diethylamino)silane, hexyldimethyl(dimethylamino)silane, hexyldimethyl(diethylamino)silane, octyldimethyl(dimethylamino)silane,

octyldimethyl(diethylamino)silane, decyldimethyl(dimethylamino)silane, decyldimethyl(diethylamino)silane, dodecyldimethyl(dimethylamino)silane and dodecyldimethyl(diethylamino)silane; or one consisting only of the mixture. Meanwhile, as the treatment liquid (B) of the liquid chemical kit, it is preferable to use: one containing a mixture of 60 to 99.9998 mass% of at least one kind of nonaqueous organic solvent selected from the group consisting of hydrofluoroethers, hydrochlorofluorocarbons, polyalcohol derivatives having no OH group and lactone-based solvents, and 0.0002 to 40 mass% of at least one kind of acid selected from the group consisting of trifluoroacetic acid, trifluoroacetic anhydride, trifluoromethanesulfonic acid, trifluoromethanesulfonic anhydride, trimethylsilyl trifluoroacetate, trimethylsilyl trifluoromethanesulfonate, dimethylsilyl trifluoroacetate, dimethylsilyl trifluoromethanesulfonate, butyldimethylsilyl trifluoroacetate, butyldimethylsilyl trifluoromethanesulfonate, hexyldimethylsilyl trifluoroacetate, hexyldimethylsilyl trifluoromethanesulfonate, octyldimethylsilyl trifluoroacetate, octyldimethylsilyl trifluoromethanesulfonate, decyldimethylsilyl trifluoroacetate, decyldimethylsilyl trifluoromethanesulfonate, dodecyldimethylsilyl trifluoroacetate and dodecyldimethylsilyl trifluoromethanesulfonate; or one consisting only of the mixture. Incidentally, at the time of preparing the liquid chemical for forming a water-repellent protective film by mixing the treatment liquid (A) and the treatment liquid (B), it is preferable to mix the nonaqueous organic solvent, the silylation reagent and the acid in an amount of 76 to 99.8999 mass %, 0.1 to 20 mass% and 0.0001 to 4 mass%, respectively, relative to the total amount of 100 mass% of the liquid chemical after preparation.

[0115] As the treatment liquid (A) of the liquid chemical kit, it is preferable to use: one containing a mixture of 60 to 99.8 mass% of at least one kind of nonaqueous organic solvent selected from the group consisting of hydrofluoroethers, hydrochlorofluorocarbons and polyalcohol derivatives having no OH group and 0.2 to 40 mass% of at least one kind of silylation

reagent selected from the group consisting of hexamethyldisilazane, tetramethyldisilazane, 1,3-dibutyltetramethyldisilazane, 1,3-dihexyltetramethyldisilazane, 1,3-dioctyltetramethyldisilazane, 1,3-didecyltetramethyldisilazane and 1,3-didodecyltetramethyldisilazane; or one consisting only of the mixture. Furthermore, as the treatment liquid (B) of the liquid chemical kit, it is preferable to use: one containing a mixture of 60 to 99.9998 mass% of at least one kind of nonaqueous organic solvent selected from the group consisting of hydrofluoroethers, hydrochlorofluorocarbons and polyalcohol derivatives having no OH group and 0.0002 to 40 mass% of at least one kind of acid selected from the group consisting of trifluoroacetic acid, trifluoroacetic anhydride, trifluoromethanesulfonic acid, trifluoromethanesulfonic anhydride, trimethylsilyl trifluoroacetate, trimethylsilyl trifluoromethanesulfonate, dimethylsilyl trifluoroacetate, dimethylsilyl trifluoromethanesulfonate, butyldimethylsilyl trifluoroacetate, butyldimethylsilyl trifluoromethanesulfonate, hexyldimethylsilyl trifluoroacetate, hexyldimethylsilyl trifluoromethanesulfonate, octyldimethylsilyl trifluoroacetate, octyldimethylsilyl trifluoromethanesulfonate, decyldimethylsilyl trifluoroacetate, decyldimethylsilyl trifluoromethanesulfonate, dodecyldimethylsilyl trifluoroacetate and dodecyldimethylsilyl trifluoromethanesulfonate; or one consisting only of the mixture. Incidentally, at the time of preparing the liquid chemical for forming a water-repellent protective film by mixing the treatment liquid (A) and the treatment liquid (B), it is preferable mix the nonaqueous organic solvent, the silylation reagent and the acid in an amount of 76 to 99.8999 mass %, 0.1 to 20 mass% and 0.0001 to 4 mass%, respectively, relative to the total amount of 100 mass% of the liquid chemical after preparation.

[0116] The liquid chemical for forming a protective film and a liquid chemical kit for forming a protective film, according to the present invention may contain another additive and the like within a range not affecting the scope of the present invention. As the additive, it is possible to cite oxidizing

agents such as hydrogen peroxide, ozone and the like, surfactants and the like.

[0117] In the liquid chemical obtained by the method of preparing a liquid chemical of the present invention or in the liquid chemical kit (a treatment liquid) obtained by the method of preparing a liquid chemical kit of the present invention, metal impurities and particles contained in the liquid chemical or the liquid chemical kit (the treatment liquid) may be eliminated by using a particle-eliminating membrane and an ion exchange resin membrane. Furthermore, the elimination of metal impurities and particles with use of the particle-eliminating membrane and the ion exchange resin membrane may be carried out at some time throughout the mixing step for the liquid chemical, the step of preparing a treatment liquid (A) for the liquid chemical and the step of preparing a treatment liquid (B) for the liquid chemical.

[0118] The liquid chemical for forming a protective film and the liquid chemical kit for forming a protective film, obtained according to the present invention are required to be low in metal impurity concentration. Hence a portion brought into contact with a liquid (e.g. the liquid chemical, the treatment liquid (A), the treatment liquid (B) and a feedstock solvent) at the time of preparing the liquid chemical or the liquid chemical kit and exemplified by a pipe brought into contact with a liquid to lead the liquid, a mixing bath and a storage bath is preferably formed of a resinous material not causing metal elution. Concrete examples of the resinous material are high-density polyethylene (HDPE), high-density polypropylene (PP), nylon-6,6, tetrafluoroethylene (PTFE), a copolymer of tetrafluoroethylene and perfluoroalkylvinylether (PFA), polychlorotrifluoroethylene (PCTFE), ethylene chlorotrifluoroethylene copolymer (ECTFE), ethylene tetrafluoroethylene (ETFE), tetrafluoroethylene hexapropylene copolymer (FEP) and the like. In addition, a liquid (e.g. the liquid chemical, the treatment liquid (A), the treatment liquid (B) and a feedstock solvent) is sometimes refined by filtration through a particle-eliminating resinous membrane and an ion exchange resin membrane, at the time of preparing the liquid chemical or the liquid chemical kit. In this case, the charge electric potential of the liquid is sometimes

increased by the contact between the liquid and the resin so as to increase the risk of causing static electricity disasters. Particularly in the case of a liquid containing a large amount of nonaqueous organic solvent, the charge electric potential tends to increase.

[0119] When conducting a discharge step of the present invention on the liquid (e.g. the liquid chemical, the treatment liquid (A), the treatment liquid (B) and a feedstock solvent) which is charged as above, the step is performed in such a manner as to bring the liquid into contact with an electrically conductive material which is grounded. The electrically conductive material can be exemplified by steel, cast iron, maraging steel, stainless steel, nickel and alloys thereof, cobalt and alloys thereof, aluminum, magnesium and alloys thereof, copper and alloys thereof, titanium, zirconium, tantalum, niobium and alloys thereof, lead and alloys thereof, noble metals such as gold, silver, platinum, palladium, rhodium, iridium, ruthenium and osmium and alloys thereof, diamond, glassy carbon and the like. The electrically conductive material is preferably one which is low in amount of metal elution into the liquid. For example, under such a condition that a charged liquid (e.g. a liquid chemical, a treatment liquid (A), a treatment liquid (B) and a feedstock solvent) is in contact with an electrically conductive material at 45°C for 700 hours, an immersion test using the liquid and a test piece of the electrically conductive material. Then, the elution amount of each of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag per unit area of the test piece in the immersion test is determined. The elution amount is converted into the concentration while adapting practical facility conditions (a contacting area formed between the liquid and the electrically conductive material and the throughput of the liquid) thereto. It is preferable to select an electrically conductive material in which the thus obtained concentration of each of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag in the liquid is less than 0.01 mass ppb, or less than the minimum determination limit concerning elements having a minimum determination limit of not less than 0.01 mass ppb. The above-mentioned "less than the minimum determination

limit" means a value less than a minimum determination limit prescribed by a larger one of: a concentration obtained by determining a standard deviation among concentrations detected by six times of blank test measurement and multiplying the standard deviation by 10; and a concentration that corresponds to the response accounting for five times the noise of an inductively coupled plasma mass spectroscope. Furthermore, one having a higher electric conductivity is more preferable. In view of the above, it is particularly preferable that the electrically conductive material is stainless steel, gold, platinum, diamond, glassy carbon and the like.

[0120] As a method for bringing an electrically charged liquid (e.g. the liquid chemical, the treatment liquid (A), the treatment liquid (B) and a feedstock solvent) into contact with the electrically conductive material in the discharge step, it is possible to bring the liquid into contact with the electrically conductive material by disposing the electrically conductive material inside a pipe for leading the liquid (in such a manner as to put the electrically conductive material into the pipe), for example. Thus, a discharging method carried out in-line so as not to be contacted with the human body is preferable in view of safety. The time during which the liquid and the electrically conductive material are contacted is preferably long in view of reducing the charge electric potential; meanwhile, in view of metal elution associated with the electrically conductive material being corroded by the liquid, the contact time is preferably short. From the above viewpoint, the contact time is preferably 0.001 to 1 second, more preferably 0.01 to 0.1 second. It is also possible to dispose two or more sections where the electrically charged liquid and the electrically conductive material are contacted, at the time of preparing the liquid chemical or the liquid chemical kit.

EXAMPLES

[0121] [Example 1]

A first refinement step was performed by the so-called one-pass filtration system where propylene glycol monomethyl ether acetate (PGMEA) was permeated through an ion exchange resin membrane (ION CLEAN SL No.

DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 1) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 1) at a flow rate of 0.6 L/min one time, thereby eliminating metal impurities from the solvent. In a mixing step, 1000 g of hexamethyldisilazane as a silylation reagent [HMDS: $(CH_3)_3SiNHSi(CH_3)_3$] and 36 g of acid (trifluoroacetic anhydride [$(CF_3CO)_2O$]) as an agent for forming a water-repellent protective film were added to 18964 g of PGMEA of after the first refinement step. Furthermore, a second refinement step was conducted by one-pass filtration system where the liquid chemical of after the mixing step was permeated through an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 2) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 2) at a flow rate of 0.3 L/min, thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles had been eliminated. The conditions for preparing the liquid chemical are shown in Table 1. As a result of measuring the metal impurity concentration of each of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag relative to the total amount of the obtained liquid chemical by using an inductively coupled plasma mass spectroscope (Agilent 7500cs model produced by Yokogawa Analytical Systems Inc.), it was confirmed to be as follows: Na=0.02 mass ppb, Mg=less than 0.03 mass ppb, K=less than 0.03 mass ppb, Ca=less than 0.08 mass ppb, Mn=less than 0.001 mass ppb, Fe=0.02 mass ppb, Cu=0.005 mass ppb, Li=less than 0.001 mass ppb, Al=less than 0.03 mass ppb, Cr=less than 0.05 mass ppb, Ni=less than 0.002 mass ppb, Zn=less than 0.04 mass ppb and Ag=less than 0.004 mass ppb (wherein "less than" means a value less than a minimum determination limit prescribed by a larger one of: a concentration obtained by determining a standard deviation among concentrations detected by six times of blank test measurement and

multiplying the standard deviation by 10; and a concentration that corresponds to the response accounting for five times the noise of an inductively coupled plasma mass spectroscope. As a result of conducting particle measurement in a liquid phase by a laser light-scattering type detector or measuring the number of particles of larger than 0.2 μm by using a laser light-scattering type measuring apparatus (KS-42AF model produced by RION Co., Ltd.), the number of particles of larger than 0.2 μm was 5 per 1 mL of the liquid chemical. The results of evaluating the obtained liquid chemical are shown in Table 2.

[0122] [Table 1]

	Silylation Reagent	Solvent	Embodiment	First Refinement Step (Solvent Refinement Method)	Second or Third Refinement Step (Liquid Chemical Refinement Method)	Preparation Method	Remarks (Number of Filters)
Example 1	HMDS	PGMEA	1st	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each 2nd Refinement: 2 each
Example 2	HMDS	PGMEA	1st	Reduced-pressure distillation	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	2nd Refinement: 2 each
Example 3	TMSDMA	PGMEA	1st	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each 2nd Refinement: 2 each
Example 4	TMDS	PGMEA	1st	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each 2nd Refinement: 2 each
Example 5	TMDS	PGMEA	1st	Reduced-pressure distillation	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	2nd Refinement: 2 each
Example 6	HMDS	PGMEA	1st	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 2 each 2nd Refinement: 4 each
Example 7	HMDS	PGMEA	1st	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each 2nd Refinement: 1 each
Example 8	HMDS	PGMEA	1st	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	2nd	3rd Refinement: 2 each
Example 9	HMDS	PGMEA	1st	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	2nd	3rd Refinement: 4 each
Comparative Example 1	HMDS	PGMEA	—	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	—	—	1st Refinement: 1 each
Comparative Example 2	HMDS	PGMEA	—	—	—	—	—

[0123] [Table 2]

	Metal impurity Concentration (mass ppb)													Number of Particles (per 1 mL)
	Na	Mg	K	Ca	Mn	Fe	Cu	Li	Al	Cr	Ni	Zn	Ag	
Example 1	0.02	<0.03	<0.03	<0.08	<0.001	0.02	0.005	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5
Example 2	0.04	<0.03	<0.03	<0.08	<0.001	0.04	0.02	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	12
Example 3	0.02	<0.03	<0.03	<0.08	<0.001	0.02	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	7
Example 4	0.02	<0.03	<0.03	<0.08	<0.001	0.02	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	8
Example 5	0.04	<0.03	<0.03	<0.08	<0.001	0.04	0.025	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	15
Example 6	<0.02	<0.03	<0.03	<0.08	<0.001	<0.02	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	4
Example 7	0.04	<0.03	<0.03	<0.08	<0.001	0.03	0.016	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	6
Example 8	0.08	<0.03	0.08	<0.08	0.003	0.09	0.012	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5
Example 9	0.06	<0.03	0.06	<0.08	<0.001	0.07	0.009	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	4
Comparative Example 1	0.06	<0.03	0.05	<0.08	<0.001	0.07	0.008	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	240
Comparative Example 2	0.58	0.12	0.28	0.37	0.024	0.42	0.078	0.007	<0.03	0.06	0.008	<0.04	<0.004	800

[0124] [Example 2]

The procedure of Example 1 was repeated with the exception that the first refinement step was carried out by distilling PGMEA under a condition of 80°C and under a reduced pressure of 10 kPa to eliminate metal impurities from the solvent, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 1 and the results of evaluating the obtained liquid chemical are shown in Table 2.

[0125] [Examples 3-5]

The agent for forming a water-repellent protective film, used in Example 1 and the first refinement step conducted in Example 1 were modified thereby obtaining a liquid chemical for forming a protective film. Incidentally, "Reduced-pressure distillation" indicated in Tables means the same operations as the reduced-pressure distillation conducted in Example 2. The conditions for preparing the liquid chemical are shown in Table 1 and the results of evaluating the obtained liquid chemical are shown in Table 2.

[0126] By the way, "TMSDMA" means trimethylsilyl dimethylamine [$(CH_3)_3SiN(CH_3)_2$], and "TMDS" means tetramethyldisilazane [$(CH_3)_2Si(H)NHSi(H)(CH_3)_2$].

[0127] [Example 6]

The procedure of Example 1 was repeated with the exception that an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 2) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of capsule filter: 2) were used in the first refinement step while an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 4) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 4) were used in the second refinement step, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 1 and the results of evaluating the obtained liquid chemical are shown in Table 2.

[0128] [Example 7]

The procedure of Example 1 was repeated with the exception that an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 1) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 1) were used in the second refinement step, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 1 and the results of evaluating the obtained liquid chemical are shown in Table 2.

[0129] [Example 8]

The first refinement step of Example 1 was not performed. In a third refinement step, a liquid chemical of after the mixing step was refined by

being permeated through the same ion exchange resin membrane and particle-eliminating membrane as those used in the second refinement step of Example 1. However, metal impurities contained in the liquid chemical were not sufficiently eliminated only by permeating the liquid through one-pass system; therefore the liquid chemical was circulated to be permeated through the membrane two or more times, thereby eliminating the metal impurities sufficiently from the liquid chemical. With the exception of the above, the procedure of Example 1 was repeated thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles have been eliminated. The conditions for preparing the liquid chemical are shown in Table 1 and the results of evaluating the obtained liquid chemical are shown in Table 2.

[0130] [Example 9]

The procedure of Example 8 was repeated with the exception that an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 4) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 4) were used in the third refinement step, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 1 and the results of evaluating the obtained liquid chemical are shown in Table 2.

[0131] [Comparative Example 1]

The procedure of Example 1 was repeated with the exception that the second refinement step was not performed, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 1 and the results of evaluating the obtained liquid chemical are shown in Table 2.

[0132] [Comparative Example 2]

The procedure of Example 1 was repeated with the exception that the first and second refinement step were not performed, thereby obtaining a

liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 1 and the results of evaluating the obtained liquid chemical are shown in Table 2.

[0133] [Example 10]

A first refinement step was performed by one-pass filtration system where isopropanol (iPA) was permeated through an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 1) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 1) at a flow rate of 0.6 L/min, thereby eliminating metal impurities from the solvent. Likewise, a first refinement step was performed by one-pass filtration system where diethylene glycol monoethyl ether acetate (DGEEA) was permeated through an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 1) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 1) at a flow rate of 0.6 L/min, thereby eliminating metal impurities from the solvent. In a mixing step, 9 g of iPA of after the first refinement step, 9990 g of DGEEA of after the first refinement step and 1 g of 2-(perfluorohexyl)ethyl phosphonic acid [FHEPA: $CF_3(CF_2)_5(CH_2)_2P(O)(OH)_2$] as an agent for forming a water-repellent protective film were mixed. Furthermore, a second refinement step was conducted by one-pass filtration system where the liquid chemical of after the mixing step was permeated through an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 2) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 2) at a flow rate of 0.3 L/min, thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles had been eliminated. The conditions for

preparing the liquid chemical are shown in Table 3 and the results of evaluating the obtained liquid chemical are shown in Table 4.

[0134] [Table 3]

	Silylation Reagent	Solvent	Embodiment	First Refinement Step (Solvent Refinement Method)	Second or Third Refinement Step (Liquid Chemical Refinement Method)	Preparation Method	Remarks (Number of Filters)
Example 10	FHEPA	iPA / DGEEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each / 2nd Refinement: 2 each
Example 11	FHEPA	iPA / DGEEA	2nd	Atmospheric-pressure distillation (iPA) / Reduced-pressure distillation (DGEEA)	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	2nd Refinement: 2 each
Example 12	FHEPA	PGME / DGEEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each / 2nd Refinement: 2 each
Example 13	FHEPA	Water / DGEEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each 2nd Refinement: 2 each
Example 14	FHEPA	iPA / PGDA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each 2nd Refinement: 2 each
Example 15	FHEPA	iPA / DPGMEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each / 2nd Refinement: 2 each
Example 16	FHEPA	iPA / 13BGDA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each / 2nd Refinement: 2 each
Example 17	OPA	iPA / DGEEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each / 2nd Refinement: 2 each
Example 18	FHEPA	iPA / DGEEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 2 each 2nd Refinement: 4 each
Example 19	FHEPA	iPA / DGEEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each / 2nd Refinement: 1 each
Example 20	FHEPA	iPA / DGEEA	2nd	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	2nd	3rd Refinement: 2 each
Example 21	FHEPA	iPA / DGEEA	2nd	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	2nd	3rd Refinement: 4 each
Example 22	ED-200	iPA / DGEEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	1st Refinement: 1 each 2nd Refinement: 2 each
Comparative Example 3	FHEPA	iPA / DGEEA	—	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	—	—	1st Refinement: 1 each
Comparative Example 4	FHEPA	iPA / DGEEA	—	—	—	—	—

[0135] [Table 4]

	Metal impurity Concentration (mass ppb)													Number of Particles (per 1 mL)
	Na	Mg	K	Ca	Mn	Fe	Cu	Li	Al	Cr	Ni	Zn	Ag	
Example 10	0.04	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	6
Example 11	0.05	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	16
Example 12	0.02	<0.03	<0.03	<0.08	<0.001	0.02	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	8
Example 13	0.02	<0.03	<0.03	<0.08	<0.001	0.02	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	4
Example 14	0.02	<0.03	<0.03	<0.08	<0.001	0.02	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	3
Example 15	0.02	<0.03	<0.03	<0.08	<0.001	0.02	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	9
Example 16	0.03	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	11
Example 17	0.02	<0.03	<0.03	<0.08	<0.001	0.02	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5
Example 18	0.02	<0.03	<0.03	<0.08	<0.001	<0.02	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5
Example 19	0.06	<0.03	0.04	<0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	9
Example 20	0.08	<0.03	0.08	0.08	0.005	0.07	0.027	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	7
Example 21	0.07	<0.03	0.07	<0.08	0.003	0.05	0.019	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	9
Example 22	0.04	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	7
Comparative Example 3	0.07	<0.03	0.06	<0.08	0.002	0.06	0.018	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	360
Comparative Example 4	0.56	0.25	0.3	0.38	0.021	0.38	0.091	<0.001	<0.03	0.07	<0.002	<0.04	<0.004	900

[0136] [Example 11]

The first refinement step was carried out by distilling iPA under a condition of 120°C and 760 kPa under atmospheric pressure to eliminate metal impurities from the solvent. Likewise, the first refinement step was carried out by distilling DGEEA under a condition of 160°C and under a reduced pressure of 5 kPa to eliminate metal impurities from the solvent. In a mixing step, 9 g of iPA of after the first refinement step, 9990 g of DGEEA of after the first refinement step and 1 g of FHEPA as an agent for forming a water-repellent protective film were mixed. Furthermore, a second refinement step was conducted by one-pass filtration system where the liquid chemical of after the mixing step was permeated through an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 2) and a

particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 2) at a flow rate of 0.3 L/min, thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles had been eliminated. The conditions for preparing the liquid chemical are shown in Table 3 and the results of evaluating the obtained liquid chemical are shown in Table 4.

[0137] [Examples 12-17]

The agent for forming a water-repellent protective film and the solvents, used in Example 10 were modified thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 3 and the results of evaluating the obtained liquid chemical are shown in Table 4.

[0138] Incidentally, "PGME" means propylene glycol monomethyl ether, "PGDA" means propylene glycol diacetate, "DPGMEA" means dipropylene glycol monomethyl ether acetate, "13BGDA" means 1,3-butylene glycol diacetate, and "OPA" means octylphosphonic acid. In the case where two kinds of solvents were used, it can be known from the section "Solvent" of the table that one indicated in the upper line was used in an amount of 9 g and the other indicated in the lower line was used in an amount of 9990 g.

[0139] [Example 18]

The procedure of Example 10 was repeated with the exception that an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 2) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of capsule filter: 2) were used in the first refinement step while an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 4) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600

cm^2, Number of filter: 4) were used in the second refinement step, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 3 and the results of evaluating the obtained liquid chemical are shown in Table 4.

[0140] [Example 19]

The procedure of Example 10 was repeated with the exception that an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 1) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 1) were used in the second refinement step, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 3 and the results of evaluating the obtained liquid chemical are shown in Table 4.

[0141] [Example 20]

The first refinement step of Example 10 was not performed. In a third refinement step, a liquid chemical of after the mixing step was refined by being permeated through the same ion exchange resin membrane and particle-eliminating membrane as those used in the second refinement step of Example 10. However, metal impurities contained in the liquid chemical were not sufficiently eliminated only by permeating the liquid through one-pass system; therefore the liquid chemical was circulated to be permeated through the membrane two or more times, thereby eliminating the metal impurities sufficiently from the liquid chemical. With the exception of the above, the procedure of Example 10 was repeated thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles have been eliminated. The conditions for preparing the liquid chemical are shown in Table 3 and the results of evaluating the obtained liquid chemical are shown in Table 4.

[0142] [Example 21]

The procedure of Example 20 was repeated with the exception that

an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 4) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 4) were used in the third refinement step, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 3 and the results of evaluating the obtained liquid chemical are shown in Table 4.

[0143] [Example 22]

The procedure of Example 10 was repeated with the exception that polyoxyethylene octyl ether phosphate ED-200 (a mixture of $C_8H_{17}OC_2H_4OP(=O)(OH)_2$ and $\{C_8H_{17}OC_2H_4O\}_2P(=O)OH$, produced by TOHO Chemical Industry Co., Ltd.) was used as the agent for forming a water-repellent protective film, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 3 and the results of evaluating the obtained liquid chemical are shown in Table 4.

[0144] [Comparative Example 3]

The procedure of Example 10 was repeated with the exception that the second refinement step was not performed, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 3 and the results of evaluating the obtained liquid chemical are shown in Table 4.

[0145] [Comparative Example 4]

The procedure of Example 10 was repeated with the exception that the first and second refinement step were not performed, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 3 and the results of evaluating the obtained liquid chemical are shown in Table 4.

[0146] [Example 23]

A fourth refinement step was performed by one-pass filtration

system where PGMEA was permeated through an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 1) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 1) at a flow rate of 0.6 L/min, thereby eliminating metal impurities from the nonaqueous organic solvent. In a step of preparing a treatment liquid (A), 9000 g of PGMEA of after the fourth refinement step and 1000 g of octyl(dimethyl)dimethylaminosilane [ODMAS: $C_8H_{17}(CH_3)_2Si\text{-}N(CH_3)_2$] as a silylation reagent were mixed. Furthermore, a fifth refinement step was conducted by one-pass filtration system where the treatment liquid (A) of after the mixing step was permeated through an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 2) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 2) at a flow rate of 0.3 L/min, thereby obtaining a treatment liquid (A) from which metal impurities and particles had been eliminated. In a step of preparing a treatment liquid (B), 9712 g of PGMEA of after the fourth refinement step and 288 g of trifluoroacetic anhydride [$(CF_3CO)_2O$]) as acid were mixed. Furthermore, a fifth refinement step was conducted by one-pass filtration system where the treatment liquid (B) of after the mixing step was permeated through an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 2) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 2) at a flow rate of 0.3 L/min, thereby obtaining a treatment liquid (B) from which metal impurities and particles had been eliminated. Then, 1000 g of the treatment liquid (A) and 1000 g of the treatment liquid (B) were mixed thereby obtaining a liquid chemical for forming a water-repellent protective film. The conditions for

preparing the treatment liquids (A) and (B) are shown in Table 5 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 6.

[0147] [Table 5]

	Silylation Reagent	Nonaqueous Organic Solvent		Fourth Refinement Step (Nonaqueous Organic Solvent Refinement Method)	Fifth or Sixth Refinement Step (Treatment Liquid Refinement Method)	Preparation Method	Remarks (Number of Filters)
		Treatment Liquid (A)	Treatment Liquid (B)				
Example 23	ODMAS	PGMEA	PGMEA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 24	ODMAS	PGMEA	PGMEA	Reduced-pressure distillation	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	5th Refinement: 2 each
Example 25	ODMAS	DGEEA	DGEEA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 26	ODMAS	PGDA	PGDA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 27	ODMAS	DPGMEA	DPGMEA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 28	ODMAS	DPGMPE	DPGMPE	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 29	ODMAS	13BGDA	13BGDA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 30	ODMAS	14BGDA	14BGDA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 31	ODMAS	14BGDA	14BGDA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 32	ODMAS	PGMEA	GBL	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 33	BDMAS	PGDA	PGDA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 34	DOTMDS	PGDA	PGDA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 2 each
Example 35	ODMAS	PGMEA	PGMEA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 2 each 5th Refinement: 4 each
Example 36	ODMAS	PGMEA	PGMEA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	4th Refinement: 1 each 5th Refinement: 1 each
Example 37	ODMAS	PGMEA	PGMEA	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	4th	6th Refinement: 2 each
Example 38	ODMAS	PGMEA	PGMEA	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	4th	6th Refinement: 4 each
Comparative Example 5	ODMAS	PGMEA	PGMEA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	—	—	4th Refinement: 1 each
Comparative Example 6	ODMAS	PGMEA	PGMEA	—	—	—	—

[0148] [Table 6]

		Metal impurity Concentration (mass ppb)													Number of Particles (per 1 mL)
		Na	Mg	K	Ca	Mn	Fe	Cu	Li	Al	Cr	Ni	Zn	Ag	
Example 23	Treatment Liquid (A)	0.05	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	4
	Treatment Liquid (B)	0.03	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	6
	Liquid Chemical	0.04	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	6
Example 24	Treatment Liquid (A)	0.07	<0.03	<0.03	0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	21
	Treatment Liquid (B)	0.03	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	17
	Liquid Chemical	0.05	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	20
Example 25	Treatment Liquid (A)	0.06	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	8
	Treatment Liquid (B)	0.03	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	6
	Liquid Chemical	0.04	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	7
Example 26	Treatment Liquid (A)	0.05	<0.03	<0.03	<0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	12
	Treatment Liquid (B)	0.03	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	17
	Liquid Chemical	0.04	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	15
Example 27	Treatment Liquid (A)	0.05	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	9
	Treatment Liquid (B)	0.03	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	17
	Liquid Chemical	0.04	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	14
Example 28	Treatment Liquid (A)	0.04	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5
	Treatment Liquid (B)	0.03	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	18
	Liquid Chemical	0.04	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	12
Example 29	Treatment Liquid (A)	0.04	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	10
	Treatment Liquid (B)	0.04	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	16
	Liquid Chemical	0.04	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	14
Example 30	Treatment Liquid (A)	0.06	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	10
	Treatment Liquid (B)	0.04	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	16
	Liquid Chemical	0.05	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	14
Example 31	Treatment Liquid (A)	0.06	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	12
	Treatment Liquid (B)	0.04	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	19
	Liquid Chemical	0.05	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	17
Example 32	Treatment Liquid (A)	0.05	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	13
	Treatment Liquid (B)	0.04	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	18
	Liquid Chemical	0.05	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	15
Example 33	Treatment Liquid (A)	0.06	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	12
	Treatment Liquid (B)	0.03	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	17
	Liquid Chemical	0.04	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	15
Example 34	Treatment Liquid (A)	0.06	<0.03	<0.03	<0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	28
	Treatment Liquid (B)	0.05	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	13
	Liquid Chemical	0.05	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	22
Example 35	Treatment Liquid (A)	0.03	<0.03	<0.03	<0.08	<0.001	0.02	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	8
	Treatment Liquid (B)	<0.02	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	3
	Liquid Chemical	0.02	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	6
Example 36	Treatment Liquid (A)	0.06	<0.03	<0.03	<0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	9
	Treatment Liquid (B)	0.05	<0.03	<0.03	<0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5
	Liquid Chemical	0.06	<0.03	<0.03	<0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	8
Example 37	Treatment Liquid (A)	0.09	<0.03	0.06	0.09	<0.001	0.08	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	4
	Treatment Liquid (B)	0.08	<0.03	0.05	0.09	<0.001	0.09	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	8
	Liquid Chemical	0.09	<0.03	0.06	0.09	<0.001	0.09	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5
Example 38	Treatment Liquid (A)	0.07	<0.03	0.04	<0.08	<0.001	0.06	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	3
	Treatment Liquid (B)	0.07	<0.03	0.04	0.08	<0.001	0.07	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5
	Liquid Chemical	0.07	<0.03	0.04	<0.08	<0.001	0.07	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5
Comparative Example 5	Treatment Liquid (A)	0.07	<0.03	0.05	0.08	<0.001	0.07	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	320
	Treatment Liquid (B)	0.06	<0.03	0.05	<0.08	<0.001	0.06	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	480
	Liquid Chemical	0.07	<0.03	0.05	<0.08	<0.001	0.07	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	400
Comparative Example 6	Treatment Liquid (A)	0.62	0.28	0.37	0.48	<0.001	0.51	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	750
	Treatment Liquid (B)	0.32	0.17	0.23	0.28	<0.001	0.62	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	900
	Liquid Chemical	0.47	0.24	0.31	0.38	<0.001	0.58	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	840

[0149] [Example 24]

The procedure of Example 23 was repeated with the exception that the fourth refinement step was carried out by distilling PGMEA under a condition of 80°C and under a reduced pressure of 10 kPa to eliminate metal impurities from the nonaqueous organic solvent, thereby obtaining treatment liquids (A) and (B). Additionally, 1000 g of the treatment liquid (A) and 1000 g of the treatment liquid (B) were mixed thereby obtaining a liquid chemical for forming a water-repellent protective film. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 5 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 6.

[0150] [Examples 25-34]

The procedure of Example 23 was repeated upon modifying the agent for forming a water-repellent protective film and the nonaqueous organic solvent, thereby obtaining treatment liquids (A) and (B). Moreover, a liquid chemical for forming a protective film was obtained from the treatment liquids (A) and (B). The conditions for preparing the treatment liquids (A) and (B) are shown in Table 5 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 6.

[0151] By the way, "DPGMPE" means dipropylene glycol methyl propyl ether, "14BGDA" means 1,4-butylene glycol diacetate, "GBL" means γ-butyrolactone, "BDMAS" means butyl(dimethyl)dimethylaminosilane [$C_4H_9(CH_3)_2Si\text{-}N(CH_3)_2$], "DOTMDS" means 1,3-dioctyltetramethyldisilazane [$C_8H_{17}(CH_3)_2SiNHSi(CH_3)_2C_8H_{17}$].

[0152] [Example 35]

The procedure of Example 23 was repeated with the exception that an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 2) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of capsule filter: 2) were used in the fourth refinement step while an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44

produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 4) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 4) were used in the fifth refinement step, thereby obtaining treatment liquids (A) and (B). Additionally, from the treatment liquids (A) and (B), a liquid chemical for forming a protective film was obtained. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 5 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 6.

[0153] [Example 36]

The procedure of Example 23 was repeated with the exception that an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 1) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of capsule filter: 1) were used in the fifth refinement step, thereby obtaining treatment liquids (A) and (B). Additionally, from the treatment liquids (A) and (B), a liquid chemical for forming a protective film was obtained. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 5 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 6.

[0154] [Example 37]

The fourth refinement step of Example 23 was not performed. In a sixth refinement step, a treatment liquid (A) of after the step for preparing a treatment liquid (A) and a treatment liquid (B) of after the step for preparing a treatment liquid (B) were refined by being independently permeated through the same ion exchange resin membrane and particle-eliminating membrane as those used in the fifth refinement step of Example 23. However, metal impurities contained in the treatment liquids were not sufficiently eliminated only by permeating them through one-pass system; therefore the treatment liquids were circulated to be permeated through the membrane two or more

times, thereby eliminating the metal impurities sufficiently from the treatment liquids. With the exception of the above, the procedure of Example 23 was repeated thereby obtaining treatment liquids (A) and (B). Additionally, from the treatment liquids (A) and (B), a liquid chemical for forming a protective film was obtained. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 5 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 6.

[0155] [Example 38]

The procedure of Example 37 was repeated with the exception that an ion exchange resin membrane (ION CLEAN SL No. DFA1SRPESW44 produced by Pall Corporation, Surface area: 1100 cm^2, Number of filter: 4) and a particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Optimizer D600 produced by Nihon Entegris K.K., Surface area: 600 cm^2, Number of filter: 4) were used in the sixth refinement step, thereby obtaining treatment liquids (A) and (B). Additionally, from the treatment liquids (A) and (B), a liquid chemical for forming a protective film was obtained. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 5 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 6.

[0156] [Comparative Example 5]

The procedure of Example 23 was repeated with the exception that the fifth refinement step was not performed, thereby obtaining treatment liquids (A) and (B). Additionally, from the treatment liquids (A) and (B), a liquid chemical for forming a protective film was obtained. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 5 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 6.

[0157] [Comparative Example 6]

The procedure of Example 23 was repeated with the exception that the fourth and fifth refinement step were not performed, thereby obtaining

treatment liquids (A) and (B). Additionally, from the treatment liquids (A) and (B), a liquid chemical for forming a protective film was obtained. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 5 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 6.

[0158] [Example 39]

A first refinement step was performed by one-pass filtration system where PGMEA was permeated through an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 4) at a flow rate of 20 L/min, thereby eliminating metal impurities from the solvent. In a mixing step, 1,910 kg of hexamethyldisilazane as a silylation reagent [HMDS: $(CH_3)_3SiNHSi(CH_3)_3$] and 69 kg of acid (trifluoroacetic anhydride [$(CF_3CO)_2O$]) as an agent for forming a water-repellent protective film were added to 36,200 kg of PGMEA of after the first refinement step. Furthermore, a second refinement step was conducted by one-pass filtration system where the liquid chemical of after the mixing step was permeated through an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 8) at a flow rate of 30 L/min, thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles had been eliminated. As the material of a portion of a pipe for leading a liquid after the mixing step which portion is to be brought into contact with the liquid, a copolymer of tetrafluoroethylene and perfluoroalkylvinylether (PFA) was employed. As a result of measuring the charged electric potential of the obtained liquid chemical by using an explosion-proof type digital static meter (KSD-0180 model produced by KASUGA DENKI, Inc.), the charged electric potential of the liquid chemical was 30 kV. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in

Table 8.

[0159] [Table 7]

	Silylation Reagent	Solvent	Embodiment	First Refinement Step (Solvent Refinement Method)	Second or Third Refinement Step (Liquid Chemical Refinement Method)	Preparation Method	Discharge Step	Remarks (Number of Filters)
Example 39	HMDS	PGMEA	1st	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	Not Performed	1st Refinement: 4 each 2nd Refinement: 8 each
Example 40	HMDS	PGMEA	1st	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	2nd	Not Performed	3rd Refinement: 8 each
Example 41	HMDS	PGMEA	1st	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	Performed	1st Refinement: 4 each 2nd Refinement: 8 each
Example 42	HMDS	PGMEA	1st	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	Performed	1st Refinement: 4 each 2nd Refinement: 8 each
Example 43	HMDS	PGMEA	1st	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	Performed	1st Refinement: 4 each 2nd Refinement: 8 each
Example 44	HMDS	PGMEA	1st	Reduced-pressure distillation	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	Performed	2nd Refinement: 8 each
Example 45	HMDS	PGMEA	1st	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	Performed	1st Refinement: 4 each 2nd Refinement: 4 each
Example 46	HMDS	PGMEA	1st	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	2nd	Performed	3rd Refinement: 8 each
Example 47	HMDS	PGMEA	1st	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	2nd	Performed	3rd Refinement: 12 each
Example 48	FHEPA	IPA DGEEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	Not Performed	1st Refinement: 4 each 2nd Refinement: 8 each
Example 49	FHEPA	IPA DGEEA	2nd	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	2nd	Not Performed	3rd Refinement: 8 each
Example 50	FHEPA	IPA DGEEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	Performed	1st Refinement: 4 each 2nd Refinement: 8 each
Example 51	FHEPA	IPA DGEEA	2nd	Atmospheric-pressure distillation (IPA) Reduced-pressure distillation (DGEEA)	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	Performed	2nd Refinement: 8 each
Example 52	FHEPA	IPA DGEEA	2nd	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	1st	Performed	1st Refinement: 4 each 2nd Refinement: 4 each
Example 53	FHEPA	IPA DGEEA	2nd	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	2nd	Performed	3rd Refinement: 8 each
Example 54	FHEPA	IPA DGEEA	2nd	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	2nd	Performed	3rd Refinement: 12 each

[0160] [Table 8]

	Metal impurity Concentration (mass ppb)													Number of Particles (per 1 mL)	Charged Potential of Liquid Chemical [kV]
	Na	Mg	K	Ca	Mn	Fe	Cu	Li	Al	Cr	Ni	Zn	Ag		
Example 39	0.03	<0.03	<0.03	<0.08	<0.001	0.04	0.008	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5	30
Example 40	0.09	<0.03	0.06	0.08	0.009	0.07	0.024	<0.001	<0.03	<0.05	0.021	<0.04	<0.004	6	36
Example 41	0.03	<0.03	<0.03	<0.08	<0.001	0.05	0.015	<0.001	<0.03	<0.05	0.008	<0.04	<0.004	8	0.4
Example 42	0.02	<0.03	<0.03	<0.08	<0.001	0.06	0.011	<0.001	<0.03	<0.05	0.005	<0.04	<0.004	10	0.6
Example 43	0.02	<0.03	<0.03	<0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	9	0.8
Example 44	0.04	<0.03	<0.03	<0.08	<0.001	0.06	0.021	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	18	0.3
Example 45	0.06	<0.03	<0.03	<0.08	<0.001	0.07	0.023	<0.001	<0.03	0.06	0.013	<0.04	<0.004	11	0.4
Example 46	0.08	<0.03	0.06	<0.08	0.015	0.08	0.028	<0.001	<0.03	<0.05	0.022	<0.04	<0.004	13	0.2
Example 47	0.07	<0.03	0.04	<0.08	0.007	0.06	0.016	<0.001	<0.03	0.06	0.015	<0.04	<0.004	8	0.2
Example 48	0.04	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	11	18
Example 49	0.07	<0.03	0.05	<0.08	0.016	0.08	0.021	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	7	23
Example 50	0.05	<0.03	<0.03	<0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	0.011	<0.04	<0.004	13	0.5
Example 51	0.05	<0.03	<0.03	<0.08	<0.001	0.06	0.009	<0.001	<0.03	<0.05	0.008	<0.04	<0.004	9	0.6
Example 52	0.06	<0.03	<0.03	<0.08	0.009	0.06	0.007	<0.001	<0.03	<0.05	0.015	<0.04	<0.004	12	0.5
Example 53	0.08	<0.03	0.07	<0.08	0.012	0.09	0.026	<0.001	<0.03	<0.05	0.024	<0.04	<0.004	8	0.6
Example 54	0.07	<0.03	0.05	<0.08	0.007	0.07	0.016	<0.001	<0.03	<0.05	0.018	<0.04	<0.004	5	0.5

[0161] [Example 40]

The first refinement step of Example 39 was not performed. In a third refinement step, a liquid chemical of after the mixing step was refined by being permeated through the same ion exchange resin membrane with particle-eliminating membrane as that used in the second refinement step of Example 39. However, metal impurities contained in the liquid chemical were not sufficiently eliminated only by permeating the liquid through one-pass system; therefore the liquid chemical was circulated to be permeated through the membrane two or more times, thereby eliminating the metal impurities sufficiently from the liquid chemical. With the exception of the above, the procedure of Example 39 was repeated thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles have been eliminated. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid

chemical are shown in Table 8.

[0162] [Example 41]

The procedure of Example 39 was repeated with the exception that the liquid chemical of after the second refinement step was led in-line through a grounded electrically conductive pipe (Material: SUS316) having an outer diameter of 34.0 mm and a length of 50 mm (wherein the time during which the electrically conductive material and the liquid chemical were contacted was 0.063 second), thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles have been eliminated. In an immersion test conducted by immersing a SUS316 test piece having a surface area of 14 cm^2 in 300 mL of a liquid chemical (the same as the liquid chemical obtained by this Example) at 45°C for 700 hours, the elution amount of each of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag was firstly determined. As a result of converting the elution amount into the concentration while adapting the conditions of this Example (Contacting area formed between the liquid chemical and the electrically conductive material: 32 cm^2, Throughput of the liquid chemical: 38,179 kg) thereto, the liquid chemical was confirmed to have a concentration of each of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag of less than 0.01 mass ppb, or less than the minimum determination limit concerning elements having a minimum determination limit of not less than 0.01 mass ppb. Accordingly, SUS316 was employed as the electrically conductive pipe. As the material of a portion of a pipe for leading a liquid after the mixing step, other than the electrically conductive pipe, PFA was employed. The charged electric potential of the obtained liquid chemical was 0.4 kV. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0163] [Example 42]

The procedure of Example 41 was repeated with the exception that an electrically conductive pipe having an outer diameter of 34.0 mm and a length of 24 mm (Material: SUS316, Time during which an electrically

conductive material and a liquid chemical are contacted: 0.030 second) was used as an electrically conductive material, thereby obtaining a liquid chemical for forming a protective film. The charged electric potential of the obtained liquid chemical was 0.6 kV. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0164] [Example 43]

The procedure of Example 41 was repeated with the exception that an electrically conductive pipe having an outer diameter of 34.0 mm and a length of 10 mm (Material: SUS316, Time during which an electrically conductive material and a liquid chemical are contacted: 0.013 second) was used as an electrically conductive material, thereby obtaining a liquid chemical for forming a protective film. The charged electric potential of the obtained liquid chemical was 0.8 kV. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0165] [Example 44]

The procedure of Example 42 was repeated with the exception that the first refinement step was carried out by distilling PGMEA under a condition of 80°C and under a reduced pressure of 10 kPa to eliminate metal impurities from the solvent, thereby obtaining a liquid chemical for forming a protective film. The charged electric potential of the obtained liquid chemical was 0.3 kV. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0166] [Example 45]

The procedure of Example 41 was repeated with the exception that an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 4) was used in the second refinement step, thereby obtaining

a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0167] [Example 46]

The first refinement step of Example 41 was not performed. In a third refinement step, a liquid chemical of after the mixing step was refined by being permeated through the same ion exchange resin membrane with particle-eliminating membrane as that used in the second refinement step of Example 41. However, metal impurities contained in the liquid chemical were not sufficiently eliminated only by permeating the liquid through one-pass system; therefore the liquid chemical was circulated to be permeated through the membrane two or more times, thereby eliminating the metal impurities sufficiently from the liquid chemical. With the exception of the above, the procedure of Example 41 was repeated thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles have been eliminated. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0168] [Example 47]

The procedure of Example 46 was repeated with the exception that an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 12) was used in the third refinement step, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0169] [Example 48]

A first refinement step was performed by one-pass filtration system where iPA was permeated through an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05

μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 4) at a flow rate of 20 L/min, thereby eliminating metal impurities from the solvent. Likewise, a first refinement step was performed by one-pass filtration system where DGEEA was permeated through an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 4) at a flow rate of 20 L/min, thereby eliminating metal impurities from the solvent. In a mixing step, 36 kg of iPA of after the first refinement step, 39,960 kg of DGEEA of after the first refinement step and 4 kg of 2-(perfluorohexyl)ethyl phosphonic acid [FHEPA: $CF_3(CF_2)_5(CH_2)_2P(O)(OH)_2$] as an agent for forming a water-repellent protective film were mixed. Furthermore, a second refinement step was conducted by one-pass filtration system where the liquid chemical of after the mixing step was permeated through an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 8) at a flow rate of 30 L/min, thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles had been eliminated. As the material of a portion of a pipe for leading a liquid after the mixing step which portion is to be brought into contact with the liquid, PFA was employed. The charged electric potential of the obtained liquid chemical was 18 kV. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0170] [Example 49]

The first refinement step of Example 48 was not performed. In a third refinement step, a liquid chemical of after the mixing step was refined by being permeated through the same ion exchange resin membrane with particle-eliminating membrane as that used in the second refinement step of Example 48. However, metal impurities contained in the liquid chemical

were not sufficiently eliminated only by permeating the liquid through one-pass system; therefore the liquid chemical was circulated to be permeated through the membrane two or more times, thereby eliminating the metal impurities sufficiently from the liquid chemical. With the exception of the above, the procedure of Example 48 was repeated thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles have been eliminated. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0171] [Example 50]

The procedure of Example 48 was repeated with the exception that the liquid chemical of after the second refinement step was led in-line through a grounded electrically conductive pipe (Material: SUS316) having an outer diameter of 34.0 mm and a length of 24 mm (wherein the time during which the electrically conductive material and the liquid chemical were contacted was 0.030 second), thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles have been eliminated. In an immersion test conducted by immersing a SUS316 test piece having a surface area of 14 cm^2 in 300 mL of a liquid chemical (the same as the liquid chemical obtained by this Example) at 45°C for 700 hours, the elution amount of each of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag was firstly determined. As a result of converting the elution amount into the concentration while adapting the conditions of this Example (Contacting area formed between the liquid chemical and the electrically conductive material: 15 cm^2, Throughput of the liquid chemical: 39,996 kg) thereto, the liquid chemical was confirmed to have a concentration of each of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag of less than 0.01 mass ppb, or less than the minimum determination limit concerning elements having a minimum determination limit of not less than 0.01 mass ppb. Accordingly, SUS316 was employed as the electrically conductive pipe. As the material of a portion of a pipe for leading a liquid after the mixing step, other than the

electrically conductive pipe, PFA was employed. The charged electric potential of the obtained liquid chemical was 0.5 kV. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0172] [Example 51]

The first refinement step was carried out by distilling iPA under a condition of 120°C and 760 kPa under atmospheric pressure to eliminate metal impurities from the solvent. Likewise, the first refinement step was carried out by distilling DGEEA under a condition of 160°C and under a reduced pressure of 5 kPa to eliminate metal impurities from the solvent. With the exception of the above, the procedure of Example 50 was repeated thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles have been eliminated. The charged electric potential of the obtained liquid chemical was 0.6 kV. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0173] [Example 52]

The procedure of Example 50 was repeated with the exception that an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 4) was used in the second refinement step, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0174] [Example 53]

The first refinement step of Example 50 was not performed. In a third refinement step, a liquid chemical of after the mixing step was refined by being permeated through the same ion exchange resin membrane with particle-eliminating membrane as that used in the second refinement step of Example 50. However, metal impurities contained in the liquid chemical

were not sufficiently eliminated only by permeating the liquid through one-pass system; therefore the liquid chemical was circulated to be permeated through the membrane two or more times, thereby eliminating the metal impurities sufficiently from the liquid chemical. With the exception of the above, the procedure of Example 50 was repeated thereby obtaining a liquid chemical for forming a protective film from which metal impurities and particles have been eliminated. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0175] [Example 54]

The procedure of Example 53 was repeated with the exception that an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 12) was used in the third refinement step, thereby obtaining a liquid chemical for forming a protective film. The conditions for preparing the liquid chemical are shown in Table 7 and the results of evaluating the obtained liquid chemical are shown in Table 8.

[0176] [Example 55]

A fourth refinement step was performed by one-pass filtration system where PGMEA was permeated through an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 4) at a flow rate of 20 L/min, thereby eliminating metal impurities from the nonaqueous organic solvent. In a step of preparing a treatment liquid (A), 34,100 kg of PGMEA of after the fourth refinement step and 3,800 kg of octyl(dimethyl)dimethylaminosilane [ODMAS: $C_8H_{17}(CH_3)_2Si\text{-}N(CH_3)_2$] as a silylation reagent were mixed. Furthermore, a fifth refinement step was conducted by one-pass filtration system where the treatment liquid (A) of after the mixing step was permeated through an ion exchange resin membrane with

particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 8) at a flow rate of 30 L/min, thereby obtaining a treatment liquid (A) from which metal impurities and particles had been eliminated. In a step of preparing a treatment liquid (B), 38,000 kg of PGMEA of after the fourth refinement step and 1,130 kg of trifluoroacetic anhydride [$(CF_3CO)_2O$]) as acid were mixed. Furthermore, a fifth refinement step was conducted by one-pass filtration system where the treatment liquid (B) of after the mixing step was permeated through an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 8) at a flow rate of 30 L/min, thereby obtaining a treatment liquid (B) from which metal impurities and particles had been eliminated. As the material of a portion of a pipe for leading each of the treatment liquids after the step for preparing a treatment liquid (A) and the step for preparing a treatment liquid (B), PFA was employed. The charged electric potential of the treatment liquid (A) was 37 kV while the charged electric potential of the treatment liquid (B) was 24 kV. Then, 1 kg of the treatment liquid (A) and 1 kg of the treatment liquid (B) were mixed thereby obtaining a liquid chemical for forming a water-repellent protective film. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 9 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 10.

[0177] [Table 9]

	Silylation Reagent	Nonaqueous Organic Solvent		Fourth Refinement Step (Nonaqueous Organic Solvent Refinement Method)	Fifth or Sixth Refinement Step (Treatment Liquid Refinement Method)	Preparation Method	Discharge Step	Remarks (Number of Filters)
		Treatment Liquid (A)	Treatment Liquid (B)					
Example 55	ODMAS	PGMEA	PGMEA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	Treatment Liquid (A): Not Performed Treatment Liquid (B): Not Performed Liquid Chemical: —	4th Refinement: 4 each 5th Refinement: 8 each
Example 56	ODMAS	PGMEA	PGMEA	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	4th	Treatment Liquid (A): Not Performed Treatment Liquid (B): Not Performed Liquid Chemical: —	6th Refinement: 8 each
Example 57	ODMAS	PGMEA	PGMEA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	Treatment Liquid (A): Performed Treatment Liquid (B): Performed Liquid Chemical: —	4th Refinement: 4 each 5th Refinement: 8 each
Example 58	ODMAS	PGMEA	PGMEA	Reduced-pressure distillation	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	Treatment Liquid (A): Performed Treatment Liquid (B): Performed Liquid Chemical: —	5th Refinement: 8 each
Example 59	ODMAS	PGMEA	PGMEA	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	One-pass refinement using ion exchange resin membrane and particle-eliminating membrane	3rd	Treatment Liquid (A): Performed Treatment Liquid (B): Performed Liquid Chemical: —	4th Refinement: 4 each 5th Refinement: 4 each
Example 60	ODMAS	PGMEA	PGMEA	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	4th	Treatment Liquid (A): Performed Treatment Liquid (B): Performed Liquid Chemical: —	6th Refinement: 8 each
Example 61	ODMAS	PGMEA	PGMEA	—	Circulation refinement using ion exchange resin membrane and particle-eliminating membrane	4th	Treatment Liquid (A): Performed Treatment Liquid (B): Performed Liquid Chemical: —	6th Refinement: 12 each

[0178] [Table 10]

		Metal impurity Concentration (mass ppb)													Number of Particles (per 1 mL)	Charged Potential of Treatment Liquid [kV]
		Na	Mg	K	Ca	Mn	Fe	Cu	Li	Al	Cr	Ni	Zn	Ag		
Example 55	Treatment Liquid (A)	0.04	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	8	37
	Treatment Liquid (B)	0.04	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	13	24
	Liquid Chemical	0.04	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	11	—
Example 56	Treatment Liquid (A)	0.08	<0.03	0.05	0.08	<0.001	0.07	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	10	32
	Treatment Liquid (B)	0.09	<0.03	0.04	0.08	<0.001	0.08	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	14	21
	Liquid Chemical	0.09	<0.03	0.05	0.08	<0.001	0.08	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	12	—
Example 57	Treatment Liquid (A)	0.06	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	6	0.5
	Treatment Liquid (B)	0.03	<0.03	<0.03	<0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	3	0.7
	Liquid Chemical	0.05	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5	—
Example 58	Treatment Liquid (A)	0.06	<0.03	<0.03	0.08	<0.001	0.03	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	13	0.6
	Treatment Liquid (B)	0.05	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	16	0.5
	Liquid Chemical	0.06	<0.03	<0.03	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	15	—
Example 59	Treatment Liquid (A)	0.07	<0.03	<0.03	<0.08	<0.001	0.06	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	7	0.6
	Treatment Liquid (B)	0.05	<0.03	0.04	<0.08	<0.001	0.04	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	6	0.7
	Liquid Chemical	0.06	<0.03	0.03	<0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	7	—
Example 60	Treatment Liquid (A)	0.09	<0.03	0.06	<0.08	<0.001	0.08	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	7	0.6
	Treatment Liquid (B)	0.07	<0.03	0.03	0.09	<0.001	0.06	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	11	0.6
	Liquid Chemical	0.08	<0.03	0.04	0.08	<0.001	0.07	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	9	—
Example 61	Treatment Liquid (A)	0.08	<0.03	0.05	<0.08	<0.001	0.07	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	9	0.5
	Treatment Liquid (B)	0.06	<0.03	0.04	<0.08	<0.001	0.05	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	5	0.6
	Liquid Chemical	0.07	<0.03	0.04	<0.08	<0.001	0.06	<0.003	<0.001	<0.03	<0.05	<0.002	<0.04	<0.004	7	—

[0179] [Example 56]

The fourth refinement step of Example 55 was not performed. In a sixth refinement step, the treatment liquid (A) of after the step of preparing a treatment liquid (A) and the treatment liquid (B) of after the step of preparing a treatment liquid (B) were refined by being independently permeated through the same ion exchange resin membrane with particle-eliminating membrane as that used in the fifth refinement step of Example 55. However, metal impurities contained in either of the treatment liquids were not sufficiently eliminated only by permeating the liquid through one-pass system; therefore the treatment liquids were circulated to be permeated through the membrane two or more times, thereby eliminating the metal impurities sufficiently from the treatment liquids. With the exception of the above, the procedure of Example 55 was repeated thereby obtaining treatment liquids (A) and (B). Additionally, from the treatment liquids (A) and (B), a liquid chemical for forming a protective film was obtained. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 9 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 10.

[0180] [Example 57]

The procedure of Example 55 was repeated with the exception that the treatment liquid (A) of after the fifth refinement step was led in-line through a grounded electrically conductive pipe (Material: platinum) having an outer diameter of 34.0 mm and a length of 24 mm (wherein the time during which the electrically conductive material and the treatment liquid were contacted was 0.030 second), thereby obtaining a treatment liquid (A) from which metal impurities and particles have been eliminated. In addition, the procedure of Example 55 was repeated with the exception that the treatment liquid (B) of after the fifth refinement step was led in-line through a grounded electrically conductive pipe (Material: platinum) having an outer diameter of 34.0 mm and a length of 24 mm (wherein the time during which the electrically conductive material and the treatment liquid were contacted was 0.030 second), thereby obtaining a treatment liquid (B) from which metal impurities and

particles have been eliminated. In an immersion test conducted by immersing a platinum test piece having a surface area of 14 cm^2 in 300 mL of each treatment liquid (the same as the treatment liquid (A) and the treatment liquid (B) obtained in this Example) at 45°C for 700 hours, the elution amount of each of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag was firstly determined. As a result of converting the elution amount into the concentration while adapting the conditions of this Example (Contacting area formed between the treatment liquid and the electrically conductive material: 15 cm^2, Throughput of the treatment liquid (A): 37,900 kg, Throughput of the treatment liquid (B): 39,130 kg) thereto, each of the treatment liquids was confirmed to have a concentration of each of the elements Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag of less than 0.01 mass ppb, or less than the minimum determination limit concerning elements having a minimum determination limit of not less than 0.01 mass ppb. Accordingly, platinum was employed as the electrically conductive pipe. As the material of a portion of a pipe for leading each of the treatment liquids after the step for preparing a treatment liquid (A) and the step for preparing a treatment liquid (B), other than the electrically conductive pipe, PFA was employed. The charged electric potential of the obtained treatment liquid (A) was 0.5 kV while the charged electric potential of the treatment liquid (B) was 0.7 kV. Then, 1 kg of the treatment liquid (A) and 1 kg of the treatment liquid (B) were mixed thereby obtaining a liquid chemical for forming a water-repellent protective film. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 9 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 10.

[0181] [Example 58]

The procedure of Example 57 was repeated with the exception that the fourth refinement step was carried out by distilling PGMEA under a condition of 80°C and under a reduced pressure of 10 kPa to eliminate metal impurities from the nonaqueous organic solvent, thereby obtaining treatment liquids (A) and (B). The charged electric potential of the obtained treatment

liquid (A) was 0.6 kV while the charged electric potential of the treatment liquid (B) was 0.5 kV. Then, 1 kg of the treatment liquid (A) and 1 kg of the treatment liquid (B) were mixed thereby obtaining a liquid chemical for forming a water-repellent protective film. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 9 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 10.

[0182] [Example 59]

The procedure of Example 57 was repeated with the exception that an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 4) was used in the fifth refinement step, thereby obtaining treatment liquids (A) and (B). Additionally, from the treatment liquids (A) and (B), a liquid chemical for forming a protective film was obtained. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 9 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 10.

[0183] [Example 60]

The fourth refinement step of Example 57 was not performed. In a sixth refinement step, the treatment liquid (A) of after the step of preparing a treatment liquid (A) and the treatment liquid (B) of after the step of preparing a treatment liquid (B) were refined by being independently permeated through the same ion exchange resin membrane with particle-eliminating membrane as that used in the fifth refinement step of Example 57. However, metal impurities contained in either of the treatment liquids were not sufficiently eliminated only by permeating the liquid through one-pass system; therefore the treatment liquids were circulated to be permeated through the membrane two or more times, thereby eliminating the metal impurities sufficiently from the treatment liquids. With the exception of the above, the procedure of Example 57 was repeated thereby obtaining treatment liquids (A) and (B).

Additionally, from the treatment liquids (A) and (B), a liquid chemical for forming a protective film was obtained. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 9 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 10.

[0184] [Example 61]

The procedure of Example 60 was repeated with the exception that an ion exchange resin membrane with particle-eliminating membrane having a particle-eliminating diameter of 0.05 μm (Protego Plus LTX No. PRLZ02PQ1K produced by Nihon Entegris K.K., Surface area: 1.38 m^2, Number of filter: 12) was used in the sixth refinement step, thereby obtaining treatment liquids (A) and (B). Additionally, from the treatment liquids (A) and (B), a liquid chemical for forming a protective film was obtained. The conditions for preparing the treatment liquids (A) and (B) are shown in Table 9 and the results of evaluating the obtained treatment liquids (A) and (B) and liquid chemical are shown in Table 10.

CLAIMS

[Claim 1] A method for preparing a liquid chemical for forming a water-repellant protective film, the liquid chemical having a solvent and an agent for forming a water-repellant protective film, the liquid chemical being for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the uneven pattern at its surface, the method being characterized by comprising:

a first refinement step for eliminating the elements (metal impurities) Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag in a solvent by distilling the solvent or by using a particle-eliminating membrane and an ion exchange resin membrane;

a mixing step for mixing the solvent of after the first refinement step and an agent for forming a water-repellant protective film; and

a second refinement step for eliminating particles in a liquid chemical of after the mixing step by using a particle-eliminating membrane.

[Claim 2] A method for preparing a liquid chemical for forming a water-repellant protective film, as claimed in claim 1, characterized by further comprising a discharge step where at least one selected from the solvent of after the first refinement step and the liquid chemical for forming a water-repellent protective film which liquid chemical is obtained after the second refinement step is brought into contact with an electrically conductive material.

[Claim 3] A method for preparing a liquid chemical for forming a water-repellant protective film, the liquid chemical having a solvent and an agent for forming a water-repellant protective film, the liquid chemical being for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the uneven pattern at its surface, the method being characterized by comprising:

a mixing step for mixing a solvent and an agent for forming a

water-repellant protective film; and

a third refinement step for eliminating the elements (metal impurities) Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag and particles in a liquid chemical obtained after the mixing step, by using a particle-eliminating membrane and an ion exchange resin membrane.

[Claim 4] A method for preparing a liquid chemical for forming a water-repellant protective film, as claimed in claim 3, characterized by further comprising a discharge step where the liquid chemical obtained after the third refinement step is brought into contact with an electrically conductive material.

[Claim 5] A method for preparing a liquid chemical for forming a water-repellant protective film, as claimed in any of claims 1 to 4, characterized in that the agent for forming a water-repellant protective film comprises at least one selected from the group consisting of silylation reagents represented by the following general formula [1] and an acid or base.

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

[In the formula [1], R^1 mutually independently represents a monovalent organic group having a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^1 mutually independently represents at least one selected from the group consisting of a monovalent functional group of which element to be bonded to a silicon element is nitrogen, a monovalent functional group of which element to be bonded to a silicon element is oxygen, a halogen group, a nitrile group and –CO–NH–$Si(CH_3)_3$ group; "a" is an integer of from 1 to 3; "b" is an integer of from 0 to 2; and the total of "a" and "b" is 1 to 3.]

[Claim 6] A method for preparing a liquid chemical for forming a water-repellant protective film, as claimed in claim 5, characterized in that the acid comprises at least one selected from the group consisting of hydrogen

chloride, sulfuric acid, perchloric acid, phosphoric acid, sulfonic acid represented by the following general formula [2] and anhydride thereof, carboxylic acid represented by the following general formula [3] and anhydride thereof, alkyl borate ester, aryl borate ester, boron tris(trifluoroacetate), trialkoxyboroxin, boron trifluoride and a silane compound represented by the following general formula [4].

$R^2S(O)_2OH$ [2]

[In the formula [2], R^2 represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s).]

R^3COOH [3]

[In the formula [3], R^3 represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s).]

$(R^4)_cSi(H)_dX^2_{4-c-d}$ [4]

[In the formula [4], R^4 mutually independently represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^2 mutually independently represents at least one selected from the group consisting of chloro group, $-OCO-R^5$ (where R^5 is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)) and $-OS(O)_2-R^6$ (where R^6 is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)); "c" is an integer of from 1 to 3; "d" is an integer of from 0 to 2; and the total of "c" and "d" is 1 to 3.]

[Claim 7] A method for preparing a liquid chemical for forming a water-repellant protective film, as claimed in claim 5, characterized in that the base comprises at least one selected from the group consisting of ammonia, N,N,N',N'-tetramethylethylenediamine, triethylenediamine, dimethylaniline, alkylamine, dialkylamine, trialkylamine, pyridine, piperazine,

N-alkylmorpholine and a silane compound represented by the following general formula [5].

$(R^7)_eSi(H)_fX^3{}_{4-e-f}$ [5]

[In the formula [5], R^7 mutually independently represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^3 mutually independently represents a monovalent functional group of which element to be bonded to a silicon element is nitrogen, the monovalent functional group possibly containing a fluorine element or a silicon element; "e" is an integer of from 1 to 3; "f" is an integer of from 0 to 2; and the total of "e" and "f" is 1 to 3.]

[Claim 8] A method for preparing a liquid chemical for forming a water-repellant protective film, as claimed in any of claims 5 to 7, characterized in that the solvent comprises at least one selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen-containing solvents, sulfoxide-based solvents, lactone-based solvents, carbonate-based solvents, polyalcohol derivatives having no OH group, and nitrogen element-containing solvents having no N–H group.

[Claim 9] A method for preparing a liquid chemical for forming a water-repellant protective film on a wafer, as claimed in any of claims 1 to 4, characterized in that the agent for forming a water-repellant protective film comprises at least one kind selected from the group consisting of compounds represented by the following general formulas [6] to [13] and their salts.

R^8–$P(=O)(OH)_g(R^9)_{2-g}$ [6]

[In the formula [6], R^8 represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); R^9 mutually independently represents a monovalent organic group having a C_1-C_3 hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); and "g" is an integer of from 0 to 2.]

R^{10}–C(=O)–X^4 [7]

[In the formula [7], R^{10} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; X^4 represents a group selected from the group consisting of fluoro group, chloro group, bromo group and iodo group.]

$R^{11}R^{12}R^{13}N$ [8]

[In the formula [8], R^{11} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; R^{12} represents a hydrogen element, a monovalent organic group having a C_1-C_{18} hydrocarbon group, or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; R^{13} represents a hydrogen element, a monovalent organic group having a C_1-C_{18} hydrocarbon group, or a monovalent organic group having a C_1-C_8 fluoroalkyl chain.]

R^{14}–C(=O)–X^5–X^6 [9]

[In the formula [9], R^{14} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; X^5 represents an oxygen element or sulfur element; X^6 represents a group selected from the group consisting of a hydrogen element, alkyl group, aromatic group, pyridyl group, quinolyl group, succinimide group, maleimide group, benzoxazole group, benzothiazole group and benzotriazole group; and a hydrogen element(s) of these groups may be substituted with an organic group.]

$R^{15}(X^7)_h$ [10]

[The formula [10] represents a compound where "h" hydrogen element(s) or fluorine element(s) of R^{15} representing a C_1-C_{18} hydrocarbon the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s) is mutually independently substituted with a group represented by X^7, the group X^7 being at least one selected from the group consisting of an isocyanate group, mercapto group, aldehyde group, –CONHOH group and a cyclic structure containing a nitrogen element, wherein "h" is an integer of from 1 to 6.]

R^{16}–X^8 [11]

[In the formula [11], X^8 represents a cyclic structure containing a sulfur element; R^{16} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain.]

R^{17}–C(=O)–X^9–C(=O)–R^{18} [12]

[In the formula [12], R^{17} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; R^{18} represents a monovalent organic group having a C_1-C_{18} hydrocarbon group or a monovalent organic group having a C_1-C_8 fluoroalkyl chain; and X^9 represents an oxygen element or a sulfur element.]

$(R^{24}–O–(R^{25}O)_t–)_uP(=O)(OH)_{3-u}$ [13]

[In the formula [13], R^{24} mutually independently represents a C_4-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); R^{25} mutually independently represents a C_2-C_6 divalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); "t" mutually independently represents an integer of from 0 to 10; and "u" is 1 or 2.]

[Claim 10] A method for preparing a liquid chemical for forming a water-repellant protective film, as claimed in claim 9, characterized in that the solvent comprises at least one selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen-containing solvents, sulfoxide-based solvents, lactone-based solvents, carbonate-based solvents, alcohols, polyalcohol derivatives, nitrogen element-containing solvents and water.

[Claim 11] A liquid chemical for forming a water-repellant protective film, prepared through the steps of the method for preparing a liquid chemical for forming a water-repellant protective film, as claimed in any of claims 1 to 10.

[Claim 12] A method for preparing a liquid chemical kit for forming a water-repellant protective film, the liquid chemical kit being for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the uneven pattern at its surface, the liquid chemical kit having a treatment liquid (A) that contains a nonaqueous organic solvent and a silylation reagent and a treatment liquid (B) that contains a nonaqueous organic solvent and an acid or base, the method being characterized by comprising:

a fourth refinement step for eliminating the elements (metal impurities) Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag in a nonaqueous organic solvent by distilling the nonaqueous organic solvent or by using a particle-eliminating membrane and an ion exchange resin membrane;

a step of preparing a treatment liquid (A) by mixing the nonaqueous organic solvent of after the fourth refinement step and a silylation reagent;

a step of preparing a treatment liquid (B) by mixing the nonaqueous organic solvent of after the fourth refinement step and an acid or base; and

a fifth refinement step for eliminating particles in the treatment liquid (A) of after the step of preparing the treatment liquid (A) and /or the treatment liquid (B) of after the step of preparing the treatment liquid (B), by using a particle-eliminating membrane.

[Claim 13] A method for preparing a liquid chemical kit for forming a water-repellant protective film, as claimed in claim 12, characterized by further comprising a discharge step where at least one selected from the nonaqueous organic solvent of after the fourth refinement step and a treatment liquid obtained after the fifth refinement step is brought into contact with an electrically conductive material.

[Claim 14] A method for preparing a liquid chemical kit for forming a water-repellant protective film, the liquid chemical kit being for forming a water-repellent protective film at least on surfaces of recessed portions of an uneven pattern of a wafer having the uneven pattern at its surface, the liquid chemical kit having a treatment liquid (A) that contains a nonaqueous organic solvent and a silylation reagent and a treatment liquid (B) that contains a nonaqueous organic solvent and an acid or base, the method being characterized by comprising:

a step of preparing a treatment liquid (A) by mixing a nonaqueous organic solvent and a silylation reagent;

a step of preparing a treatment liquid (B) by mixing a nonaqueous organic solvent and an acid or base; and

a sixth refinement step for eliminating the elements (metal impurities) Na, Mg, K, Ca, Mn, Fe, Cu, Li, Al, Cr, Ni, Zn and Ag and particles in the treatment liquid (A) of after the step of preparing the treatment liquid (A) and /or the treatment liquid (B) of after the step of preparing the treatment liquid (B), by using a particle-eliminating membrane and an ion exchange resin membrane.

[Claim 15] A method for preparing a liquid chemical kit for forming a water-repellant protective film, as claimed in claim 14, characterized by further comprising a discharge step where the treatment liquid (A) and/or the treatment liquid (B) obtained after the sixth refinement step is brought into contact with an electrically conductive material.

[Claim 16] A method for preparing a liquid chemical kit for forming a water-repellant protective film, as claimed in any of claims 12 to 15, characterized in that the nonaqueous organic solvent comprises at least one selected from the group consisting of hydrocarbons, esters, ethers, ketones, halogen-containing solvents, sulfoxide-based solvents, lactone-based solvents, carbonate-based solvents, polyalcohol derivatives having no OH group, and

nitrogen element-containing solvents having no N–H group.

[Claim 17] A method for preparing a liquid chemical kit for forming a water-repellant protective film, as claimed in any of claims 12 to 16, characterized in that the silylation reagent comprises at least one selected from the group consisting of silicon compounds represented by the following general formula [1].

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

[In the formula [1], R^1 mutually independently represents a monovalent organic group having a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^1 mutually independently represents at least one selected from the group consisting of a monovalent functional group of which element to be bonded to a silicon element is nitrogen, a monovalent functional group of which element to be bonded to a silicon element is oxygen, a halogen group, a nitrile group and –CO–NH–$Si(CH_3)_3$ group; "a" is an integer of from 1 to 3; "b" is an integer of from 0 to 2; and the total of "a" and "b" is 1 to 3.]

[Claim 18] A method for preparing a liquid chemical kit for forming a water-repellant protective film, as claimed in any of claims 12 to 17, characterized in that the silylation reagent comprises a silicon compound represented by the following general formula [14].

$R^{19}_iSiX^{10}_{4-i}$ [14]

[In the formula [14], R^{19} mutually independently represents at least one group selected from a hydrogen group and a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s), wherein the total number of carbons contained in all of the hydrocarbon groups bonded to a silicon element is not smaller than 6; X^{10} mutually independently represents at least one group selected from a monovalent functional group of which element to be bonded to a silicon element is nitrogen, a monovalent functional group of which element

to be bonded to a silicon element is oxygen, a halogen group, a nitrile group and –CO–NH–$Si(CH_3)_3$ group; "i" is an integer of from 1 to 3.]

[Claim 19] A method for preparing a liquid chemical kit for forming a water-repellant protective film, as claimed in any of claims 12 to 18, characterized in that the acid comprises at least one selected from the group consisting of hydrogen chloride, sulfuric acid, perchloric acid, phosphoric acid, sulfonic acid represented by the following general formula [2] and anhydride thereof, carboxylic acid represented by the following general formula [3] and anhydride thereof, alkyl borate ester, aryl borate ester, boron tris(trifluoroacetate), trialkoxyboroxin, boron trifluoride and a silane compound represented by the following general formula [4].

$R^2S(O)_2OH$ [2]

[In the formula [2], R^2 represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s).]

R^3COOH [3]

[In the formula [3], R^3 represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s).]

$(R^4)_cSi(H)_dX^2_{4-c-d}$ [4]

[In the formula [4], R^4 mutually independently represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^2 mutually independently represents at least one selected from the group consisting of chloro group, –OCO–R^5 (where R^5 is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)) and –$OS(O)_2$–R^6 (where R^6 is a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s)); "c" is an integer of from 1 to 3; "d" is an integer of from 0 to 2; and the total of "c" and "d" is 1 to 3.]

[Claim 20] A method for preparing a liquid chemical kit for forming a water-repellant protective film, as claimed in any of claims 12 to 18, characterized in that the base comprises at least one selected from the group consisting of ammonia, N,N,N',N'-tetramethylethylenediamine, triethylenediamine, dimethylaniline, alkylamine, dialkylamine, trialkylamine, pyridine, piperazine, N-alkylmorpholine and a silane compound represented by the following general formula [5].

$$(R^7)_eSi(H)_fX^3_{4-e-f} \quad [5]$$

[In the formula [5], R^7 mutually independently represents a C_1-C_{18} monovalent hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s); X^3 mutually independently represents a monovalent functional group of which element to be bonded to a silicon element is nitrogen, the monovalent functional group possibly containing a fluorine element or a silicon element; "e" is an integer of from 1 to 3; "f" is an integer of from 0 to 2; and the total of "e" and "f" is 1 to 3.]

[Claim 21] A liquid chemical kit for forming a water-repellant protective film, prepared through the steps of the method for preparing a liquid chemical kit for forming a water-repellant protective film, as claimed in any of claims 12 to 20.