SPECIFICATION

TITLE OF THE INVENTION:

LIQUID CHEMICAL FOR FORMING PROTECTING FILM

TECHNICAL FIELD

[0001] The present invention relates to a technique of cleaning a substrate (a wafer) in semiconductor device fabrication or the like.

BACKGROUND ART

[0002] Semiconductor devices for use in networks or digital household electric appliances are desired to be further sophisticated and multifunctional, and to be low in power consumption. Accordingly, the trend toward micro-patterning for circuits is continuing. Together with the continuation of micro-patterning, a pattern collapse in the circuits has become a significant problem. In semiconductor device fabrication, a cleaning step is greatly used for the purpose of removing particles and metal impurities. As a result of this, the cleaning step occupies 30-40% of the whole of the semiconductor fabrication step. A phenomenon observed in the cleaning step when an aspect ratio of pattern is high due to the micro-patterning for semiconductor device is a pattern collapse, in which a gas-liquid interface that comes about collapses the pattern at the time of passing therethrough and at the time of drying the wafer after cleaning or rinsing.

[0003] In Patent Publication 1, there is disclosed a method of suppressing the pattern collapse, i.e., a technique of changing a cleaning liquid from water to 2-propanol before the gas-liquid interface passes through a pattern. However, this is said to have some constraints, for example, in that an adaptable aspect ratio of pattern is not higher than 5.

[0004] Additionally, Patent Publication 2 discloses a technique directed toward a resist pattern as a method of suppressing the pattern collapse. This is a method of decreasing a capillary force as far as possible thereby suppressing the pattern collapse.

[0005] However, the thus disclosed technique is directed toward the resist pattern and is for reforming a resist itself. Moreover, it can finally be removed together with the resist so as not to need to estimate a process of removing a treatment agent after drying. Therefore, this cannot be applied to the objects of the present invention.

[0006] Additionally, there is set forth in Patent Publication 3 a cleaning process for: conducting surface-reforming of a wafer surface formed having an uneven pattern with a film containing silicon, by oxidation or the like; forming a water-repellent protecting film on the surface by using a water-soluble surfactant or a silane coupling agent; reducing the capillary force; and preventing the pattern collapse.

[0007] Furthermore, in Patent Publications 4 and 5, there is disclosed a technique for preventing the pattern collapse by conducting a hydrophobicity-imparting treatment in the use of a treatment liquid containing: a silylation agent represented by *N,N*-dimethylaminotrimethylsilane; and a solvent.

Prior Art Document

Patent Publication

[0008] Patent Publication 1: Japanese Patent Application Publication No. 2008-198958

Patent Publication 2: Japanese Patent Application Publication No. 5-299336

Patent Publication 3: Japanese Patent No. 4403202

Patent Publication 4: Japanese Patent Application Publication No. 2010-129932

Patent Publication 5: International Application Publication No. 10/47196 Pamphlet

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0009] The present invention relates to a technique for cleaning a substrate (a wafer) in semiconductor device fabrication and the like, the objective of

which is to enhance the production yield of devices having such a circuit pattern as to be particularly fine and high in aspect ratio, and more particularly to a water-repellent liquid chemical and the like with the objective of improving a cleaning step which tends to induce a wafer having at its surface an uneven pattern to cause an uneven pattern collapse.

Hitherto, there has generally been used a wafer containing silicon element at its surface; however, a wafer containing at its surface an element such as titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium (hereinafter, they may sometimes be referred to as "metal-based element") has become used together with the diversification of the pattern. However, in a case where a wafer having at its surface a substance that does not sufficiently contain reactive functional groups (e.g., silanol groups), such as the wafer containing the above-mentioned metal-based element at its surface, it is not possible to form a water-repellent protecting film for preventing the pattern collapse even if the treatment liquid or treatment method discussed in Patent Publications 3 to 5 is used, which is a problem in that the pattern collapse cannot be prevented.

Challenges for the present invention are: to form a water-repellent protecting film on a wafer having an uneven pattern at its surface and containing at least one kind element of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern (hereinafter, such a wafer sometimes be referred to as "a metal-based wafer" or merely "a wafer"), at least on the surfaces of the recessed portions so as to reduce interaction between a liquid retained in the recessed portions and the surfaces of the recessed portions thereby improving a cleaning step which tends to induce the pattern collapse; and to provide a liquid chemical for forming the protecting film, i.e., a liquid chemical which able to form the water-repellent protecting film.

Means for Solving the Problems

[0010] The pattern collapse is to occur when an gas-liquid interface passes through the pattern at the time of drying a wafer after cleaning the wafer with

a cleaning liquid. The reason therefor is said that a difference in height of residual liquid of the cleaning liquid between a part having high aspect ratio and a part having low aspect ratio causes a difference in capillary force which acts on the pattern.

[0011] Accordingly, it is expected, by decreasing the capillary force, that the difference in capillary force due to the difference in height of residual liquid is reduced thereby resolving the pattern collapse. The magnitude of the capillary force is the absolute value of P obtained by the equation as shown below. It is expected from this equation that the capillary force can be reduced by decreasing γ or $\cos\theta$.

[0012] $P = 2 \times \gamma \times \cos\theta / S$

(In the equation, γ represents the surface tension of a liquid retained in the recessed portions, θ represents the contact angle of the liquid retained in the recessed portions to the surfaces of the recessed portions, and S represents the width of the recessed portions.)

[0013] In the present invention, there is formed a water-repellent protecting film at least on the surfaces of the recessed portions of the uneven pattern when a liquid that remains in the recessed portions after the protecting film has been formed is removed from the recessed portions or dried. Therefore, the capillary force which acts on the recessed portions is so reduced that the pattern collapse becomes difficult to occur. Additionally, the protecting film is to be removed after the drying step.

[0014] A liquid chemical for forming a water-repellent protecting film, according to the present invention (hereinafter, the liquid chemical may sometimes be referred to as "a liquid chemical for forming a protecting film" or merely "a liquid chemical") is a liquid chemical including:

an agent for forming a water-repellent protecting film (hereinafter, the agent may sometimes be referred to as merely "a protecting-film-forming agent"), the agent being for forming a water-repellent protecting film (hereinafter, the film may sometimes be referred to as merely "a protecting film") on a wafer after a cleaning step for the wafer and before a drying step for

the wafer , the wafer having at its surface an uneven pattern and containing at least one kind element of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern, the water-repellent protecting film being formed at least on the surfaces of the recessed portions; and

a solvent,

the liquid chemical being characterized in that the agent for forming a water-repellent protecting film is a compound represented by the following general formula [1].

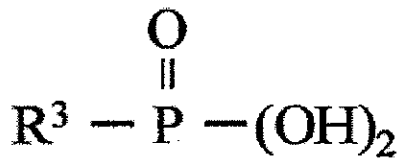
$$R^1 - \overset{\overset{O}{\|}}{P} - (OH)_a(R^2)_{2-a} \qquad [1]$$

(In the formula [1], R^1 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^2 mutually independently represents a monovalent organic group having a C_1-C_{18} hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s). a is an integer of from 0 to 2.)

[0015] By using the protecting-film-forming agent represented by the above-mentioned general formula [1], it becomes possible to form a water-repellent protecting film at least on the surfaces of the recessed portions of the metal-based wafer. In the protecting-film-forming agent, P–OH group and/or P=O group (hereinafter, these may sometimes be referred to as "a functional moiety") have compatibility with a substance containing the metal-based element. Incidentally, "having compatibility" means that Van der Waals force, a static interaction or the like acts between the surface of the substance containing the metal-based element and the functional moiety of the protecting-film-forming agent thereby causing adsorption and/or that the surface of the substance is reacted with the functional moiety of the protecting-film-forming agent to build a chemical bond thereby causing

adsorption. Additionally, R^1 is a hydrophobic moiety of the protecting-film-forming agent. Therefore, when the protecting-film-forming agent is adsorbed on the metal-based element of the metal-based wafer, hydrophobic moieties are arranged outward from the surface of the wafer thereby imparting repellency to the wafer surface.

[0016] Furthermore, it is preferable that the protecting-film-forming agent is a compound represented by the following general formula [2].



[2]

(In the formula [2], 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).)

[0017] As the metal-based wafer, it is possible to cite those containing at least one kind element of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at the surfaces of the recessed portions of the uneven pattern, preferably those containing at least one kind element of titanium, tungsten, aluminum and ruthenium, and particularly preferably those containing titanium element. In a case of a wafer containing silicon element at the surfaces of the recessed portions of the uneven pattern, there are a multitude of silanol groups (SiOH groups) on the surfaces. These silanol groups serve as reaction points to be reacted with a silane coupling agent, so that the water-repellent protecting film can easily be formed on the surfaces of the recessed portions. On the other hand, in a case of the metal-based wafer, the surface has fewer reaction points like the silanol groups, so that it is difficult to form the protecting film with a compound such as the silane coupling agent. Additionally, in the present invention, the wafer having at its surface an uneven pattern means a wafer which is in a condition where the uneven pattern has already been formed on the surface by etching, imprint or the like. Moreover, it is possible to adopt a wafer on which another process such as

metal routing has been performed, as far as the wafer has an uneven pattern at its surface.

[0018] The liquid chemical for forming a protecting film, according to the present invention is used in such a manner as to substitute a cleaning liquid with the liquid chemical during a cleaning step for the metal-based wafer. Additionally, the substituted liquid chemical may be substituted with another cleaning liquid.

[0019] Furthermore, a water-repellent protecting film of the present invention is a water-repellent protecting film formed on a wafer after a cleaning step for the wafer and before a drying step for the wafer, the wafer having at its surface an uneven pattern and containing at least one kind element of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern, the water-repellent protecting film being formed at least on the surfaces of the recessed portions by retaining the liquid chemical for forming a water-repellent protecting film at least in the recessed portions. The water-repellent protecting film is characterized by being formed of a compound represented by the general formula [1] and serving as an agent for forming a water-repellent protecting film. Incidentally, the water-repellent protecting film of the present invention may be such as to contain a reaction product having as the primary component a compound represented by the general formula [1].

[0020] The cleaning liquid is substituted with the liquid chemical for forming a protecting film after the cleaning step, and the liquid chemical is retained at least in the recessed portions of the uneven pattern as discussed above, during which the protecting film is formed at least on the surfaces of the recessed portions of the uneven pattern. The protecting film of the present invention may be not necessarily continuously formed and not necessarily uniformly formed. However, in order to impart more excellent water repellency, it is preferable to form the protecting film continuously and uniformly.

[0021] In the present invention, the protecting film means a film formed on the wafer surface so as to reduce the wettability of the wafer surface, i.e., a film imparting water repellency to the same. In the present invention, the 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 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 such a reduction of the interaction, the contact angle of the liquid to the article surface can be increased.

[0022] Furthermore, a method for cleaning a wafer, according to the present invention is a method for cleaning a wafer having at its surface an uneven pattern and containing at least one kind element of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern. The method including at least:

a protecting-film-forming step where a liquid chemical for forming a protecting film is retained at least in the recessed portions of the uneven pattern;

a drying step of removing liquid from the uneven pattern by drying; and

a film-removing step of removing the protecting film,

wherein the liquid chemical for forming a protecting film is a liquid chemical containing an agent for forming a water-repellent protecting film, the agent being for forming a water-repellent protecting film at least on the surfaces of the recessed portions,

the cleaning method being characterized in that the water-repellent protecting film is formed of a compound represented by the general formula [1] and serving as an agent for forming a water-repellent protecting film.

Effects of the Invention

[0023] The protecting film formed from the liquid chemical for forming a

protecting film, according to the present invention is excellent in water repellency. Therefore, in a wafer having at its surface an uneven pattern and containing at least one kind element of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern, the film reduces the interaction between liquid retained in the recessed portions and the surfaces of the recessed portions, and by extension brings about the effect of preventing the pattern collapse. By using the liquid chemical, a cleaning step conducted in a method for producing the wafer having at its surface an uneven pattern is improved without lowering throughput. Accordingly, the method for producing the wafer having the uneven pattern at its surface, conducted in the use of the liquid chemical for forming a protecting film of the present invention, is excellent in productivity.

[0024] The liquid chemical for forming a protecting film, according to the present invention is adaptable to uneven patterns having the aspect ratio expected to rise more and more, for example, an aspect ratio of not less than 7, which allows cost reduction in producing more sophisticated semiconductor devices. In addition, the liquid chemical is adaptable without considerably modifying conventional apparatuses and therefore results in being one applicable in production of various kinds of semiconductor devices.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] Fig. 1 is a schematic perspective view of a wafer 1 of which surface is made into a surface having an uneven pattern 2.

Fig. 2 is a schematic view showing a part of a-a' cross section of Fig. 1.

Fig. 3 is a schematic view showing a condition where a liquid chemical 8 for forming a protecting film is retained in recessed portions 4 in a cleaning step.

Fig. 4 is a schematic view showing a condition where a liquid is retained in the recessed portions 4 on which the protecting film is formed.

MODE(S) FOR CARRYING OUT THE INVENTION

[0026] As the metal-based wafer, it is possible to cite: those obtained by

coating a surface of 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, various compound semiconductor wafers, a plastic wafer or the like 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; those in which at least one layer of a multilayer film formed on the wafer is the layer formed of a matter containing the above-mentioned metal-based elements. The step of forming the uneven pattern is conducted on a layer including a layer of a matter containing the above-mentioned metal-based elements. Additionally, there are also included those in which at least a part of the surfaces having the uneven pattern becomes a matter containing at least one kind element of the above-mentioned metal-based elements at the time of forming the uneven pattern.

[0027] In general, a surface treatment using a liquid chemical for forming a protecting film of the present invention mostly undergoes, before it is conducted, the following pretreatment steps as exemplified by:

a pretreatment step 1 of making a wafer surface into a surface having an uneven pattern;

a pretreatment step 2 of cleaning the wafer surface by using a water-based cleaning liquid; and

a pretreatment step 3 of substituting the water-based cleaning liquid with a cleaning liquid A different from the water-based cleaning liquid (hereinafter it may sometimes be referred to as merely "a cleaning liquid A").

Incidentally, either the pretreatment step 2 or the pretreatment step 3 may be omitted in some cases.

[0028] In the pretreatment step 1 as a pattern-forming method, a resist is applied to the wafer surface first of all. Thereafter, the resist is exposed through a resist mask, followed by conducting an etching removal on the exposed resist or an unexposed resist, thereby producing a resist having a desired uneven pattern. Additionally, the resist having an uneven pattern can be obtained also by pushing a mold having a pattern onto the resist. Then, the wafer is subjected to etching. At this time, the parts of the wafer surface which corresponding to recessed portions of a resist pattern are etched selectively. Finally, the resist is stripped off thereby obtaining a wafer having an uneven pattern.

[0029] By the above-mentioned pretreatment step 1, it becomes possible to obtain a wafer having at its surface an uneven pattern and containing at least one kind element of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern.

[0030] Examples of the water-based cleaning liquid used in the pretreatment step 2 are water and an aqueous solution obtained by mixing at least one kind of an organic solvent, hydrogen peroxide, ozone, acid, alkali and surfactant with water (the aqueous solution having a water content of not less than 10 mass%, for example).

[0031] Furthermore, in the pretreatment step 2, the substitution with the water-based cleaning liquid may be conducted twice or more. The water-based cleaning liquids to be used in this case may be those different from each other.

[0032] If recessed portions have a small width and projected portions have a large aspect ratio, and if the surface is cleaned with the water-based cleaning liquid in the pretreatment step 2 and subsequently the water-based cleaning liquid is removed by drying and the like or if water is removed by drying and the like after substituting the water-based cleaning liquid with water, a pattern collapse is to easily occur. The uneven pattern is defined as shown in Fig. 1 and Fig. 2. Fig. 1 is one example of a schematic perspective view of a wafer 1 of which surface is made into a surface having an uneven pattern 2.

Fig. 2 shows a part of an a-a' cross section in Fig. 1. A width 5 of recessed portions is defined by an interval between a projected portion 3 and the projected portion 3, as shown in Fig. 2. The aspect ratio of projected portions is expressed by dividing a height 6 of the projected portions by a width 7 of the projected portions. The pattern collapse in the cleaning step is to easily occur when the recessed portions have a width of not more than 70 nm, particularly not more than 45 nm and when the aspect ratio is not less than 4, particularly not less than 6.

[0033] The cleaning liquid A used in the pretreatment step 3 refers to an organic solvent, a mixture of the organic solvent and a water-based cleaning liquid, or a cleaning liquid into which at least one kind of acid, alkali and surfactant is mixed with these. Furthermore, it is preferable to perform a step of retaining the liquid chemical for forming a protecting film at least in the recessed portions of the uneven pattern upon substituting the cleaning liquid A with the liquid chemical for forming a protecting film of the present invention (the protecting-film-forming step).

[0034] In the present invention, a style for cleaning the wafer is not particularly limited so long as the liquid chemical or the cleaning liquid can be retained at least in the recessed portions of the uneven pattern of the wafer. Examples of the style for cleaning the wafer are: a single cleaning style represented by spin cleaning where a generally horizontally held wafer is rotated and cleaned one by one while supplying a liquid to the vicinity of the center of the rotation; and a batch style where a plurality of wafer sheets are immersed in a cleaning bath to be cleaned. Incidentally, the form of the liquid chemical or the cleaning liquid at the time of supplying the liquid chemical or the cleaning liquid 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 time of being retained in the recessed portions, and is exemplified by liquid, vapor or the like.

[0035] The organic solvent, which serves as one of the preferable examples of the cleaning liquid A, are exemplified by hydrocarbons, esters, ethers,

ketones, halogen-element containing solvents, sulfoxide-based solvents, lactone-based solvents, carbonate-based solvents, alcohols, polyalcohol derivatives, nitrogen element-containing solvents and the like.

[0036] Examples of hydrocarbons are toluene, benzene, xylene, hexane, heptane, octane and the like. Examples of esters are ethyl acetate, propyl acetate, butyl acetate, ethyl acetoacetate and the like. Examples of ethers are diethyl ether, dipropyl ether, dibutyl ether, tetrahydrofuran, dioxane and the like. Examples of ketones are acetone, acetylacetone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, cyclohexanone and the like. Examples of the halogen-element containing solvents are: 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. Examples of the sulfoxide-based solvents are dimethyl sulfoxide and the like. Examples of the lactone-based solvents are 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. Examples of the carbonate-based solvents are

dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, propylene carbonate and the like. Examples of alcohols are methanol, ethanol, propanol, buthanol, 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 and the like. Examples of the polyalcohol derivatives are 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, 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 buthyl 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. Examples of the nitrogen element-containing solvents are formamide, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, diethylamine, triethylamine, pyridine and the like.

[0037] Incidentally, it is preferable that the cleaning liquid A is an organic solvent or a mixture liquid of water and an organic solvent in view of the cleanliness. Furthermore, it is preferable that the organic solvent contains a water-soluble organic solvent (so as to have a solubility of not smaller than 5 mass parts by weight relative to 100 parts by weight of water) because it can be easily substituted for the water-based cleaning liquid.

[0038] Additionally, in the pretreatment step 3, the substitution with the cleaning liquid A may be conducted twice or more. More specifically, the water-based cleaning liquid used in the pretreatment step 2 may be

substituted with a first kind of cleaning liquid A, and successively, the first kind of cleaning liquid A may be substituted with two or more kinds of cleaning liquid A different from the above-mentioned cleaning liquid A, and then the liquid chemical for forming a protecting film may be substituted therefor.

[0039] Moreover, in a case where the water-based cleaning liquid used in the pretreatment step 2 can be substituted directly with the liquid chemical for forming a protecting film, the substitution with the cleaning liquid A (the pretreatment step 3) may be omitted.

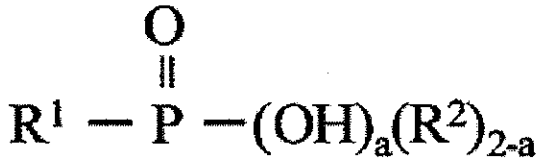
[0040] Fig. 3 is a schematic view showing a condition where the liquid chemical 8 for forming a protecting film is retained in recessed portions 4 in the protecting-film-forming step. The wafer of the schematic view of Fig.3 shows a part of the a-a' cross section in Fig. 1. At this time, a protecting film is formed on the surfaces of the recessed portions 4 thereby imparting water repellency to the surfaces.

[0041] Incidentally, where the protecting film can be formed by the liquid chemical of the present invention is on a surface of a portion of the matter containing at least one kind of element among the metal-based elements, in the uneven pattern. Accordingly, the protecting film may be formed at least on a part of the surfaces of the recessed portions of the metal-based wafer. Additionally, also on a wafer formed of a plurality of components including the matter containing at least one kind of element of the metal-based elements, it is possible to form the protecting film on the surface of the matter containing at least one kind of element of the metal-based elements. Examples of the wafer formed of a plurality of components further include: those in which the matter containing at least one kind of element of the metal-based elements 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 becomes the matter containing at least one kind of element of the metal-based elements at the time of forming the uneven pattern.

[0042] Incidentally, the liquid chemical for forming a protecting film, according to the present invention can easily form an excellent water-repellent

protecting film on the surface of an article containing titanium element at its surface. Therefore, it is preferable that the wafer is a wafer having at its surface an uneven pattern and containing titanium element at the surfaces of the recessed portions of the uneven pattern.

[0043] The liquid chemical for forming a protecting film is a liquid chemical containing a protecting-film-forming agent for forming a protecting film after a cleaning step for a metal-based wafer and before a drying step for the metal based wafer at least on the surfaces of the recessed portions and an organic solvent, and is characterized in that the agent for forming a water-repellent protecting film is a compound represented by the following general formula [1].



[1]

(In the formula [1], R^1 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^2 mutually independently represents a monovalent organic group having a C_1-C_{18} hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s). a is an integer of from 0 to 2.)

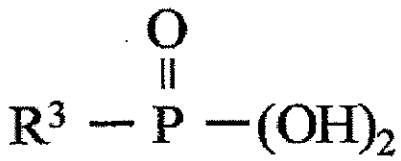
[0044] A hydrocarbon group contained in R^2 of the general formula [1] is exemplified by alkyl group, alkylene group, those in which hydrogen elements are partially or entirely substituted with a fluorine element(s), and the like.

[0045] Additionally, it is preferable that the above-mentioned R^2 is $-OR^4$ (R^4 is a hydrocarbon group having a carbon number of 1 to 18). Additionally, it is preferable that R^4 has a carbon number of 1 to 8 and particularly 1 to 4, since the water repellency is more excellently imparted thereby. Moreover, R^4 is preferably a straight-chained alkyl group.

[0046] As the compound represented by the general formula [1], it is possible to cite $CH_3P(O)(OH)_2$, $C_2H_5P(O)(OH)_2$, $C_3H_7P(O)(OH)_2$, $C_4H_9P(O)(OH)_2$, $C_5H_{11}P(O)(OH)_2$, $C_6H_{13}P(O)(OH)_2$, $C_7H_{15}P(O)(OH)_2$,

$C_8H_{17}P(O)(OH)_2$, $C_9H_{19}P(O)(OH)_2$, $C_{10}H_{21}P(O)(OH)_2$, $C_{11}H_{23}P(O)(OH)_2$, $C_{12}H_{25}P(O)(OH)_2$, $C_{13}H_{27}P(O)(OH)_2$, $C_{14}H_{29}P(O)(OH)_2$, $C_{15}H_{31}P(O)(OH)_2$, $C_{16}H_{33}P(O)(OH)_2$, $C_{17}H_{35}P(O)(OH)_2$, $C_{18}H_{37}P(O)(OH)_2$, $C_6H_5P(O)(OH)_2$, $CF_3P(O)(OH)_2$, $C_2F_5P(O)(OH)_2$, $C_3F_7P(O)(OH)_2$, $C_4F_9P(O)(OH)_2$, $C_5F_{11}P(O)(OH)_2$, $C_6F_{13}P(O)(OH)_2$, $C_7F_{15}P(O)(OH)_2$, $C_8F_{17}P(O)(OH)_2$, $CF_3C_2H_4P(O)(OH)_2$, $C_2F_5C_2H_4P(O)(OH)_2$, $C_3F_7C_2H_4P(O)(OH)_2$, $C_4F_9C_2H_4P(O)(OH)_2$, $C_5F_{11}C_2H_4P(O)(OH)_2$, $C_6F_{13}C_2H_4P(O)(OH)_2$, $C_7F_{15}C_2H_4P(O)(OH)_2$, $C_8F_{17}C_2H_4P(O)(OH)_2$, and those obtained by substituting $-P(O)(OH)_2$ group of the above 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.

[0047] Furthermore, in the protecting-film-forming agent, it is preferable that a of the general formula [1] is 1 or 2 in order to impart a better water repellency. The protecting-film-forming agent is more preferably a compound represented by the following general formula [2] in which a is 2.



[2]

(In the formula [2], 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).)

[0048] Examples of R^1 and R^3 of the general formulas [1] and [2] are: alkyl group; phenyl group; phenyl group the hydrogen element of which is substituted with alkyl group; naphthyl group; these hydrocarbon groups whose hydrogen elements are partially or entirely substituted with a fluorine element(s); and the like.

[0049] Moreover, it is preferable that R^1 and R^3 of the general formulas [1] and [2] have a carbon number of 2 to 16, particularly preferably 4 to 14 and much more preferably 6 to 14, since the water repellency is more excellently imparted thereby. Additionally, it is preferable that the hydrocarbon group whose hydrogen elements may partially or entirely be substituted with a

fluorine element(s) is alkyl group and particularly a straight-chained alkyl group. If a straight-chained alkyl group is used as the hydrocarbon group, hydrophobic moieties of the protecting-film-forming agent tend to be arranged perpendicularly to the surface of the protecting film at the time of forming the protecting film thereby more excellently imparting a water-repellency-imparting effect, which is further preferable. Moreover, R^1 and R^3 of the general formulas [1] and [2] bring about a far better water repellency so as to preferably be a hydrocarbon group whose hydrogen elements are partially or entirely be substituted with a fluorine element(s).

[0050] Additionally, the protecting-film-forming agent may exist in the form of a salt represented by the general formulas [1] and [2]. The salt can be cited by ammonium salt, amine salt and the like.

[0051] Furthermore, the protecting-film-forming agent contained in the liquid chemical for forming a protecting film preferably has a concentration of 0.0005 to 2 mass% relative to the total quantity of 100 mass% of the liquid chemical. A concentration of smaller than 0.0005 mass% tends to make the water-repellency-imparting effect insufficient, while that of larger than 2 mass% tends to be insoluble in an organic solvent. A concentration of 0.001 to 1 mass% is more preferable, and 0.0015 to 0.8 mass% is particularly preferable.

[0052] As the organic solvent used for the liquid chemical for forming a protecting film, it is preferable to use, for example, water, an organic solvent, a mixture liquid of water and an organic solvent. The organic solvent is exemplified by hydrocarbons, esters, ethers, ketones, halogen-element containing solvents, sulfoxide-based solvents, lactone-based solvents, carbonate-based solvents, alcohols, polyalcohol derivatives, nitrogen element-containing solvents, and a mixture of these.

[0053] As concrete examples of the organic solvent, it is possible to cite the same as those that have been applied to the cleaning liquid A.

[0054] Additionally, it is preferable to use a nonflammable one as a part or the entire of the solvent since the liquid chemical for forming a protecting film

becomes nonflammable or increases in flash point thereby reducing the risk of the liquid chemical. Most of the halogen-element containing solvents are nonflammable, so that such a halogen element-containing nonflammable solvent can be preferably used as a nonflammable organic solvent. Furthermore, water can be preferably used as the nonflammable solvent too.

[0055] Additionally, in view of safety under the fire protection law, it is preferable to use a solvent having a flash point exceeding 70°C as the above-mentioned solvent.

[0056] Moreover, 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 protecting film tends to have a flash point exceeding 93°C even if the solvent is not nonflammable one. Hence the liquid chemical hardly applies to "the flammable liquid", which is preferable in view of safety.

[0057] Additionally, most of the lactone-based solvents, carbonate-based solvents, alcohols having a high molecular weight or two or more OH groups and the polyalcohol derivatives have high flash point. It is therefore preferable to use these solvents because the risk of the liquid chemical for forming a protecting film can be reduced. In view of the safety, as the above-mentioned solvent, it is more preferable to use those having a flash point exceeding 70°C 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, propylene carbonate, heptanol, octanol, 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 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, 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, ethylene glycol dibutyl ether, ethylene glycol monobutyl ether acetate, ethylene glycol diacetate, diethylene glycol ethyl methyl ether, diethylene glycol diethyl ether, diethylene glycol buthyl 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.

Additionally, as the above-mentioned solvent, it is much more preferable to use those having a flash point exceeding 93°C such as 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, 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, ethylene glycol diacetate, diethylene glycol buthyl 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.

[0058] Furthermore, from reasons of imparting a more excellent water repellency, it is preferable to use: hydrocarbons, esters, ethers, ketones, lactone-based solvents, carbonate-based solvents, polyalcohol derivatives having no hydroxy group, water, or a mixture liquid of these. Additionally, in consideration of substitutability with the water-based cleaning liquid, it is preferable to use: polyalcohol derivatives having no hydroxyl group; water; or a mixture liquid of these. In order to more greatly dissolve the protecting-film-forming agent, the above-mentioned solvent may contain some alcohols. In this case the concentration of the alcohols is preferably not larger than 10 mass%, particularly preferably not larger than 5 mass%, much more preferably not larger than 3 mass% relative to 100 mass% of the liquid chemical for forming a protecting film.

[0059] Additionally, in order to accelerate the formation of the protecting film due to the protecting-film-forming agent, a catalyst may be added to the liquid chemical for forming a protecting film. The added amount of the catalyst is preferably 0.01 to 50 mass% relative to the total quantity of 100 mass% of the protecting-film-forming agent.

[0060] When increasing the temperature of the liquid chemical for forming a protecting film, the protecting film can be formed in a shorter time. A temperature at which a uniform protecting film can be readily formed is not lower than 10°C and lower than the boiling point of the liquid chemical. Particularly, it is preferable to keep a temperature of not lower than 15°C and not higher than a temperature 10 °C lower than the boiling point of the liquid chemical. It is preferable that the temperature of the liquid chemical is kept

at the above-mentioned temperature while the liquid chemical is being retained at least in the recessed portions of the uneven pattern. Incidentally, the boiling point of the liquid chemical means the boiling point of a component having the most amount among components contained in the water-repellent liquid chemical, in mass ratio.

[0061] After the protecting film-forming step, the liquid chemical that remains at least in the recessed portions of the uneven pattern may be substituted (hereinafter, this may sometimes be referred to as "a subsequent cleaning step") with a cleaning liquid different from the above-mentioned liquid chemical (hereinafter, this cleaning liquid may sometimes be referred to as "a cleaning liquid B"), and may subsequently be brought into a drying step. Examples of the cleaning liquid B are: a water-based cleaning liquid, an organic solvent; a mixture of the water-based cleaning liquid and the organic solvent; those into which at least one kind of acid, alkali and a surfactant is mixed; those in which the protecting-film-forming agent used for the liquid chemical for forming a protecting film is contained at a concentration lower than that of the liquid chemical; and the like. From the viewpoint of removing particles and metal impurities, it is more preferable that the cleaning liquid B is water, an organic solvent or a mixture of water and the organic solvent.

[0062] Furthermore, in the subsequent cleaning step, the substitution with the cleaning liquid B may be conducted twice or more. More specifically, the liquid chemical for forming a protecting film may be substituted with a first kind of cleaning liquid B, and successively, it may further be substituted with two or more kinds of cleaning liquid B different from the first kind of cleaning liquid B. The liquid chemical may be brought into the drying step thereafter.

[0063] The organic solvent, which is one of the preferable examples of the cleaning liquid B, is exemplified by hydrocarbons, esters, ethers, ketones, halogen-element containing solvents, sulfoxide-based solvents, alcohols, polyalcohol derivatives, nitrogen element-containing solvents, and the like.

[0064] As concrete examples of the organic solvent, it is possible to cite the

same as those that have been applied to the cleaning liquid A.

[0065] Moreover, if an organic solvent is used as the cleaning liquid B, the water repellency of the protecting film formed on the wafer surface by the liquid chemical of the present invention tends to reduce little by the subsequent cleaning step.

[0066] There is shown in Fig. 4 a schematic view showing a state where a liquid is retained in the recessed portions 4 provided with water repellency by the liquid chemical for forming a protecting film. The wafer as shown in the schematic view of Fig. 4 shows a part of the a-a' cross section in Fig. 1. The surface formed having the uneven pattern is coated with a protecting film 10 by the liquid chemical thereby being provided with water repellency. Furthermore, the protecting film 10 is retained on the wafer surface even when the liquid 9 is removed from the uneven pattern.

[0067] When the protecting film 10 is formed at least on the surfaces of the recessed portions of the uneven pattern of the wafer by the liquid chemical for forming a protecting film, a contact angle of from 50 to 130° is preferable on the assumption that water is retained on the surfaces, because the pattern collapse becomes difficult to occur thereby. The closer to 90° the contact angle is, the smaller the capillary force acting on the recessed portions becomes. It is therefore further preferable that the contact angle is 60 to 120°, particularly preferably 65 to 115° because the pattern collapse becomes further difficult to occur. Furthermore, the capillary force is preferably not higher than 2.1 MN/m^2. The capillary force of not higher than 2.1 MN/m^2 is preferable because the pattern collapse becomes difficult to occur. Additionally, a lower capillary force makes the pattern collapse more difficult to occur, so that a capillary force of 1.6 MN/m^2 or lower is further preferable and that of not higher than 1.4 MN/m^2 is particularly preferable. Furthermore, it is ideal to put the capillary force close to 0.0 MN/m^2 as much as possible by adjusting the contact angle to the liquid to around 90°.

[0068] Then, as discussed in the drying step, there is conducted a step of removing a liquid from the uneven pattern by drying, the liquid being retained

in the recessed portions 4 on which the protecting film is formed by the liquid chemical. At this time, the liquid retained in the recessed portions may be the liquid chemical used in the protecting-film-forming step, the cleaning liquid B used in the subsequent cleaning step, or a mixture liquid of these. The mixture liquid is one in which the protecting-film-forming agent is contained in the liquid chemical for forming a protecting film at a concentration lower than that of the liquid chemical. The mixture liquid may be a liquid which is on the way to substitution of the liquid chemical with the cleaning liquid B, or a mixture liquid obtained by previously mixing the protecting-film-forming agent with the cleaning liquid B. In view of the cleanliness of the wafer, it is particularly use water, an organic solvent, or a mixture of water and the organic solvent. Additionally, it is possible to bring the cleaning liquid B retained on the unevenly patterned surface after once removing liquid from the unevenly patterned surface. Drying may be conducted thereafter.

[0069] Incidentally, in a case of performing a cleaning treatment (the subsequent cleaning step) after a surface treatment with the liquid chemical, a time for this step, i.e. a time to retain the cleaning liquid B is preferably not shorter than 10 seconds, more preferably not shorter than 20 seconds from the viewpoint of removing particles and impurities from the unevenly patterned surface. In view of the effect of maintaining a water-repellent performance of the protecting film formed on the unevenly patterned surface, if an organic solvent is used as the cleaning liquid B, the water repellency of the wafer surface tends to become easily maintained even after conducting the subsequent cleaning step. On the other hand, a too long time for the cleaning treatment can reduce the productivity, and therefore the time is preferably within 15 minutes.

[0070] In the drying step, a liquid retained on the uneven pattern is removed by drying. The drying is preferably conducted by a conventionally known drying method such as spin drying, IPA (2-propanol) steam drying, Marangoni drying, heating drying, warm air drying, vacuum drying and the like.

[0071] Then, as discussed in the film-removing step, there is performed a step of removing the protecting film 10. In the case of removing the water-repellent protecting film, it is effective to cleave C-C bond and C-F bond in the water-repellent protecting film. A method therefor is not particularly limited so long as it is possible to cleave the above-mentioned bonds, and exemplified by: irradiating the wafer surface with light; heating the wafer; exposing the wafer to ozone; irradiating the wafer surface with plasma; subjecting the wafer surface to corona discharge; and the like.

[0072] In the case of removing the protecting film 10 by light irradiation, it is preferable to conduct an irradiation with ultraviolet rays having a wavelength of shorter than 340 nm and 240 nm (corresponding to bond energies of C-C bond and C-F bond in the water-repellent film, i.e., 83 kcal/mol and 116 kcal/mol, respectively). As the light source therefor, there is used a metal halide lamp, a low-pressure mercury lamp, a high-pressure mercury lamp, an excimer lamp, a carbon arc or the like. In the case of the metal halide lamp, the intensity of the ultraviolet irradiation is preferably not less than 100 mW/cm^2, particularly preferably not less than 200 mW/cm^2, as a measurement value obtained by the illuminance meter (Intensity meter UM-10 produced by Konica Minolta Sensing, Inc., Light-Receptor UM-360 [Peak sensitivity wavelength: 365 nm, Measured wavelength range: 310 to 400 nm]). Incidentally, an irradiation intensity of less than 100 mW/cm^2 takes a long time to remove the protecting film 10. Additionally, in the case of the low-pressure mercury lamp, the ultraviolet irradiation is performed with shorter wavelengths so that removal of the protecting film 10 is achieved in a short time even if the intensity is low, which is therefore preferable.

[0073] Additionally, in the case of removing the protecting film 10 by light irradiation, it is particularly preferable to generate ozone in parallel with decomposing the components of the protecting film 10 by ultraviolet rays and then to induce oxidation-volatilization of the components of the protecting film 10 by the ozone, since a treatment time is saved thereby. As the light source therefor, the low-pressure mercury lamp, the excimer lamp or the like is used.

Moreover, the wafer may be heated while being subjected to light irradiation.

[0074] In the case of heating the wafer, heating of the wafer is conducted at 400 to 1000 °C, preferably at 500 to 900 °C. The heating time is preferably kept from 10 seconds to 60 minutes, more preferably from 30 seconds to 10 minutes. Additionally, this step may be conducted in combination with ozone exposure, plasma irradiation, corona discharge or the like. Furthermore, the light irradiation may be conducted while heating the wafer.

[0075] As the method for removing the protecting film 10 by heating, there are a method of bringing a wafer into contact with a heat source, a method of bringing a wafer into a heated atmosphere such as a heat treatment furnace, and the like. The method of bringing a wafer into a heated atmosphere can easily and uniformly provide the wafer surface with energy for removing the protecting film 10 even in a case where two or more wafers are subjected to a treatment. This method is operationally convenient, achieves the treatment within a short period of time and has high treatment ability. Therefore, this is an industrially advantageous method.

[0076] In the case of exposing the wafer to ozone, it is preferable to expose the wafer surface to ozone generated by ultraviolet irradiation using the low-pressure mercury lamp, low-temperature discharge using high voltages or the like. The wafer may be irradiated with light or heated while being exposed to ozone.

[0077] In the film-removing step, the protecting film on the wafer surface can be efficiently removed by combining the above-mentioned light irradiation, heating, ozone exposure, plasma irradiation and corona discharge.

EXAMPLES

[0078] To make a wafer surface into a surface having an uneven pattern and to substitute a cleaning liquid retained at least in recessed portions of the uneven pattern with another cleaning liquid are techniques that have been variously studied and already been established as discussed in other literatures and the like. Accordingly, in the present invention, evaluations of a liquid chemical for forming a protecting film were mainly performed.

Additionally, as apparent from the following equation, a pattern collapse greatly depends on the contact angle of the cleaning liquid to the wafer surface, i.e. the contact angle of liquid drop, and on the surface tension of the cleaning liquid.

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

(In the equation, γ represents the surface tension of a liquid retained in the recessed portions, θ represents the contact angle of the liquid retained in the recessed portions to the surfaces of the recessed portions, and S represents the width of the recessed portions.)

In a case of a cleaning liquid retained in recessed portions 4 of an uneven pattern 2, the contact angle of liquid drop and the capillary force acting on the recessed portions (which force is regarded as an equivalent of the pattern collapse) are in correlation with each other, so that it is also possible to derive the capillary force from the equation and the evaluations made on the contact angle of liquid drop to a protecting film 10. In Examples, a representative of a water-based cleaning liquid, water, was used as the cleaning liquid.

[0079] However, in the case of a wafer having an unevenly patterned surface, it is not possible to exactly evaluate the contact angle of the protecting film 10 itself, the protecting film being formed on the unevenly patterned surface.

[0080] An evaluation of the contact angle of waterdrop is conducted by dropping several microliters of waterdrop on a surface of a sample (a substrate) and then by measuring an angle formed between the waterdrop and the substrate surface, as discussed in JIS R 3257 (Testing method of wettability of glass substrate surface). However, in the case of the wafer having a pattern, the contact angle is enormously large. This is because Wenzel's effect or Cassie's effect is caused so that an apparent contact angle of the waterdrop is increased under the influence of a surface shape (roughness) of the substrate upon the contact angle.

[0081] In view of the above, in the present examples, the liquid chemical is provided to a wafer having a smooth surface to form a protecting film on the

wafer surface, on which various evaluations were performed by regarding the protecting film as the protecting film 10 formed on a surface of a wafer 1 having at its surface the uneven pattern 2). In the present examples, "a wafer having a titanium nitride film" (represented by TiN in Tables) which has a titanium nitride layer on a silicon wafer having a smooth surface, "a wafer having a tungsten film" (represented by W in Tables) which has a tungsten layer on a silicon wafer having a smooth surface, and "a wafer having a ruthenium film" (represented by Ru in Tables) which has a ruthenium layer on a silicon wafer having a smooth surface were used as the wafer having the smooth surface.

[0082] Details will be discussed below. Hereinafter, there will be discussed: a method for evaluating a wafer to which a liquid chemical for forming a protecting film is provided; a preparation of the liquid chemical for forming a protecting film; and evaluation results after providing the liquid chemical for forming a protecting film to the wafer.

[0083] [Method for evaluating Wafer to which Liquid Chemical for forming Protecting Film is provided]

As a method for evaluating a wafer to which a liquid chemical for forming a protecting film is provided, the following evaluations (1) to (4) were performed.

[0084] (1) Evaluation of Contact Angle of Protecting Film formed on Wafer Surface

About 2 μl of pure water was dropped on a wafer surface on which a protecting film was formed, followed by measuring an angle (contact angle) formed between the waterdrop and the wafer surface by using a contact angle meter (produced by Kyowa Interface Science Co., Ltd.: CA-X Model). In this evaluation, a wafer having a contact angle within a range of from 50 to 130° to the protecting film was classified as an acceptable one.

[0085] (2) Evaluation of Capillary Force

The capillary force (the absolute value of P) was obtained by calculating P by using the following equation.

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

(In the equation, γ represents the surface tension of a liquid retained in the recessed portions, θ represents the contact angle of the liquid retained in the recessed portions to the surfaces of the recessed portions, and S represents the width of the recessed portions.)

Incidentally, the present example was made on the assumption that a wafer formed having a line-and-space pattern the line width (the width of the recessed portions) of which was 45 nm, as an example of a pattern shape. The pattern having a line width of 45 nm tends to cause its collapse in a case where a cleaning liquid used when a gas-liquid interface passes through the uneven pattern is water, while the pattern collapse tends to be difficult to occur in a case of 2-propanol. If the wafer surface is titanium nitride, tungsten or ruthenium, for example, the contact angle of 2-propanol to the surface is 0.5° in either case, and similarly the contact angle of water is 2° in either case. Also concerning the other matters containing titanium element, tungsten element or ruthenium element (such as titanium, titanium oxide, tungsten oxide and ruthenium oxide), the degree of the contact angle is as much as the above. In a case where the pattern width is 45 nm and the wafer surface is titanium nitride (the wafer having the titanium nitride film), tungsten (the wafer having the tungsten film) or ruthenium (the wafer having the ruthenium film) and where the cleaning liquid is 2-propanol (Surface tension: 22 mN/m), the capillary force is 0.98 MN/m^2. On the other hand, in a case of water (Surface tension: 72 mN/m) having the largest surface tension among liquids other than mercury, the capillary force results in 3.2 MN/m^2.

[0086] (3) Removability of Protecting Film

Under the following conditions, a sample was irradiated with UV rays from a metal halide lamp for 2 hours, upon which an evaluation of removability of the protecting film at the film-removing step was made. A sample on which waterdrop had a contact angle of not larger than 30° after the irradiation was classified as acceptable one.

・ Lamp: M015-L312 produced by EYE GRAPHICS CO., LTD.

(Intensity: 1.5 kW)

・Illuminance: 128 mW/cm^2 as a measurement value obtained under the following conditions

・Measuring Apparatus: Ultraviolet Intensity Meter (UM-10 produced by Konica Minolta Sensing, Inc.)

・Light-Receptor: UM-360 (Light-Receptive Wavelength : 310-400 nm, Peak Wavelength: 365 nm)

・Measuring Mode: Irradiance Measurement

[0087] (4) Evaluation of Surface Smoothness of Wafer after removing Protecting Film

The surface was observed by atomic force microscope (produced by Seiko Instruments Inc.: SPI3700, 2.5 micrometer square scan). Then, there was obtained a difference ΔRa (nm) in the centerline average surface roughness Ra (nm) of the surface of the wafer between before and after the cleaning. Incidentally, Ra is a three-dimensionally enlarged one obtained by applying the centerline average roughness defined by JIS B 0601 to a measured surface and is calculated as "an average value of absolute values of difference from standard surface to designated surface" from the following equation.

[0088]

$$Ra = \frac{1}{S_0}\int_{Y_T}^{Y_B}\int_{X_L}^{X_R} |F(X,Y) - Z_0| \, dXdY$$

Here, X_L and X_R, and Y_B and Y_T represent a measuring range in the X coordinate and the Y coordinate, respectively. S_0 represents an area on the assumption that the measured surface is ideally flat, and is a value obtained by $(X_R\text{-}X_L)\times(Y_B\text{-}Y_T)$. Additionally, F(X,Y) represents the height at a measured point (X,Y). Z_0 represents the average height within the measured surface.

[0089] The Ra value of the wafer surface before the protecting film was formed thereon and the Ra value of the wafer surface after the protecting film was removed therefrom were measured. If a difference between them (ΔRa)

was within ±1nm, the wafer surface was regarded as not being eroded by the cleaning and as not leaving residues of the protecting film thereon, and therefore classified as an acceptable one.

[0090] [Example 1]

(I-1) Preparation of Liquid Chemical for forming Protecting Film

A mixture of 0.002 g of octadecylphosphonic acid [$C_{18}H_{37}P(O)(OH)_2$] serving as an agent for forming a water-repellent protecting film and 99.998 g of propylene glycol monomethyl ether acetate (hereinafter referred to as "PGMEA") serving as an organic solvent was stirred for about 18 hours thereby obtaining a liquid chemical for forming a protecting film, in which liquid chemical the protecting-film-forming agent had a concentration of 20 mass ppm relative to the total quantity of the liquid chemical for forming a protecting film (hereinafter referred to as "a protecting-film-forming agent concentration").

[0091] (I-2) Step of Cleaning Wafer (Pretreatment Step)

As a pretreatment step 2, a wafer having a smooth titanium nitride film (a silicon wafer formed having on its surface a titanium nitride layer of 50 nm thickness) was immersed in 1 mass% aqueous hydrogen peroxide for 1 minute at room temperature, and then immersed in pure water for 1 minute. Furthermore, as a pretreatment step 3, the wafer was immersed in isopropyl alcohol (hereinafter referred to as "iPA") for 1 minute.

[0092] (I-3) From Step of Forming Protecting Film on Wafer Surface to Drying Step

As a protecting-film-forming step, the wafer having the titanium nitride film was immersed in the liquid chemical for forming a protecting film at 20 °C for 10 minutes, the liquid chemical having been prepared in the above "(I-1) Preparation of Liquid Chemical for forming Protecting Film" section, thereby forming a protecting film on the wafer surface. Thereafter, the wafer having the titanium nitride film was immersed in iPA for 1 minute, as a subsequent cleaning step. Then, as a drying step, the wafer having the titanium nitride film was taken out of iPA, followed by spraying air thereon to

remove iPA from the surface.

[0093] As a result of evaluating the obtained wafer having the titanium nitride film in a manner discussed in the above [Method for evaluating Wafer to which Liquid Chemical for forming Protecting Film is provided] section, a wafer in which an initial contact angle before the surface treatment was smaller than 10° was confirmed to have a contact angle of 106° after the surface treatment, as shown in Table 1. With this, a water-repellency-imparting effect was excellently exhibited. Additionally, as a result of calculating the capillary force at the time of retaining water by using the equation discussed in the above "Evaluation of Capillary Force" section, the capillary force was so small as to be 0.9 MN/m^2. Additionally, the contact angle after UV irradiation was smaller than 10°, so that removal of the protecting film was achieved. Furthermore, the ΔRa value of the wafer after UV irradiation was within ±0.5nm, with which it was confirmed that the wafer was not eroded at the time of cleaning and that residues of the protecting film did not remain after UV irradiation.

[0094] [Table 1]

	Liquid chemical for forming protecting film			Wafer	Cleaning liquid for pretreatment step 3	Protecting-film-forming step		Subsequent cleaning step		Evaluation results				
	Protecting-film-forming agent	Solvent	Protecting-film-forming agent concentration [mass ppm]			Temperature [C°]	Time [min]	Cleaning liquid for subsequent cleaning step	Time [min]	Initial contact angle [°]	Contact angle after surface treatment ([°])	Capillary force ([MN/m^2]) <Calculated value>	Removability of protecting film (Contact angle [°])	Surface smoothness (ΔRa[nm])
Example 1	$C_{18}H_{37}P(O)(OH)_2$	PGMEA	20	TiN	iPA	20	10	iPA	1	<10	106	0.9	<10	Within ±0.5
Example 2	$C_{12}H_{25}P(O)(OH)_2$	PGMEA	20	TiN	iPA	20	10	iPA	1	<10	98	0.5	<10	Within ±0.5
Example 3	$C_{12}H_{25}P(O)(OH)_2$	PGMEA	30	TiN	iPA	20	10	iPA	1	<10	98	0.5	<10	Within ±0.5
Example 4	$C_{12}H_{25}P(O)(OH)_2$	PGMEA	50	TiN	iPA	20	10	iPA	1	<10	100	0.6	<10	Within ±0.5
Example 5	$C_{12}H_{25}P(O)(OH)_2$	PGMEA	50	TiN	iPA	20	1	iPA	1	<10	98	0.5	<10	Within ±0.5
Example 6	$C_{12}H_{25}P(O)(OH)_2$	PGMEA	50	TiN	iPA	40	10	iPA	1	<10	101	0.6	<10	Within ±0.5
Example 7	$C_{12}H_{25}P(O)(OH)_2$	Cyclohexanone	50	TiN	iPA	20	10	iPA	1	<10	100	0.6	<10	Within ±0.5
Example 8	$C_{12}H_{25}P(O)(OH)_2$	iPA	50	TiN	iPA	20	10	iPA	1	<10	70	1.1	<10	Within ±0.5
Example 9	$C_{12}H_{25}P(O)(OH)_2$	THF	50	TiN	iPA	20	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 10	$C_{12}H_{25}P(O)(OH)_2$	Water	20	TiN	iPA	20	10	iPA	1	<10	98	0.5	<10	Within ±0.5
Example 11	$C_{10}H_{21}P(O)(OH)_2$	PGMEA	30	TiN	iPA	20	10	iPA	1	<10	95	0.3	<10	Within ±0.5
Example 12	$C_{10}H_{21}P(O)(OH)_2$	PGMEA	50	TiN	iPA	20	10	iPA	1	<10	98	0.4	<10	Within ±0.5
Example 13	$C_{10}H_{21}P(O)(OH)_2$	PGMEA	50	TiN	iPA	20	1	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 14	$C_{10}H_{21}P(O)(OH)_2$	Cyclohexanone	50	TiN	iPA	20	10	iPA	1	<10	98	0.4	<10	Within ±0.5
Example 15	$C_{10}H_{21}P(O)(OH)_2$	iPA	50	TiN	iPA	20	10	iPA	1	<10	68	1.2	<10	Within ±0.5
Example 16	$C_{10}H_{21}P(O)(OH)_2$	Water	50	TiN	iPA	20	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 17	$C_{10}H_{21}P(O)(OH)_2$	PGMEA	50	TiN	iPA	40	10	iPA	1	<10	99	0.5	<10	Within ±0.5
Example 18	$C_{10}H_{21}P(O)(OC_2H_5)_2$	PGMEA	1000	TiN	iPA	40	10	iPA	1	<10	54	1.9	<10	Within ±0.5
Example 19	$C_8H_{17}P(O)(OH)_2$	PGMEA	50	TiN	iPA	20	10	iPA	1	<10	85	0.3	<10	Within ±0.5
Example 20	$C_8H_{17}P(O)(OH)_2$	PGMEA	100	TiN	iPA	20	10	iPA	1	<10	93	0.2	<10	Within ±0.5
Example 21	$C_8H_{17}P(O)(OH)_2$	PGMEA	300	TiN	iPA	20	10	iPA	1	<10	94	0.2	<10	Within ±0.5
Example 22	$C_8H_{17}P(O)(OH)_2$	Cyclohexanone	300	TiN	iPA	20	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 23	$C_8H_{17}P(O)(OH)_2$	iPA	300	TiN	iPA	20	10	iPA	1	<10	64	1.4	<10	Within ±0.5
Example 24	$C_8H_{17}P(O)(OH)_2$	Water	300	TiN	iPA	20	10	iPA	1	<10	94	0.2	<10	Within ±0.5
Example 25	$C_8H_{17}P(O)(OH)_2$	PGMEA	300	TiN	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 26	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGMEA	50	TiN	iPA	20	10	iPA	1	<10	108	1	<10	Within ±0.5
Example 27	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGMEA	100	TiN	iPA	20	10	iPA	1	<10	108	1	<10	Within ±0.5
Example 28	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGMEA	100	TiN	iPA	40	10	iPA	1	<10	110	1.1	<10	Within ±0.5
Example 29	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGMEA	100	TiN	iPA	70	10	iPA	1	<10	110	1.1	<10	Within ±0.5
Example 30	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGMEA/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5

[0095] [Examples 2 to 84]

Upon suitably modifying those used in Example 1 (i.e., the protecting-film-forming agent, the solvent for the liquid chemical for forming a protecting film, the protecting-film-forming agent concentration, the time for the protecting-film-forming step, the temperature of the protecting-film-forming step and the cleaning liquid for the subsequent cleaning step), the surface treatment was conducted on a wafer. Then, evaluations were performed thereon. The results are shown in Table 1 to Table 3.

[0096] [Table 2]

	Liquid chemical for forming protecting film			Wafer	Cleaning liquid for pretreatment step 3	Protecting-film-forming step		Subsequent cleaning step		Evaluation results				
	Protecting-film-forming agent	Solvent	Protecting-film-forming agent concentration [mass ppm]			Temperature [C°]	Time [min]	Cleaning liquid for subsequent cleaning step	Time [min]	Initial contact angle [°]	Contact angle after surface treatment ([°])	Capillary force ([MN/m^2]) <Calculated value>	Removability of protecting film (Contact angle [°])	Surface smoothness (ΔRa [nm])
Example 31	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	Cyclohexanone	100	TiN	iPA	20	10	iPA	1	<10	108	1	<10	Within ±0.5
Example 32	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	iPA	100	TiN	iPA	20	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 33	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	Water	100	TiN	iPA	20	10	iPA	1	<10	110	1.1	<10	Within ±0.5
Example 34	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	Water	100	TiN	iPA	40	10	iPA	1	<10	110	1.1	<10	Within ±0.5
Example 35	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	PGME	100	TiN	iPA	20	10	iPA	1	<10	98	0.4	<10	Within ±0.5
Example 36	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DEGME	100	TiN	iPA	20	10	iPA	1	<10	98	0.4	<10	Within ±0.5
Example 37	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DEGDEE	100	TiN	iPA	20	10	iPA	1	<10	110	1.1	<10	Within ±0.5
Example 38	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DEGEEA	100	TiN	iPA	20	10	iPA	1	<10	108	1	<10	Within ±0.5
Example 39	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DEGEEA/iPA	100	TiN	iPA	20	10	iPA	1	<10	108	1	<10	Within ±0.5
Example 40	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DEGEEA/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 41	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DEGEEA/iPA/Water	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 42	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	GBL/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 43	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	GBL/iPA/Water	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 44	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	PGDA/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 45	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	PGDA/iPA/Water	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 46	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	TPGDME/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 47	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	13BGDA/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 48	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	13BGDA/iPA/Water	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 49	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	14BGDA/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 50	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DPGMEA/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 51	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DPGMEA/iPA/Water	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 52	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	TEGBME/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 53	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	TEGBME/iPA/Water	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 54	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	GBL/DPGMEA/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 55	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	GBL/DPGMEA/iPA/Water	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 56	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	GBL/PGMEA/iPA	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 57	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	GBL/PGMEA/iPA/Water	500	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 58	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DEGEEA/PGME-3	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 59	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DEGEEA/iPA	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 60	C_6F_{13}-C_2H_4-P (O) $(OH)_2$	DEGEEA/iPA/Water	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5

[0097] [Table 3]

	Liquid chemical for forming protecting film			Wafer	Cleaning liquid for pretreatment step 3	Protecting-film-forming step		Subsequent cleaning step		Evaluation results				
	Protecting-film-forming agent	Solvent	Protecting-film-forming agent concentration [mass ppm]			Temperature [C°]	Time [min]	Cleaning liquid for subsequent cleaning step	Time [min]	Initial contact angle [°]	Contact angle after surface treatment ([°])	Capillary force ([MN/m^2]) <Calculated value>	Removability of protecting film (Contact angle [°])	Surface smoothness (ΔRa [nm])
Example 61	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DPGMEA/iPA/Water	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 62	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	TEGBME/iPA	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 63	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	TEGBME/iPA/Water	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 64	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/DPGMEA/iPA/Water	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 65	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/PGMEA/iPA/Water	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 66	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/DPGA/iPA/Water	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 67	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/13BGDA/iPA/Water	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 68	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/TEGBME/iPA/Water	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 69	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/DEGEEA/iPA/Water	1000	TiN	iPA	20	10	iPA	1	<10	112	1.2	<10	Within ±0.5
Example 70	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA	1000	TiN	iPA	20	10	Water	1	<10	104	0.8	<10	Within ±0.5
Example 71	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/PGME-10	1500	TiN	iPA	20	10	iPA	1	<10	114	1.3	<10	Within ±0.5
Example 72	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	TEGDME	100	TiN	iPA	20	10	iPA	1	<10	108	1	<10	Within ±0.5
Example 73	$C_4F_9-C_2H_4-P(O)(OH)_2$	PGMEA	100	TiN	iPA	20	10	iPA	1	<10	104	0.8	<10	Within ±0.5
Example 74	$C_4F_9-C_2H_4-P(O)(OH)_2$	DEGEEA	100	TiN	iPA	20	10	iPA	1	<10	104	0.8	<10	Within ±0.5
Example 75	$C_6H_{13}P(O)(OH)_2$	PGMEA	300	TiN	iPA	20	10	iPA	1	<10	80	0.6	<10	Within ±0.5
Example 76	$C_6H_{13}P(O)(OH)_2$	PGMEA	500	TiN	iPA	20	10	iPA	1	<10	88	0.1	<10	Within ±0.5
Example 77	$C_6H_{13}P(O)(OH)_2$	PGMEA	1000	TiN	iPA	20	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 78	$C_6H_{13}P(O)(OH)_2$	Cyclo-hexanone	500	TiN	iPA	20	10	iPA	1	<10	86	0.2	<10	Within ±0.5
Example 79	$C_6H_{13}P(O)(OH)_2$	iPA	500	TiN	iPA	20	10	iPA	1	<10	64	1.4	<10	Within ±0.5
Example 80	$C_6H_{13}P(O)(OH)_2$	PGMEA	500	TiN	iPA	40	10	iPA	1	<10	94	0.2	<10	Within ±0.5
Example 81	$C_6H_{13}P(O)(OH)_2$	Water	500	TiN	iPA	20	10	iPA	1	<10	90	0	<10	Within ±0.5
Example 82	$C_4H_9P(O)(OH)_2$	PGMEA	500	TiN	iPA	20	10	iPA	1	<10	64	1.4	<10	Within ±0.5
Example 83	$C_4H_9P(O)(OH)_2$	PGMEA	1000	TiN	iPA	20	10	iPA	1	<10	64	1.4	<10	Within ±0.5
Example 84	$C_6H_5P(O)(OH)_2$	PGMEA	1000	TiN	iPA	20	10	iPA	1	<10	62	1.5	<10	Within ±0.5

[0098] Incidentally, in the Table, "$C_{12}H_{25}P(O)(OH)_2$" means dodecylphosphonic acid. "$C_{10}H_{21}P(O)(OH)_2$" means decylphosphonic acid. "$C_{10}H_{21}P(O)(OC_2H_5)_2$" means diethyl decylphosphonate. "$C_8H_{17}P(O)(OH)_2$" means octylphosphonic acid. "$C_6F_{13}-C_2H_4-P(O)(OH)_2$" means perfluorohexylethylphosphonic acid. "$C_4F_9-C_2H_4-P(O)(OH)_2$" means perfluorobutylethylphosphonic acid. "$C_6H_{13}P(O)(OH)_2$" means hexylphosphonic acid. "$C_4H_9P(O)(OH)_2$" means butylphosphonic acid. "$C_6H_5P(O)(OH)_2$" means phenylphosphonic acid. Additionally, "PGME" means propylene glycol monomethyl ether. "DEGME" means diethylene glycol monomethyl ether. "DEGDEE" means diethylene glycol diethyl ether. "DEGEEA" means diethylene glycol monoethyl ether acetate. "GBL" means γ-butyrolactone. "PGDA" means propylene glycol diacetate. "TPGDME" means tripropylene glycol dimethyl ether. "13BGDA" means 1,3-butylene glycol diacetate. "14BGDA" means 1,4-butylene glycol diacetate. "DPGMEA" means dipropylene glycol monomethyl ether acetate. "TEGBME" means triethylene glycol butyl methyl ether. "TEGDME" means triethylene glycol dimethyl ether. Furthermore, "PGMEA/iPA" means a solvent obtained by combining PGMEA and iPA at a mass ratio of 99.5:0.5. Furthermore, "DEGEEA/iPA" means a solvent obtained by combining DEGEEA and iPA at a mass ratio of 99.5:0.5. "DEGEEA/iPA/water" means a solvent obtained by combining DEGEEA, iPA and water at a mass ratio of 94.9:0.1:5. "GBL/iPA" means a solvent obtained by combining GBL and iPA at a mass ratio of 95:5. "GBL/iPA/water" means a solvent obtained by combining GBL, iPA and water at a mass ratio of 95:4:1. "PGDA/iPA" means a solvent obtained by combining PGDA and iPA at a mass ratio of 99.5:0.5. "PGDA/iPA/water" means a solvent obtained by combining PGDA, iPA and water at a mass ratio of 94.9:0.1:5. "TPGDME/iPA" means a solvent obtained by combining TPGDME and iPA at a mass ratio of 99.5:0.5. "13BGDA/iPA" means a solvent obtained by combining 13BGDA and iPA at a mass ratio of 99.5:0.5. "13BGDA/iPA/water" means a solvent obtained by combining 13BGDA, iPA and water at a mass ratio of 94.9:0.1:5. "14BGDA/iPA" means a solvent obtained by combining 14BGDA

and iPA at a mass ratio of 99.5:0.5. "DPGMEA/iPA" means a solvent obtained by combining DPGMEA and iPA at a mass ratio of 99.5:0.5. "DPGMEA/iPA/water" means a solvent obtained by combining DPGMEA, iPA and water at a mass ratio of 94.9:0.1:5. "TEGBME/iPA" means a solvent obtained by combining TEGBME and iPA at a mass ratio of 99.5:0.5. "TEGBME/iPA/water" means a solvent obtained by combining TEGBME, iPA and water at a mass ratio of 94.9:0.1:5. "GBL/DPGMEA/iPA" means a solvent obtained by combining GBL, DPGMEA and iPA at a mass ratio of 49.75:49.75:0.5. "GBL/DPGMEA/iPA/water" means a solvent obtained by combining GBL, DPGMEA, iPA and water at a mass ratio of 47.45:47.45:0.1:5. "GBL/PGMEA/iPA" means a solvent obtained by combining GBL, PGMEA and iPA at a mass ratio of 49.75:49.75:0.5. "GBL/PGMEA/iPA/water" means a solvent obtained by combining GBL, PGMEA, iPA and water at a mass ratio of 47.45:47.45:0.1:5. "DEGEEA/PGME-3" means a solvent obtained by combining DEGEEA and PGME at a mass ratio of 97:3. "DEGEEA/iPA-2" means a solvent obtained by combining DEGEEA and iPA at a mass ratio of 98:2. "TEGBME/iPA-2" means a solvent obtained by combining TEGBME and iPA at a mass ratio of 98:2. "GBL/DPGA/iPA/water" means a solvent obtained by combining GBL, DPGA, iPA and water at a mass ratio of 47.45:47.45:0.1:5. "GBL/13BGDA/iPA/water" means a solvent obtained by combining GBL, 13BGDA, iPA and water at a mass ratio of 47.45:47.45:0.1:5. "GBL/TEGBME/iPA/water" means a solvent obtained by combining GBL, TEGBME, iPA and water at a mass ratio of 47.45:47.45:0.1:5. "GBL/DEGEEA/iPA/water" means a solvent obtained by combining GBL, DEGEEA, iPA and water at a mass ratio of 47.45:47.45:0.1:5. "DEGEEA/PGME-10" means a solvent obtained by combining DEGEEA and PGME at a mass ratio of 90:10.

[0099] [Example 85]

(II-1) Preparation of Liquid Chemical for forming Protecting Film

A mixture of 0.002 g of octadecylphosphonic acid [$C_{18}H_{37}P(O)(OH)_2$] serving as an agent for forming a water-repellent protecting film and 99.998 g

of PGMEA serving as an organic solvent was stirred for about 18 hours thereby obtaining a liquid chemical for forming a protecting film, in which liquid chemical the protecting-film-forming agent concentration was 20 mass ppm.

[0100] (II-2) Step of Cleaning Wafer (Pretreatment Step)

As a pretreatment step 2, a wafer having a smooth tungsten film (a silicon wafer formed having on its surface a tungsten layer of 50 nm thickness) was immersed in 1 mass% aqueous ammonia for 1 minute at room temperature, and then immersed in pure water for 1 minute. Furthermore, as a pretreatment step 3, the wafer was immersed in iPA for 1 minute.

[0101] (II-3) From Step of Forming Protecting Film on Wafer Surface to Drying Step

As a protecting-film-forming step, the wafer having the tungsten film was immersed in the liquid chemical for forming a protecting film at 20 °C for 10 minutes, the liquid chemical having been prepared in the above "(II-1) Preparation of Liquid Chemical for forming Protecting Film" section. Thereafter, the wafer having the tungsten film was immersed in iPA for 1 minute as a subsequent cleaning step. Then, as a drying step, the wafer having the tungsten film was taken out of iPA, followed by spraying air thereon to remove iPA from the surface.

[0102] As a result of evaluating the obtained wafer having the tungsten film in a manner discussed in the above [Method for evaluating Wafer to which Liquid Chemical for forming Protecting Film is provided] section, a wafer in which an initial contact angle before the surface treatment was smaller than 10° was confirmed to have a contact angle of 68° after the surface treatment, as shown in Table 4. With this, the water-repellency-imparting effect was exhibited. Additionally, as a result of calculating the capillary force at the time of retaining water by using the equation discussed in the above "Evaluation of Capillary Force" section, the capillary force was so small as to be 1.2 MN/m^2. Additionally, the contact angle after UV irradiation was smaller than 10°, so that removal of the protecting film was achieved. Furthermore, the ΔRa value of the wafer after UV irradiation was within

±0.5nm, with which it was confirmed that the wafer was not eroded at the time of cleaning and that residues of the protecting film did not remain after UV irradiation.

[0103] [Table 4]

	Liquid chemical for forming protecting film			Wafer	Cleaning liquid for pretreatment step 3	Protecting-film-forming step		Subsequent cleaning step		Evaluation results				
	Protecting-film-forming agent	Solvent	Protecting-film-forming agent concentration [mass ppm]			Temperature [C°]	Time [min]	Cleaning liquid for subsequent cleaning step	Time [min]	Initial contact angle [°]	Contact angle after surface treatment ([°])	Capillary force ([MN/m^2]) <Calculated value>	Removability of protecting film (Contact angle [°])	Surface smoothness (ΔRa[nm])
Example 85	$C_{18}H_{37}P(O)(OH)_2$	PGMEA	20	W	iPA	20	10	iPA	1	<10	68	1.2	<10	Within ±0.5
Example 86	$C_{12}H_{25}P(O)(OH)_2$	PGMEA	50	W	iPA	20	10	iPA	1	<10	60	1.6	<10	Within ±0.5
Example 87	$C_{12}H_{25}P(O)(OH)_2$	PGMEA	50	W	iPA	40	10	iPA	1	<10	70	1.1	<10	Within ±0.5
Example 88	$C_{12}H_{25}P(O)(OH)_2$	Cyclo-hexanone	50	W	iPA	40	10	iPA	1	<10	70	1.1	<10	Within ±0.5
Example 89	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGMEA	100	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 90	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	Cyclo-hexanone	100	W	iPA	40	10	iPA	1	<10	88	0.1	<10	Within ±0.5
Example 91	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA	100	W	iPA	40	10	iPA	1	<10	90	0	<10	Within ±0.5
Example 92	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA	100	W	iPA	40	10	iPA	1	<10	90	0	<10	Within ±0.5
Example 93	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA /Water	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 94	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGMEA/iPA	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 95	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 96	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/iPA	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 97	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/iPA/ Water	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 98	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGDA/iPA	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 99	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	TPGDME/iPA	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 100	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	13BGDA/iPA	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 101	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	14BGDA/iPA	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 102	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DPGMEA/iPA	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 103	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DPGMEA/iPA /Water	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 104	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	TEGBME/iPA	500	W	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 105	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA	1000	W	iPA	20	10	iPA	1	<10	94	0.2	<10	Within ±0.5
Example 106	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA /Water	1000	W	iPA	20	10	iPA	1	<10	94	0.2	<10	Within ±0.5
Example 107	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/DEGEEA /iPA/Water	1000	W	iPA	20	10	iPA	1	<10	94	0.2	<10	Within ±0.5
Example 108	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/DPGMEA /iPA/Water	1000	W	iPA	20	10	iPA	1	<10	94	0.2	<10	Within ±0.5
Example 109	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/PGMEA/ iPA/Water	1000	W	iPA	20	10	iPA	1	<10	94	0.2	<10	Within ±0.5

[0104] [Examples 86 to 109]

Upon suitably modifying those used in Example 85 (i.e., the protecting-film-forming agent, the solvent, the protecting-film-forming agent concentration, and the temperature of the protecting-film-forming step), the surface treatment was conducted on a wafer. Then, evaluations were performed thereon. The results are shown in Table 4.

[0105] [Example 110]

(III-1) Preparation of Liquid Chemical for forming Protecting Film

A mixture of 0.002 g of octadecylphosphonic acid [$C_{18}H_{37}P(O)(OH)_2$] serving as an agent for forming a water-repellent protecting film and 99.998 g of PGMEA serving as an organic solvent was stirred for about 18 hours thereby obtaining a liquid chemical for forming a protecting film, in which liquid chemical the protecting-film-forming agent concentration was 20 mass ppm.

[0106] (III-2) Step of Cleaning Wafer (Pretreatment Step)

As a pretreatment step 2, a wafer having a smooth ruthenium film (a silicon wafer formed having on its surface a ruthenium layer of 300 nm thickness) was immersed in 1 mass% aqueous ammonia for 1 minute at room temperature, and then immersed in pure water for 1 minute. Furthermore, as a pretreatment step 3, the wafer was immersed in iPA for 1 minute.

[0107] (III-3) From Step of Forming Protecting Film on Wafer Surface to Drying Step

As a protecting-film-forming step, the wafer having the ruthenium film was immersed in the liquid chemical for forming a protecting film at 20 °C for 10 minutes, the liquid chemical having been prepared in the above "(III-1) Preparation of Liquid Chemical for forming Protecting Film" section. Thereafter, the wafer having the ruthenium film was immersed in iPA for 1 minute as a subsequent cleaning step. Then, as a drying step, the wafer having the ruthenium film was taken out of iPA, followed by spraying air thereon to remove iPA from the surface.

[0108] As a result of evaluating the obtained wafer having the ruthenium film in a manner discussed in the above [Method for evaluating Wafer to which

Liquid Chemical for forming Protecting Film is provided] section, a wafer in which an initial contact angle before the surface treatment was smaller than 10° was confirmed to have a contact angle of 72° after the surface treatment, as shown in Table 5. With this, the water-repellency-imparting effect was exhibited. Additionally, as a result of calculating the capillary force at the time of retaining water by using the equation discussed in the above "Evaluation of Capillary Force" section, the capillary force was so small as to be 1.0 MN/m^2. Additionally, the contact angle after UV irradiation was smaller than 10°, so that removal of the protecting film was achieved. Furthermore, the ΔRa value of the wafer after UV irradiation was within ±0.5nm, with which it was confirmed that the wafer was not eroded at the time of cleaning and that residues of the protecting film did not remain after UV irradiation.

[0109] [Table 5]

	Liquid chemical for forming protecting film			Wafer	Cleaning liquid for pretreatment step 3	Protecting-film-forming step		Subsequent cleaning step		Evaluation results				
	Protecting-film-forming agent	Solvent	Protecting-film-forming agent concentration [mass ppm]			Temperature [C°]	Time [min]	Cleaning liquid for subsequent cleaning step	Time [min]	Initial contact angle [°]	Contact angle after surface treatment ([°])	Capillary force ([MN/m^2]) <Calculated value>	Removability of protecting film (Contact angle [°])	Surface smoothness (△Ra[nm])
Example 110	$C_{18}H_{37}P(O)(OH)_2$	PGMEA	20	Ru	iPA	20	10	iPA	1	<10	72	1	<10	Within ±0.5
Example 111	$C_{12}H_{25}P(O)(OH)_2$	PGMEA	50	Ru	iPA	20	10	iPA	1	<10	64	1.4	<10	Within ±0.5
Example 112	$C_{12}H_{25}P(O)(OH)_2$	PGMEA	50	Ru	iPA	40	10	iPA	1	<10	66	1.3	<10	Within ±0.5
Example 113	$C_{12}H_{25}P(O)(OH)_2$	Cyclo-hexanone	50	Ru	iPA	40	10	iPA	1	<10	74	0.9	<10	Within ±0.5
Example 114	$C_{12}H_{25}P(O)(OH)_2$	Water	20	Ru	iPA	40	10	iPA	1	<10	70	1.1	<10	Within ±0.5
Example 115	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGMEA	100	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 116	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	Cyclo-hexanone	100	Ru	iPA	40	10	iPA	1	<10	90	0	<10	Within ±0.5
Example 117	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	Water	100	Ru	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 118	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA	100	Ru	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 119	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA	100	Ru	iPA	40	10	iPA	1	<10	92	0.1	<10	Within ±0.5
Example 120	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGMEA/iPA	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 121	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 122	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA/Water	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 123	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/iPA	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 124	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/iPA/Water	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 125	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	PGDA/iPA	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 126	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	TPGDME/iPA	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 127	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	13BGDA/iPA	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 128	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	14BGDA/iPA	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 129	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DPGMEA/iPA	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 130	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DPGMEA/iPA/Water	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 131	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	TEGBME/iPA	500	Ru	iPA	40	10	iPA	1	<10	96	0.3	<10	Within ±0.5
Example 132	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA	1000	Ru	iPA	40	10	iPA	1	<10	98	0.4	<10	Within ±0.5
Example 133	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	DEGEEA/iPA/Water	1000	Ru	iPA	40	10	iPA	1	<10	98	0.4	<10	Within ±0.5
Example 134	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/DEGEEA/iPA/Water	1000	Ru	iPA	40	10	iPA	1	<10	98	0.4	<10	Within ±0.5
Example 135	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/DPGMEA/iPA/Water	1000	Ru	iPA	40	10	iPA	1	<10	98	0.4	<10	Within ±0.5
Example 136	$C_6F_{13}-C_2H_4-P(O)(OH)_2$	GBL/PGMEA/iPA/Water	1000	Ru	iPA	40	10	iPA	1	<10	98	0.4	<10	Within ±0.5

[0110] [Examples 111 to 136]

Upon suitably modifying those used in Example 110 (i.e., the protecting-film-forming agent, the solvent, the protecting-film-forming agent concentration, and the temperature of the protecting-film-forming step), the surface treatment was conducted on a wafer. Then, evaluations were performed thereon. The results are shown in Table 5.

[0111] [Comparative Example 1]

The procedure of Example 1 was repeated with the exception that the liquid chemical for forming a protecting film was not provided to the wafer having the titanium nitride film. In other words, the present Comparative Example was such as to evaluate a wafer the surface of which was not coated with the protecting film. From the evaluation results shown in Table 6, it was confirmed that the contact angle on the wafer was so small as to be 14° and that the capillary force at the time of retaining water was so large as to be 3.1 MN/m^2.

[0112] [Table 6]

	Liquid chemical for forming protecting film			Wafer	Cleaning liquid for pretreatment step 3	Protecting-film-forming step		Subsequent cleaning step		Evaluation results				
	Protecting-film-forming agent	Solvent	Protecting-film-forming agent concentration [mass ppm]			Temperature [C°]	Time [min]	Cleaning liquid for subsequent cleaning step	Time [min]	Initial contact angle [°]	Contact angle after surface treatment ([°])	Capillary force ([MN/m^2]) <Calculated value>	Removability of protecting film (Contact angle [°])	Surface smoothness (△Ra [nm])
Comparative Example 1	-	-	-	TiN	iPA	-	-	iPA	1	<10	14	3.1	-	-
Comparative Example 2	$(CH_3)_3SiCl$	Toluene	30000	TiN	iPA	20	10	iPA	1	<10	18	3	-	-
Comparative Example 3	$[(CH_3)_3Si]_2NH$	Toluene	30000	TiN	iPA	20	10	iPA	1	<10	20	3	-	-
Comparative Example 4	$(CH_3)_3SiN(CH_3)_2$	Toluene	30000	TiN	iPA	20	10	iPA	1	<10	20	3	-	-
Comparative Example 5	-	-	-	W	iPA	-	-	iPA	1	<10	14	3.1	-	-
Comparative Example 6	$(CH_3)_3SiCl$	Toluene	30000	W	iPA	20	10	iPA	1	<10	14	3.1	-	-
Comparative Example 7	$[(CH_3)_3Si]_2NH$	Toluene	30000	W	iPA	20	10	iPA	1	<10	8	3.2	-	-
Comparative Example 8	$(CH_3)_3SiN(CH_3)_2$	Toluene	30000	W	iPA	20	10	iPA	1	<10	10	3.2	-	-
Comparative Example 9	-	-	-	Ru	iPA	-	-	iPA	1	<10	14	3.1	-	-
Comparative Example 10	$(CH_3)_3SiCl$	Toluene	30000	Ru	iPA	20	10	iPA	1	<10	14	3.1	-	-
Comparative Example 11	$[(CH_3)_3Si]_2NH$	Toluene	30000	Ru	iPA	20	10	iPA	1	<10	20	3	-	-
Comparative Example 12	$(CH_3)_3SiN(CH_3)_2$	Toluene	30000	Ru	iPA	20	10	iPA	1	<10	22	3	-	-

[0113] [Comparative Example 2]

First of all, a mixture of 3 g of trimethylsilyl chloride [$(CH_3)_3SiCl$] (a silane coupling agent) serving as a protecting-film-forming agent and 97 g of toluene serving as a solvent was stirred for about 5 minutes thereby obtaining a liquid chemical for forming a protecting film, in which liquid chemical the protecting-film-forming agent concentration was 30000 mass ppm. Then, the cleaning and the surface treatment were conducted on a wafer having a titanium nitride film by the same method as Example 1. From the evaluation results as shown in Table 6, it was confirmed that the contact angle on the wafer after the surface treatment was 18°. The water-repellency-imparting effect was not observed. Additionally, the capillary force at the time of retaining water was so large as to be 3.0 MN/m^2.

[0114] [Comparative Example 3]

The procedure of Comparative Example 2 was repeated with the exception that hexamethyldisilazane ($[(CH_3)_3Si]_2NH$) was used as the protecting-film-forming agent. From the results as shown in Table 6, it was confirmed that the contact angle after the surface treatment was 20°. The water-repellency-imparting effect was not observed. Additionally, the capillary force at the time of retaining water was so large as to be 3.0 MN/m^2.

[0115] [Comparative Example 4]

The procedure of Comparative Example 2 was repeated with the exception that trimethylsilyl dimethylamine [$(CH_3)_3SiN(CH_3)_2$] was used as the protecting-film-forming agent. From the results as shown in Table 6, it was confirmed that the contact angle after the surface treatment was 20°. The water-repellency-imparting effect was not observed. Additionally, the capillary force at the time of retaining water was so large as to be 3.0 MN/m^2.

[0116] [Comparative Example 5]

The procedure of Example 85 was repeated with the exception that the liquid chemical for forming a protecting film was not provided to the wafer having the tungsten film. In other words, the present Comparative Example was such as to evaluate a wafer the surface of which was not coated with the

protecting film. From the evaluation results shown in Table 6, it was confirmed that the contact angle on the wafer was so small as to be 14° and that the capillary force at the time of retaining water was so large as to be 3.1 MN/m^2.

[0117] [Comparative Example 6]

First of all, a mixture of 3 g of trimethylsilyl chloride [$(CH_3)_3SiCl$] (a silane coupling agent) serving as a protecting-film-forming agent and 97 g of toluene serving as a solvent was stirred for about 5 minutes thereby obtaining a liquid chemical for forming a protecting film, in which liquid chemical the protecting-film-forming agent concentration was 30000 mass ppm. Then, the cleaning and the surface treatment were conducted on a wafer having a tungsten film by the same method as Example 85. From the evaluation results as shown in Table 6, it was confirmed that the contact angle after the surface treatment was 14°. The water-repellency-imparting effect was not observed. Additionally, the capillary force at the time of retaining water was so large as to be 3.1 MN/m^2.

[0118] [Comparative Example 7]

The procedure of Comparative Example 6 was repeated with the exception that hexamethyldisilazane ($[(CH_3)_3Si]_2NH$) was used as the protecting-film-forming agent. From the evaluation results as shown in Table 6, it was confirmed that the contact angle after the surface treatment was 8°. The water-repellency-imparting effect was not observed. Additionally, the capillary force at the time of retaining water was so large as to be 3.2 MN/m^2.

[0119] [Comparative Example 8]

The procedure of Comparative Example 6 was repeated with the exception that trimethylsilyl dimethylamine [$(CH_3)_3SiN(CH_3)_2$] was used as the protecting-film-forming agent. From the evaluation results as shown in Table 6, it was confirmed that the contact angle after the surface treatment was 10°. The water-repellency-imparting effect was not observed. Additionally, the capillary force at the time of retaining water was so large as to be 3.2 MN/m^2.

[0120] [Comparative Example 9]

The procedure of Example 110 was repeated with the exception that the liquid chemical for forming a protecting film was not provided to the wafer having the ruthenium film. In other words, the present Comparative Example was such as to evaluate a wafer the surface of which was not coated with the protecting film. From the evaluation results shown in Table 6, it was confirmed that the contact angle on the wafer was so small as to be 14° and that the capillary force at the time of retaining water was so large as to be 3.1 MN/m^2.

[0121] [Comparative Example 10]

First of all, a mixture of 3 g of trimethylsilyl chloride [$(CH_3)_3SiCl$] (a silane coupling agent) serving as a protecting-film-forming agent and 97 g of toluene serving as a solvent was stirred for about 5 minutes thereby obtaining a liquid chemical for forming a protecting film, in which liquid chemical the protecting-film-forming agent concentration was 30000 mass ppm. Then, the cleaning and the surface treatment were conducted on a wafer having a ruthenium film by the same method as Example 110. From the evaluation results as shown in Table 6, it was confirmed that the contact angle after the surface treatment was 14°. The water-repellency-imparting effect was not observed. Additionally, the capillary force at the time of retaining water was so large as to be 3.1 MN/m^2.

[0122] [Comparative Example 11]

The procedure of Comparative Example 10 was repeated with the exception that hexamethyldisilazane ($[(CH_3)_3Si]_2NH$) was used as the protecting-film-forming agent. From the evaluation results as shown in Table 6, it was confirmed that the contact angle after the surface treatment was 20°. The water-repellency-imparting effect was not observed. Additionally, the capillary force at the time of retaining water was so large as to be 3.0 MN/m^2.

[0123] [Comparative Example 12]

The procedure of Comparative Example 10 was repeated with the exception that trimethylsilyl dimethylamine [$(CH_3)_3SiN(CH_3)_2$] was used as

the protecting-film-forming agent. From the evaluation results as shown in Table 6, it was confirmed that the contact angle after the surface treatment was 22°. The water-repellency-imparting effect was not observed. Additionally, the capillary force at the time of retaining water was so large as to be 3.0 MN/m^2.

Explanation of Reference Numerals

[0124]

1 Wafer

2 Uneven pattern of a surface of the wafer

3 Projected portions of the pattern

4 Recessed portions of the pattern

5 Width of the recessed portions

6 Height of the projected portions

7 Width of the projected portions

8 Liquid chemical for forming a protecting film, retained in the recessed portions 4

9 Liquid retained in the recessed portions 4

10 Protecting Film

CLAIMS

[Claim 1] A liquid chemical for forming a water-repellent protecting film, the liquid chemical including:

an agent for forming a water-repellent protecting film, the agent being for forming a water-repellent protecting film on a wafer after a cleaning step for the wafer and before a drying step for the wafer, the wafer having at its surface an uneven pattern and containing at least one kind element of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern, the water-repellent protecting film being formed at least on the surfaces of the recessed portions; and

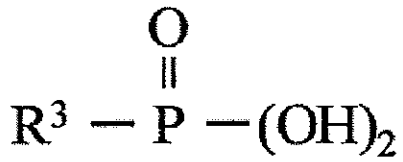
a solvent,

the liquid chemical being characterized in that the agent for forming a water-repellent protecting film is a compound represented by the following general formula [1].

$$R^1 - \overset{\overset{O}{\|}}{P} - (OH)_a(R^2)_{2-a} \qquad [1]$$

(In the formula [1], R^1 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^2 mutually independently represents a monovalent organic group having a C_1-C_{18} hydrocarbon group the hydrogen elements of which may partially or entirely be replaced with a fluorine element(s). "a" is an integer of from 0 to 2.)

[Claim 2] A liquid chemical for forming a water-repellent protecting film, as claimed in Claim 1, characterized in that the agent for forming a water-repellent protecting film is a compound represented by the following general formula [2].



[2]

(In the formula [2], 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).)

[Claim 3] A water-repellent protecting film formed on a wafer after a cleaning step for the wafer and before a drying step for the wafer, the wafer having at its surface an uneven pattern and containing at least one kind element of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern, the water-repellent protecting film being formed at least on the surfaces of the recessed portions by retaining a liquid chemical for forming a water-repellent protecting film as claimed in Claim 1 at least in the recessed portions,

the water-repellent protecting film being characterized by being formed of a compound represented by the general formula [1] and serving as an agent for forming a water-repellent protecting film.

[Claim 4] A method for cleaning a wafer, the wafer having at its surface an uneven pattern and containing at least one kind element of titanium, tungsten, aluminum, copper, tin, tantalum and ruthenium at surfaces of recessed portions of the uneven pattern, the method including at least:

a protecting-film-forming step where a liquid chemical for forming a protecting film is retained at least in the recessed portions of the uneven pattern;

a drying step of removing liquid from the uneven pattern by drying; and

a film-removing step of removing the protecting film,

wherein the liquid chemical for forming a protecting film is a liquid

chemical containing an agent for forming a water-repellent protecting film, the agent being for forming a water-repellent protecting film at least on the surfaces of the recessed portions,

the cleaning method being characterized in that the water-repellent protecting film is formed of a compound represented by the general formula [1] and serving as an agent for forming a water-repellent protecting film.