

DESCRIPTION

COMPOUND, COPOLYMER COMPRISING THE COMPOUND, AND RESIST PROTECTIVE FILM COMPOSITION COMPRISING THE COPOLYMER

5 Technical Field

The present invention relates to a compound, a copolymer containing the compound, and a resist protective film composition containing the copolymer. More particularly, the present invention relates to a compound which can be used in a resist protective film which has sufficient light transmissivity, is not easily intermixed with a resist film, has appropriate hydrophilic or hydrophobic characteristics, does not exhibit a phenomenon of pattern shape deterioration, is easily dissolved in alkali developer solutions, and decreases the occurrence of various defects during the process of immersion or dry exposure; a copolymer containing the compound; and a resist protective film composition containing the copolymer.

1.5

Background Art

Along with the recent trend of high integration of LSI and increases in processing speed, there is a demand for finer pattern formation in photoresists. As the exposure light for use in resist pattern formation, exposure light utilizing the g-line (436 nm) or the i-line (365 nm) of a mercury lamp or the like as a light source has been used.

It is believed that attempts to bring an improvement of resolution, which is a property related to the exposure light wavelength, are now substantially approaching a limit. However, there is a demand for finer photoresist patterning, and a method of using exposure light having a shorter wavelength may be effective as a means for this purpose. Therefore, KrF excimer laser light having a shorter wavelength (248 nm) or the like is

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used in place of the i-line (365 nm).

In regard to ArF immersion lithography, it has been suggested to enclose water between a projection lens and a wafer substrate. Such a method has enabled pattern formation even when a lens having a numerical aperture (NA) value of 1.0 or greater is used, by using the refractive index of water at 193 nm, and this method is called as immersion exposure technique. However, since the resist film is brought into contact with pure water, an acid that is generated by a photoacid generator or an amine compound that has been incorporated into the resist film as a quencher is dissolved in water, and accordingly, various defects such as a shape change in the resist pattern, pattern destruction due to swelling, bubbling defects, and watermark defects, tend to occur.

Therefore, for the purpose of forming a barrier between a photoresist film and a medium such as water, there has been suggested a method of forming a protective film or an overlay film between the resist film and water. Such a resist protective film is required to have characteristics such as having a sufficient light transmittance to the wavelength of the exposure light so that the protective film does not interrupt exposure, not causing intermixing with the resist film, being capable of formation on a photoresist film, causing no elution into a medium such as water at the time of immersion exposure, forming and maintaining a stable film, and being easily dissoluble in an alkali solution which serves as a developer solution.

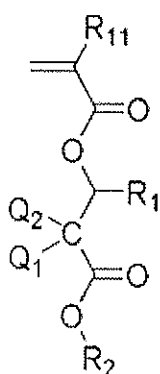
Disclosure of the Invention

It is an object of the present invention to provide a compound which can be used in a resist protective film which has sufficient light transmissivity, is not easily intermixed with resist films, has appropriate hydrophilic or hydrophobic characteristics, does not exhibit a phenomenon of pattern shape deterioration, is easily dissolved in alkali developer

solutions, and decreases the occurrence of various defects during the process of immersion or dry exposure; a copolymer containing the compound; and a resist protective film composition containing the copolymer.

In order to achieve the object described above, there is provided a compound represented by the following formula (1) according to an aspect of the present invention.

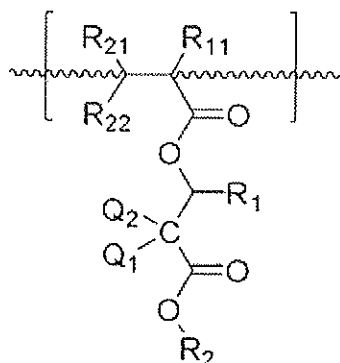
[Formula 1]



In the formula (1), R_{11} represents any one selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 8 carbon atoms, and a halogenated alkyl group having 1 to 5 carbon atoms; R_1 represents any one selected from the group consisting of an alkyl group, a heteroalkyl group, an aryl group, a heteroaryl group, a cycloalkyl group, a heterocycloalkyl group, an alkyl ether group, and an alkylcarbonyl group; R_2 represents any one selected from the group consisting of a hydrogen atom and an alkyl group having 1 to 5 carbon atoms; and Q_1 and Q_2 each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom.

According to another aspect of the present invention, there is provided a copolymer including a repeating unit represented by the following formula (1-a).

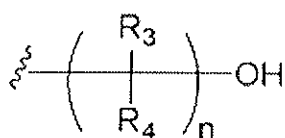
[Formula 1-a]



In the formula (1-a), R₁₁, R₂₁ and R₂₂ each independently represent any one selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 8 carbon atoms, and a halogenated alkyl group having 1 to 5 carbon atoms; R₁ represents any one selected from the group consisting of an alkyl group, a heteroalkyl group, an aryl group, a heteroaryl group, a cycloalkyl group, a heterocycloalkyl group, an alkyl ether group, and an alkylcarbonyl group; R₂ represents any one selected from the group consisting of a hydrogen atom and an alkyl group having 1 to 5 carbon atoms; and Q₁ and Q₂ each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom.

The copolymer may further include a repeating unit which contains a functional group represented by the following formula (2).

[Formula 2]



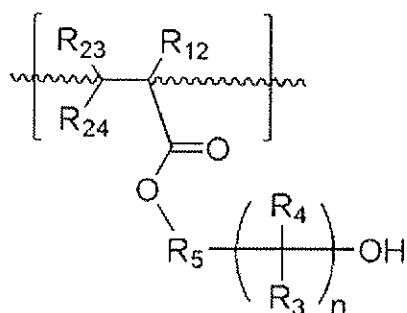
In the formula (2), R₃ and R₄ each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, and

a halogenated alkyl group having 1 to 10 carbon atoms; any one selected from the group consisting of R_3 , R_4 and a combination thereof is a halogenated alkyl group; and n represents an integer from 1 to 6.

The repeating unit containing a functional group represented by the formula (2)

5 may be a repeating unit represented by the following formula (3-a).

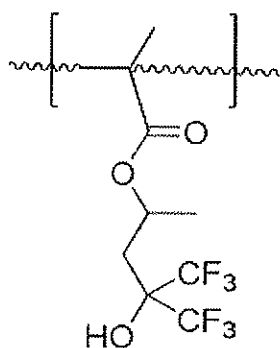
[Formula 3-a]



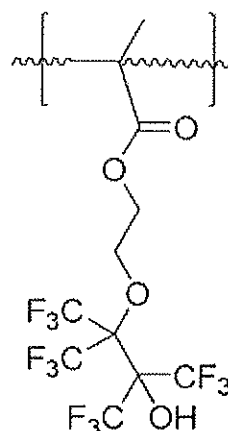
In the formula (3-a), R_{12} , R_{23} and R_{24} each independently represent any one selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 8 carbon atoms, and a halogenated alkyl group having 1 to 5 carbon atoms; R_3 and R_4 each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, and a halogenated alkyl group having 1 to 10 carbon atoms; any one selected from the group consisting of R_3 , R_4 and a combination thereof is a halogenated alkyl group; R_5 represents a divalent hydrocarbon group; and n represents an integer from 1 to 6.

The repeating unit represented by the formula (3-a) may be a repeating unit represented by any one selected from the group consisting of the following formulas (4-a), (5-a), (6-a), (7-a) and combinations thereof.

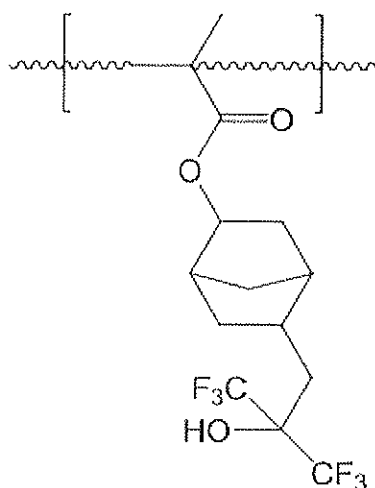
[Formula 4-a]



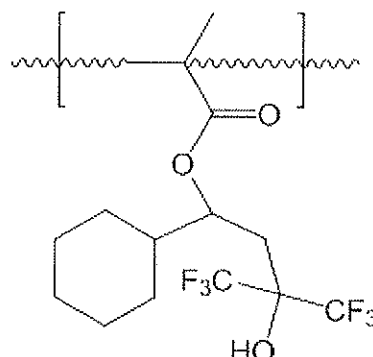
[Formula 5-a]



[Formula 6-a]



[Formula 7-a]



5 The copolymer may be such that the molar proportion m of the repeating unit represented by the formula (1-a) is $0.01 \leq m \leq 0.6$, the molar proportion l of the repeating unit represented by the formula (3-a) is $0.4 \leq l \leq 0.99$, and the sum of m and l is 1.

The copolymer may have a weight average molecular weight as measured by gel permeation chromatography of 1,000 to 500,000.

10 According to another aspect of the present invention, there is provided a resist protective film composition containing the copolymer.

The resist protective film composition may further contain an alcohol solvent having 4 to 8 carbon atoms.

Hereinafter, the present invention will be described in more detail.

The terms used in the present specification are defined as follows.

5 Unless particularly stated otherwise herein, the halogen atom means any one selected from the group consisting of fluorine, chlorine, bromine and iodine.

Unless particularly stated otherwise herein, examples of the alkyl group include a primary alkyl group, a secondary alkyl group, and a tertiary alkyl group.

10 Unless particularly stated otherwise herein, all of the compounds and substituents may be substituted or unsubstituted. Here, being substituted means that a hydrogen atom has been replaced with any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a cyano group, a nitro group, an amino group, a thio group, a methylthio group, an alkoxy group, a nitrile group, an aldehyde group, an epoxy group, an ether group, an ester group, a carbonyl group, an acetal group, a ketone group,
15 an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an allyl group, a benzyl group, an aryl group, a heteroaryl group, derivatives thereof, and combinations thereof.

Unless particularly stated otherwise herein, the prefix "hetero-" means that carbon atoms are substituted with one to three heteroatoms selected from the group consisting of N, O, S and P. For example, a heteroalkyl group means that one to three carbon atoms
20 among the carbon atoms of an alkyl group are substituted with heteroatoms.

Unless particularly stated otherwise herein, the term "halogenated" means that a hydrogen atom has been substituted with any one selected from the group consisting of fluorine, chlorine, bromine and iodine.

Unless particularly stated otherwise herein, examples of the cycloalkyl group
25 include monocyclic, bicyclic, tricyclic and tetracyclic cycloalkyl groups. Examples of the

cycloalkyl group also include polycyclic cycloalkyl groups, including an adamantyl group and a norbornyl group.

Unless particularly stated otherwise herein, the alkyl ether group means a compound containing an ether group and an alkyl group, or a derivative of the compound.

5 For example, the alkyl ether may be a linear ether or a cyclic ether.

Unless particularly stated otherwise, the alkylcarbonyl group means a compound containing the moiety -CO-, or a derivative of the compound. For example, the alkylcarbonyl group may be a compound having an alkyl group in which a carbon atom is substituted with -CO-.

1.0 Unless particularly stated otherwise, the alkyl group means a linear or branched alkyl group having 1 to 30 carbon atoms; the heteroalkyl group means an heteroalkyl group having 1 to 3 carbon atoms; the aryl group means an aryl group having 6 to 30 carbon atoms; the heteroaryl group means a heteroaryl group having 2 to 30 carbon atoms; the cycloalkyl group means a cycloalkyl group having 3 to 32 carbon atoms; the
1.5 heterocycloalkyl group means a heterocycloalkyl group having 2 to 32 carbon atoms; the alkyl ether group means an alkyl ether group having 1 to 20 carbon atoms; the alkylcarbonyl group means an alkylcarbonyl group having 1 to 20 carbon atoms; and the alkoxy group means an alkoxy group having 1 to 10 carbon atoms.

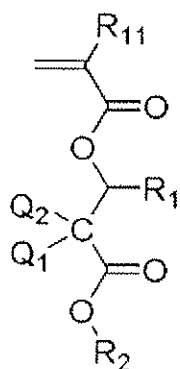
Unless particularly stated otherwise herein, examples of the divalent hydrocarbon
2.0 group include an alkanediyl and an alkenediyl, and also include a heteroalkanediyl and a heteroalkenediyl, in which one to three carbon atoms of the alkanediyl or the alkenediyl are substituted with one to three heteroatoms selected from the group consisting of N, O, S and P.

Unless particularly stated otherwise, the alkanediyl is a divalent atomic group
2.5 obtained by detaching two hydrogen atoms from an alkane, and can be represented by

formula: $-C_nH_{2n}-$. The alkenediyl is a divalent atomic group obtained by detaching two hydrogen atoms from an alkene, and can be represented by formula $-C_nH_n-$.

The compound according to an aspect of the present invention is represented by the following formula (1).

5 [Formula 1]



In the formula (1), R₁₁ represents any one selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 8 carbon atoms, and a halogenated alkyl group having 1 to 5 carbon atoms. R₁₁ is preferably any one selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 5 carbon atoms, and a halogenated alkyl group having 1 to 3 carbon atoms.

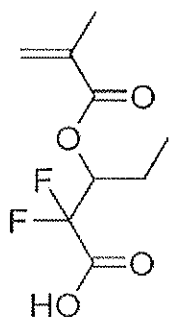
R₁ represents any one selected from the group consisting of an alkyl group, a heteroalkyl group, an aryl group, a heteroaryl group, a cycloalkyl group, a heterocycloalkyl group, an alkyl ether group, and an alkylcarbonyl group. R₁ is preferably an alkyl group having 1 to 10 carbon atoms, a heteroalkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 20 carbon atoms, a heteroaryl group having 6 to 20 carbon atoms, a cycloalkyl group having 3 to 20 carbon atoms, a heterocycloalkyl group having 3 to 20 carbon atoms, an alkyl ether group having 1 to 10 carbon atoms, and an alkylcarbonyl group having 1 to 10 carbon atoms.

Furthermore, R_1 may be substituted or unsubstituted as defined herein, and when R_1 is substituted, it is preferable that a hydrogen atom of R_1 be substituted with a halogen atom.

R_2 represents any one selected from the group consisting of a hydrogen atom and an alkyl group having 1 to 5 carbon atoms, and Q_1 and Q_2 each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom. Q_1 and Q_2 are each preferably a fluorine atom.

The compound represented by the formula (1) may be a compound represented by the following formula (6).

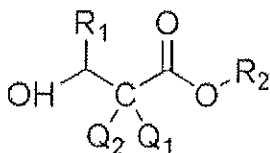
[Formula 6]



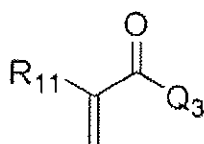
The compound represented by the formula (1) can be synthesized by a method described below.

That is, the method for producing the compound represented by the formula (1) includes the steps of dissolving a compound represented by the following formula (7) and a compound represented by the following formula (8) in a solvent, and allowing the compounds to react in the presence of a basic catalyst to obtain the compound of the following formula (1).

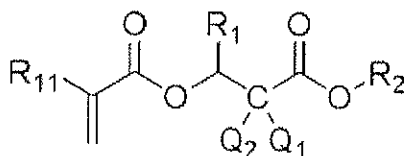
[Formula 7]



[Formula 8]



[Formula 1]



5

In the formula (7), formula (8) and formula (1), Q_3 represents a halogen atom, and is preferably chlorine.

R_{11} , R_1 , R_2 , Q_1 and Q_2 have the same meanings as defined in connection with the compound represented by the formula (1), and therefore, descriptions thereon will not be repeated.

10

Specifically, the method for producing the compound represented by the formula (1) includes a Step 1 process of dissolving the compound represented by the formula (7) in a solvent, dissolving the compound represented by the formula (8) into the solvent while slowly adding the compound dropwise, and thereby preparing a reaction mixture liquid.

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The process of producing a reaction mixture liquid by slowly adding dropwise the compound represented by the formula (8) into the solvent may be carried out in an ice

bath.

As the solvent, any one selected from the group consisting of esters, ethers, lactones, ketones, amides, alcohols, and combinations thereof can be used, and the solvent is preferably any one selected from the group consisting of dichloromethane, chloroform, dichloroethane, acetonitrile, toluene, methyl acetate, ethyl acetate, and combinations thereof.

The method for producing the compound represented by the formula (1) may include a process of allowing the reaction mixture liquid prepared in the Step 1 process to react in the presence of a basic catalyst.

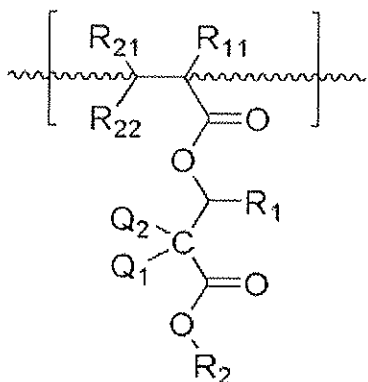
As the basic catalyst, any one selected from the group consisting of triethylamine, diethylamine, pyridine, diethylisopropylamine, and combinations thereof can be used, and triethylamine may be used with preference. When the reaction mixture liquid is allowed to react in the presence of a basic catalyst in the Step 2 process, the desired product can be obtained in a minimal reaction time, and thus the reaction yield can be increased.

The reaction time for reacting the reaction mixture liquid may be 1 to 6 hours, and is preferably 1 to 3 hours.

The compound represented by the formula (1) may be obtained by washing the reaction mixture liquid obtained after completion of the reaction, with a hydrochloric acid solution (2% HCl) to remove the basic catalyst, subsequently collecting the organic layer, and removing the solvent of the organic layer by distillation under reduced pressure. However, the present invention is not intended to be limited thereto.

The copolymer according to another aspect of the present invention includes a repeating unit represented by the following formula (1-a).

[Formula 1-a]



In the formula (1-a), R_{11} , R_{21} and R_{22} each independently represent any one selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 8 carbon atoms, and a halogenated alkyl group having 1 to 5 carbon atoms.

- 5 R_{11} , R_{21} and R_{22} are each preferably any one selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 5 carbon atoms, and a halogenated alkyl group having 1 to 3 carbon atoms.

R_1 represents any one selected from the group consisting of an alkyl group, a heteroalkyl group, an aryl group, a heteroalkyl group, a cycloalkyl group, a heterocycloalkyl group, an alkyl ether group, and an alkylcarbonyl group. R_1 is preferably

10 any one selected from the group consisting of an alkyl group having 1 to 10 carbon atoms, a heteroalkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 20 carbon atoms, a heteroaryl group having 6 to 20 carbon atoms, a cycloalkyl group having 3 to 20 carbon atoms, a heterocycloalkyl group having 3 to 20 carbon atoms, an alkyl ether group

15 having 1 to 10 carbon atoms, and an alkylcarbonyl group having 1 to 10 carbon atoms.

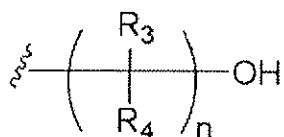
Furthermore, R_1 may be substituted or unsubstituted as defined herein, and when R_1 is substituted, it is preferable that a hydrogen atom of R_1 be substituted with a halogen atom.

R_2 represents any one selected from the group consisting of a hydrogen atom and

an alkyl group having 1 to 5 carbon atoms, and Q₁ and Q₂ each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom. Q₁ and Q₂ are each preferably a fluorine atom.

The copolymer may further include a repeating unit containing a functional group
5 represented by the following formula (2).

[Kagaku 2]

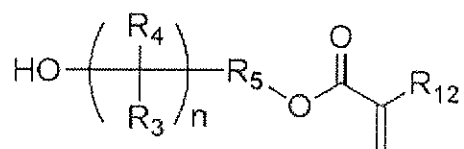


In the formula (2), R₃ and R₄ each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, and
10 a halogenated alkyl group having 1 to 10 carbon atoms. R₃ and R₄ are each preferably any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, and a halogenated alkyl group having 1 to 7 carbon atoms, and more preferably any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, and a fluoroalkyl group having 1 to 4 carbon atoms. Any one
15 selected from the group consisting of R₃, R₄ and a combination thereof is a halogenated alkyl group.

n represents an integer from 1 to 6, and n is preferably an integer from 1 to 3.

The repeating unit containing a functional group represented by the formula (2) may be derived from a compound represented by the following formula (3).

20 [Kagaku 3]



In the formula (3), R₁₂ represents any one selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 8 carbon atoms, and a halogenated alkyl group having 1 to 5 carbon atoms, and R₁₂ is preferably any one
 5 selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 5 carbon atoms, and a halogenated alkyl group having 1 to 3 carbon atoms.

R₃ and R₄ each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, and a halogenated alkyl group having 1 to 10 carbon atoms, and preferably, R₃ and R₄ each independently present
 10 any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 7 carbon atoms, and a halogenated alkyl group having 1 to 7 carbon atoms, and more preferably any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, and a fluoroalkyl group having 1 to 4 carbon atoms. Any one selected from the group consisting of R₃, R₄ and a combination thereof is a halogenated
 15 alkyl group.

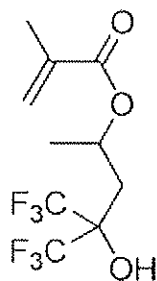
n represents an integer from 1 to 6, and n is preferably an integer from 1 to 3.

R₅ represents a divalent hydrocarbon group, and is preferably any one selected from the group consisting of an alkanediyl having 1 to 20 carbon atom, an alkenediyl having 2 to 20 carbon atoms, a heteroalkanediyl having 1 to 20 carbon atoms, a
 20 heteroalkenediyl having 2 to 20 carbon atoms, a cycloalkanediyl having 3 to 30 carbon atoms, a cycloalkenediyl having 3 to 30 carbon atoms, a heterocycloalkanediyl having 2 to 30 carbon atoms, and a heterocycloalkenediyl having 3 to 30 carbon atoms.

R₅ is more preferably any one selected from the group consisting of -OCH₂-, -OCH(Cl)-, -CO-, -COCH₂-, -COCH₂CH₂-, -CH₂-O-CH₂-, -CH₂-O-CH₂CH₂-, -CH₂CH₂-O-CH₂-, -CH₂-O-CH₂CH₂CH₂-, -CH₂CH₂-O-CH₂CH₂-, -CH₂CH₂CH₂-O-CH₂-, -C(CH₃)₂CH₂-, -CH(CH₃)CH₂-, -CH(CH₂CH₃)-, -CH(OCH₃)-, -C(CF₃)(OCH₃)-, -CH₂-S-CH₂-, -CH₂-S-CH₂CH₂-, -CH₂CH₂-S-CH₂-, -CH₂-S-CH₂CH₂CH₂-, -CH₂CH₂-S-CH₂CH₂-, -CH₂CH₂CH₂-S-CH₂-, -CH(CH₂)CH-, -C(CH₂CH₂)-, -CH₂CO-, -CH₂CH₂CO-, -CH(CH₃)CH₂CO-, -CH(OH)-, -C(OH)(CH₃)-, -CH(F)-, -CH(Br)-, -CH(Br)CH(Br)-, -CH=CH-, -CH₂CH=CH-, -CH=CHCH₂-, -CH=CHCO-, -C₇H₉- and -C₁₀H₁₄-. The hydrogen atoms of R₅ may be each substituted with any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, and combinations thereof.

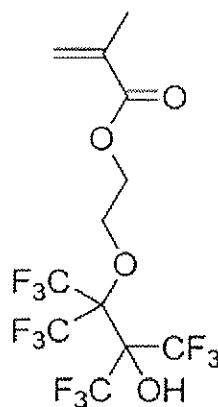
The compound represented by the formula (3) may be a compound represented by any one selected from the group consisting of the following formulas (4) to (7).

[Formula 4]

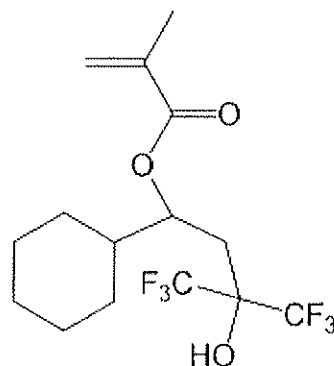
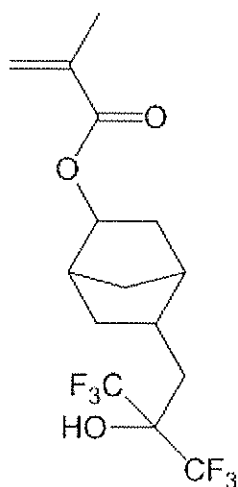


[Formula 6]

[Formula 5]

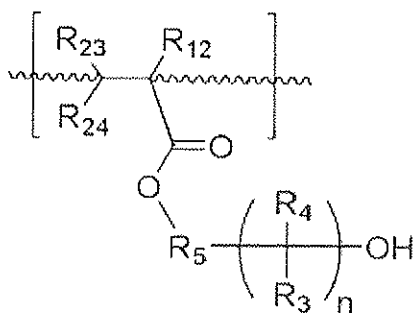


[Formula 7]



The repeating unit containing a functional group represented by the formula (2) may be a repeating unit represented by the following formula (3-a).

[Formula 3-a]



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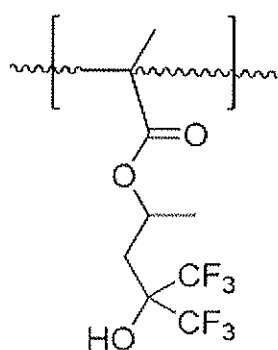
In the formula (3-a), R_{23} and R_{24} each independently represent any one selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 8 carbon atoms, and a halogenated alkyl group having 1 to 5 carbon atoms, and R_{23} and R_{24} are each preferably any one selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 5 carbon atoms, and a halogenated alkyl group having 1 to 3 carbon atoms.

In the formula (3-a), R_{12} , R_3 , R_4 , R_5 and n respectively have the same meanings as defined in connection with the formula (3), and thus further explanation will not be

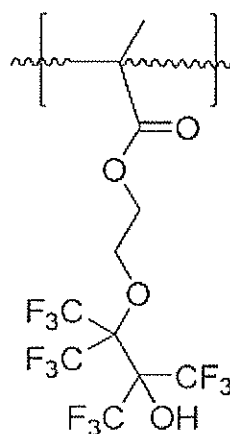
repeated.

The repeating unit represented by the formula (3-a) may be a repeating unit represented by any one selected from the group consisting of the following formula (4-a), formula (5-a), formula (6-a), formula (7-a), and combinations thereof.

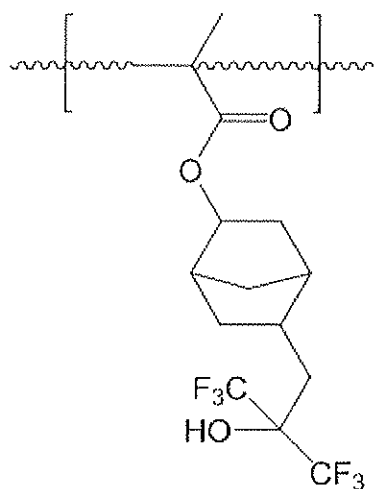
5 [Formula 4-a]



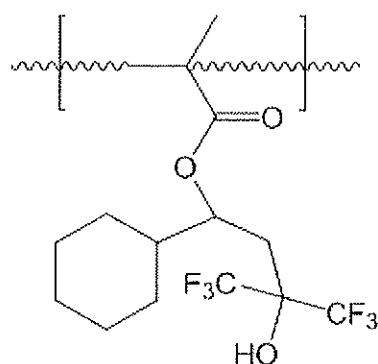
[Formula 5-a]



[Formula 6-a]



[Formula 7-a]



When the copolymer is used in a resist protective film composition containing the
 10 copolymer, the copolymer may have characteristics such as that the copolymer is
 transparent to the exposure light, is not compatible with the liquid for exposure during

immersion exposure, and does not cause intermixing with the resist. Furthermore, the copolymer has appropriate hydrophilic or hydrophobic characteristics, so that the copolymer can reduce the occurrence of various defects during the exposure process. Specifically, if the surface of the resist protective film does not have appropriate

5 hydrophilicity, bubble defects or watermark defects may occur depending on the scan speed of the exposure apparatus. However, since the resist protective composition of the present invention contains a copolymer which includes a repeating unit represented by the formula (1) as well as a repeating unit containing a functional group represented by the formula (2), the resist protective film composition has appropriate hydrophilicity and
10 solubility and forms a film having improved surface properties so that the level of defects occurring in the film can be lowered.

The copolymer may be such that the molar proportion m of the repeating unit represented by the formula (1-a) is $0.01 \leq m \leq 0.6$, the molar proportion l of the repeating unit represented by the formula (3-a) is $0.4 \leq l \leq 0.99$, and the sum of m and l is 1.

15 Preferably, the copolymer may be such that the molar proportion m is $0.01 \leq m \leq 0.3$, the molar proportion l is $0.7 \leq l \leq 0.99$, and the sum of m and l is 1.

When the proportions of the repeating units of the copolymer are in the ranges described above, in case where the resist protective film composition containing the copolymer is applied to an immersion exposure method, the composition may exhibit
20 appropriate hydrophobic characteristics with low affinity to water.

The copolymer may have a weight average molecular weight as measured by gel permeation chromatography of 1,000 to 500,000, and preferably a weight average molecular weight of 2,000 to 100,000. When a copolymer having a weight average molecular weight in the range described above is used, removal of the protective film
25 containing the copolymer by the solvent intended for protective film removal can be easily

achieved, and the protective film may be easily dissolved in the developer solution.

If the weight average molecular weight of the copolymer is too small, intermixing of the copolymer may occur, or elution of the copolymer into pure water may occur in the case of immersion exposure. If the weight average molecular weight is too large,

5 appropriate film formation may not be easily achieved, or the solubility of the copolymer in alkali may be decreased.

The resist protective film composition according to another aspect of the present invention contains the copolymer. The term resist protective film composition means an overlay film forming composition which forms a protective film over a photoresist film
10 when radiation-induced pattern formation is carried out.

The resist protective film composition can be prepared by further adding a solvent to the copolymer. When the resist protective film composition is prepared by adding a solvent to the copolymer, film formability of the resist protective film composition can be improved.

15 In the resist protective film composition, the solvent is used such that the content of the copolymer based on the total amount of the resist protective film composition is 0.1% to 20% by weight, preferably 0.1% to 10% by weight, and more preferably 0.5% to 5% by weight. When the solvent is used in an amount resulting in the copolymer content range described above, the film formability of the resist protective film composition can be
20 appropriately regulated.

As the solvent, any one selected from the group consisting of esters, ethers, lactones, ketones, alcohols, and combinations thereof can be used, and preferably, any one selected from the group consisting of alcohols, ethers, and combinations thereof can be used.

25 An alcohol-based solvent may include any one selected from the group consisting

of a monohydric alcohol, a dihydric alcohol, a trihydric alcohol, and combinations thereof, and a monohydric alcohol is preferably used. When the solvent includes a monohydric alcohol as described above, the solubility of the protective film composition may be increased, and damage of the resist film can be minimized.

5 More preferably, a monohydric alcohol having 4 to 12 carbon atoms can be used as the alcohol-based solvent, or a monohydric alcohol having 4 to 8 carbon atoms can also be used. When a monohydric alcohol having 4 to 8 carbon atoms is used as the alcohol-based solvent, the solubility of the resist protective film composition can be increased, and damage of the resist film can be minimized.

10 Specific examples of the monohydric alcohol having 4 to 8 carbon atoms include 1-butyl alcohol, 2-butyl alcohol, isobutyl alcohol, tert-butyl alcohol, 1-pentanol, 2-pentanol, 3-pentanol, tert-amyl alcohol, neopentyl alcohol, 2-methyl-1-butanol, 3-methyl-1-butanol, 3-methyl-3-pentanol, cyclopentanol, 1-hexanol, 2-hexanol, 3-hexanol, 2,3-dimethyl-2-butanol, 3,3-dimethyl-1-butanol, 3,3-dimethyl-2-butanol, 2-ethyl-1-butanol, 2-methyl-1-pentanol, 2-methyl-2-pentanol, 2-methyl-3-pentanol, 3-methyl-1-pentanol, 3-methyl-2-pentanol, 3-methyl-3-pentanol, 4-methyl-1-pentanol, 4-methyl-2-pentanol, 4-methyl-3-pentanol, cyclohexanol, 1-octanol, and combinations thereof.

15 As an ether-based solvent, any one selected from the group consisting of di-n-butyl ether, diisobutyl ether, di-sec-butyl ether, di-n-pentyl ether, diisopentyl ether, di-sec-pentyl ether, di-t-amyl ether, di-n-hexyl ether, and combinations thereof can be used, but the present invention is not limited to these.

25 The resist protective film composition containing the copolymer can maintain a pKa value similar to the value obtainable when a vinylsulfonic acid type protective film composition is used in order to prevent the occurrence of defects at the film surface, and can also improve the polymerization yield or properties.

As a method for forming a pattern using the resist protective film composition, a conventional pattern forming method can be used. Specifically, such a method includes the steps of forming a photoresist film on a substrate, forming a resist protective film on the photoresist film using the resist protective film composition, exposing the system, and
5 developing the photoresist film using a developer solution.

The compound of the present invention, the copolymer containing this compound, and the resist protective film composition containing the copolymer can be used in a resist protective film which has sufficient light transmissivity, is not easily intermixed with the resist film, has appropriate hydrophilic or hydrophobic characteristics, does not exhibit a
10 phenomenon of pattern shape deterioration, is easily dissolved in alkali developer solutions, and is capable of reducing the occurrence of various defects in the process of immersion or dry exposure.

Best Mode for Carrying Out the Invention

15 Hereinafter, the present invention will be described in detail by way of Examples so that a person having ordinary skill in the art can carry out the present invention. However, the present invention can be realized in various different embodiments and is not intended to be limited to the Examples described herein.

[Preparation Example: Synthesis of monomer and polymer]

(Synthesis Example 1)

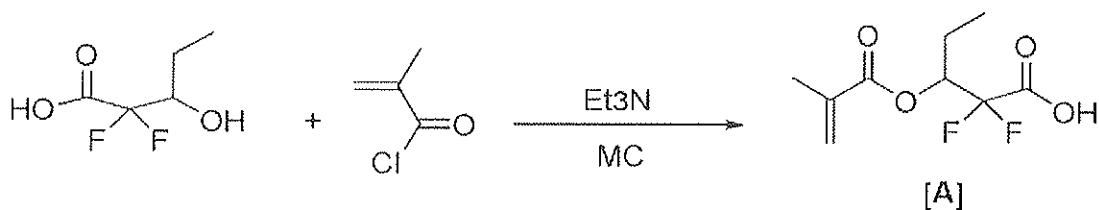
Synthesis of 2-methylacrylic acid 1-(carboxydifluoromethyl)propyl ester monomer

In a 1-L flask, 100 g of 2,2-difluoro-3-hydroxypentanoic acid was dissolved in 300 ml of dichloromethane (also called as methylene chloride, MC), and thus a reaction solution was prepared. 67 g of methacryloyl chloride was slowly added to the flask in an
25 ice bath. The flask with added methacryloyl chloride was stirred for about 20 minutes in

the ice bath, and then 78.5 g of triethylamine (Et₃N) was slowly added dropwise to the flask. After completion of the dropwise addition, the flask was stirred for about 2 hours at normal temperature, and thus a reaction liquid was obtained. The reaction liquid was washed two times with a 2% hydrochloric acid (HCl) solution, and then the organic layer was combined. The solvent of the organic layer was distilled off under reduced pressure, and thus a compound represented by formula [A] in the following reaction scheme (1) was obtained. 101 g (yield 75%) of 2-methylacrylic acid 1-(carboxydifluoromethyl)propyl ester (2,2-difluoro-3-(methacryloyloxy)pentanoic acid), which is the compound represented by formula [A] in the following reaction scheme (1), was obtained, and the structure was confirmed by ¹H-NMR.

¹H NMR δ= 0.96(t, 3H), 1.40-1.55(m, 2H), 1.93(s, 3H), 3.75(m, 1H), 5.58(d, 1H), 6.15(d, 1H)

[Reaction scheme 1]



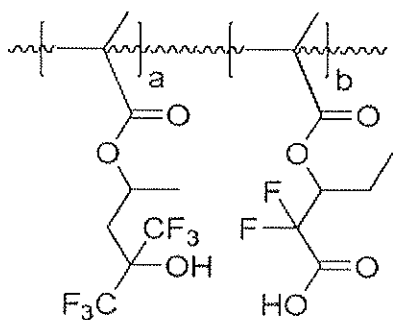
(Polymer Synthesis Example 1)

10 g of 2-methylacrylic acid 1-(carboxydifluoromethyl)propyl ester (2,2-difluoro-3-(methacryloyloxy)pentanoic acid), which is the compound represented by formula [A] in the reaction scheme (1), and 75 g of 2-methylacrylic acid 4,4,4-trifluoro-3-hydroxy-1-methyl-3-trifluoromethylbutyl ester were dissolved in 255 g of 1,4-dioxane, and thus a reaction solution was prepared. The reaction solution was introduced to a jacketed reactor together with 5.5 g of dimethylazobisbutyronitrile (DMAB), which is a polymerization initiator, the mixture was stirred, and thus a reaction liquid was prepared.

The temperature of an agitator was set to 65°C, and the temperature was slowly raised. Subsequently, the reaction liquid was placed in the agitator, and the reaction liquid was allowed to react under stirring at 65°C for 8 hours.

When the reaction of the reaction liquid was completed, the reaction liquid was added dropwise to 3.4 L of n-hexane to induce precipitation, and a precipitate thus obtained was filtered and dried in a vacuum. After the precipitate was dried in a vacuum as such, a polymer having a structure represented by the following formula (9) was obtained. The weight average molecular weight of the polymer relative to polystyrene standards was measured, and the molecular weight was found to be 7,800.

[Formula 9]



In the formula (9) shown above, a is 0.9, and b is 0.1.

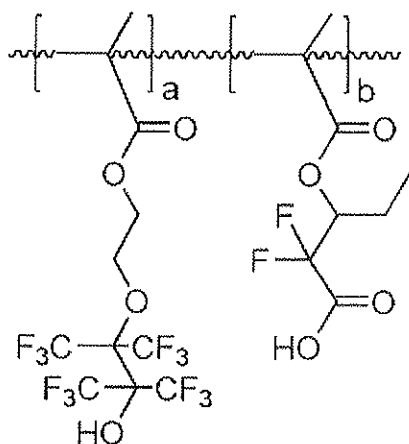
(Polymer Synthesis Example 2)

10 g of 2-methylacrylic acid 1-(carboxydifluoromethyl)propyl ester (2,2-difluoro-3-(methacryloyloxy)pentanoic acid), which is the compound represented by formula [A] in the reaction scheme (1), and 113 g of 2-methylacrylic acid 2-(3,3,3-trifluoro-2-hydroxy-1,1,2-tris(trifluoromethyl)propoxy)ethyl ester were dissolved in 255 g of 1,4-dioxane, and then the solution was introduced into a jacketed reactor together with 5.5 g of DMAB (dimethylazobisbutyronitrile) as a polymerization initiator. The mixture was stirred, and thus a reaction liquid was prepared.

The temperature of an agitator was set to 65°C, and the temperature was slowly raised. Subsequently, the reaction liquid was placed in the agitator, and the reaction liquid was allowed to react under stirring at 65°C for 8 hours.

When the reaction of the reaction liquid was completed, the reaction liquid was added dropwise to 5 L of n-hexane to induce precipitation, and a precipitate thus obtained was filtered and dried in a vacuum. After the precipitate was dried in a vacuum as such, a polymer having a structure represented by the following formula (10) was obtained. The weight average molecular weight of the polymer relative to polystyrene standards was measured, and the molecular weight was found to be 7,500.

[Formula 10]



In the formula (10) shown above, a is 0.9, and b is 0.1.

(Polymer Synthesis Example 3)

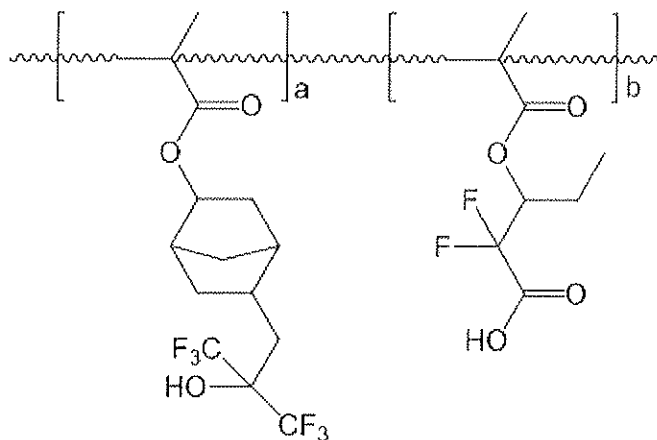
5 g of 2-methylacrylic acid 1-(carboxydifluoromethyl)propyl ester (2,2-difluoro-3-(methacryloyloxy)pentanoic acid), which is the compound represented by formula [A] in the reaction scheme (1), and 70 g of acrylic acid 5-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethylpropyl)-bicyclo[2.2.1]hept-2-yl ester were dissolved in 255 g of 1,4-

dioxane, and then the solution was introduced into a jacketed reactor together with 5.5 g of DMAB (dimethylazobisbutyronitrile) as a polymerization initiator. The mixture was stirred, and thus a reaction liquid was prepared.

The temperature of an agitator was set to 65°C, and the temperature was slowly raised. Subsequently, the reaction liquid was placed in the agitator, and the reaction liquid was allowed to react under stirring at 65°C for 8 hours.

When the reaction of the reaction liquid was completed, the reaction liquid was added dropwise to 5 L of n-hexane to induce precipitation, and a precipitate thus obtained was filtered and dried in a vacuum. After the precipitate was dried in a vacuum as such, a polymer having a structure represented by the following formula (11) was obtained. The weight average molecular weight of the polymer relative to polystyrene standards was measured, and the molecular weight was found to be 6,509 g/mol.

[Formula 11]



In the formula (11) shown above, a is 0.9, and b is 0.1.

(Polymer Synthesis Example 4)

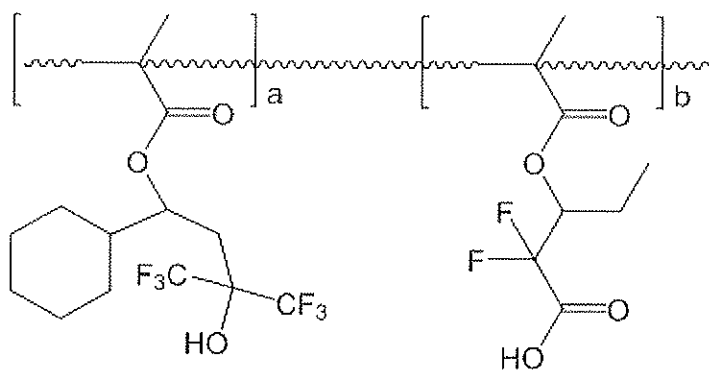
5 g of 2-methylacrylic acid 1-(carboxydifluoromethyl)propyl ester (2,2-difluoro-3-(methacryloyloxy)pentanoic acid), which is the compound represented by formula [A] in the reaction scheme (1), and 73 g of 2-methylacrylic acid 1-cyclohexyl-4,4,4-trifluoro-3-

hydroxy-3-trifluoromethylbutyl ester were dissolved in 234 g of 1,4-dioxane, and then the solution was introduced into a jacketed reactor together with 5.5 g of DMAB (dimethylazobisbutyronitrile) as a polymerization initiator. The mixture was stirred, and thus a reaction liquid was prepared.

5 The temperature of an agitator was set to 65°C, and the temperature was slowly raised. Subsequently, the reaction liquid was placed in the agitator, and the reaction liquid was allowed to react under stirring at 65°C for 8 hours.

When the reaction of the reaction liquid was completed, the reaction liquid was added dropwise to 3.4 L of n-hexane to induce precipitation, and a precipitate thus
10 obtained was filtered and dried in a vacuum. After the precipitate was dried in a vacuum as such, a polymer having a structure represented by the following formula (12) was obtained. The weight average molecular weight of the polymer relative to polystyrene standards was measured, and the molecular weight was found to be 7,359 g/mol.

[Formula 12]



15 In the formula (12) shown above, a is 0.9, and b is 0.1.

(Comparative Polymer Synthesis Example 1)

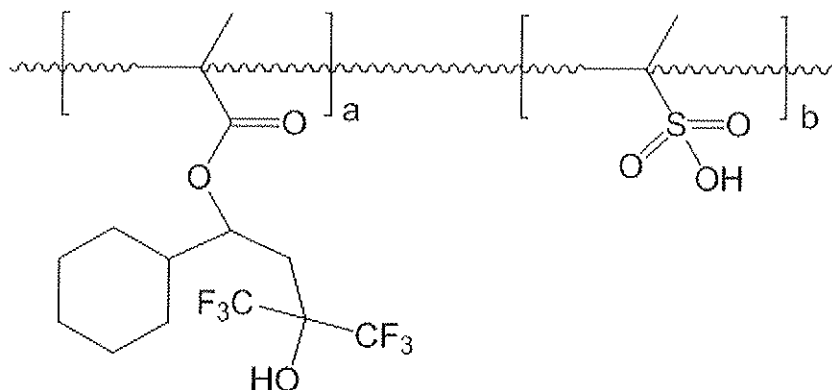
73 g of 2-methylacrylic acid 1-cyclohexyl-4,4,4-trifluoro-3-hydroxy-3-trifluoromethylbutyl ester and 4.9 g of vinylsulfonic acid were dissolved in 234 g of 1,4-
20 dioxane, and then the solution was introduced into a jacketed reactor together with 5.5 g of

DMAB (dimethylazobisbutyronitrile) as a polymerization initiator. The mixture was stirred, and thus a reaction liquid was prepared.

The temperature of an agitator was set to 65°C, and the temperature was slowly raised. Subsequently, the reaction liquid was placed in the agitator, and the reaction liquid was allowed to react under stirring at 65°C for 8 hours.

When the reaction of the reaction liquid was completed, the reaction liquid was added dropwise to 3.4 L of n-hexane to induce precipitation, and a precipitate thus obtained was filtered and dried in a vacuum. After the precipitate was dried in a vacuum as such, a polymer having a structure represented by the following formula (13) was obtained. The weight average molecular weight of the polymer relative to polystyrene standards was measured, and the molecular weight was found to be 7,800 g/mol.

[Formula 13]



In the formula (13) shown above, a is 0.9, and b is 0.1.

[Experiment Example: Formation of resist protective film and analysis of characteristics of protective film thus produced]

(Examples 1 to 4 and Comparative Example 1)

As the polymer compound for resist protective film material, the respective polymers represented by formulas (9) to (12) and formula (13) synthesized in Polymer

Synthesis Examples 1 to 4 and Comparative Polymer Synthesis Example 1 were used.

1.0 g of each of the polymers was dissolved in 25 g of 4-methylpentanol, and the solution was filtered through a 0.2- μ m polypropylene filter. Thus, a resist protective film material solution was prepared.

5 The resist protective film material solution was spin coated on a silicon substrate, and the substrate was baked for 60 seconds at 100°C. Thus, a resist protective film having a film thickness of 50 nm was formed, and the refractive index at 193 nm was measured.

10 The silicon substrate with the resist protective film formed thereon was rinsed with pure water for 5 minutes, and an observation was made on the change in the thickness of the resist protective film before and after rinsing.

Furthermore, the silicon substrate with the resist protective film formed thereon was developed with a 2.38 wt% aqueous solution of tetramethylammonium hydroxide (TMAH), and an observation was made on the thickness of the resist protective film after development.

15 Furthermore, the substrate with the resist protective film formed thereon was maintained horizontal, and 50 μ l of pure water was dropped on the protective film to form a water droplet. Subsequently, the silicon substrate was slowly slanted, and the angle of the silicon substrate at which the water droplet began to slide (sliding angle) and the receding contact angle were measured.

20 The measurement results are presented in the following Table 1.

[Table 1]

Resist protective film	Polymer compound for resist protective film	Refractive index at 193 nm	Change in film thickness before and after rinsing (nm)	Film thickness after development (nm)	Sliding angle (°)	Receding contact angle (°)
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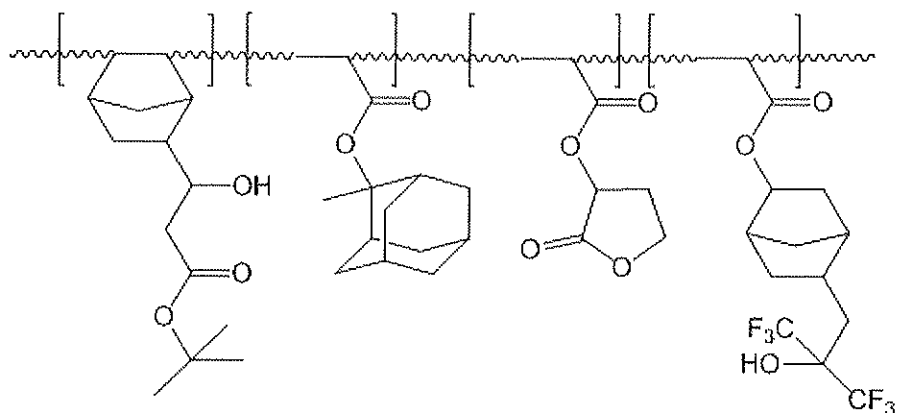
Example 1	Formula 9	1.57	0	0	11	71
Example 2	Formula 10	1.58	0	0	11	75
Example 3	Formula 11	1.54	0	0	14	76
Example 4	Formula 12	1.57	0	0	15	77
Comparative Example 1	Formula 13	1.56	0	0	13	71

From the results shown in Table 1, it can be seen that the resist protective films of Examples 1 to 4 have high water repellency and are not easily dissolved in water. It can also be seen that the resist protective films have high alkali solubility and can be conveniently removed using an alkali developer solution at the time of development.

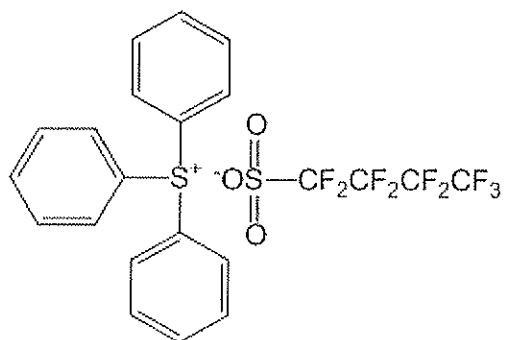
5 Furthermore, it can be seen that although the polymer compounds of Examples 1 to 4 (Formulas (9) to (12)) have an amino group or a sulfonamide group introduced at the polymer ends, there are almost no adverse effects on the sliding angle or the receding contact angle as compared with the Comparative Example.

10 5 g of a resist polymer represented by the following formula (14), 0.31 g of a photoacid generator represented by the following formula (15) (Mw: 8,500 g/mol, Mw/Mn: 1.75, the molar ratio of the respective repeating units is 1:1:1:1), and 0.07 g of an inhibitor (triisopropanol amine) were dissolved in 80 g of propylene glycol monoethyl ether acetate (PGMEA), and the solution was filtered through a 0.2- μ m polypropylene filter. Thus, a solution of photoresist film materials was prepared.

15 [Formula 14]



[Formula 15]



A bottom anti-reflective film (BARC) having a thickness of 90 nm was formed on
 5 a silicon substrate, and the solution of photoresist film materials prepared as described
 above was applied on the substrate where the anti-reflective film was formed. The
 substrate was baked for 60 seconds at 110°C, and thus a photoresist film having a
 thickness of 120 nm was formed. On this photoresist film, each of the resist protective
 film materials prepared in Examples 1 to 4 and Comparative Example 1 was applied, and
 10 the substrate was baked for 60 seconds at 100°C. Thus, resist protective films (Examples
 5 to 8 and Comparative Example 2) were respectively formed.

Subsequently, in order to reproduce immersion exposure, the films obtained after
 exposure were subjected to rinsing with pure water for 5 minutes. That is, each of the
 substrates was exposed to an ArF scanner, 306C (NA = 0.78, 6% halftone mask)

manufactured by Nikon Corp., and the substrate was rinsed with pure water for 5 minutes. Post-exposure bake (PEB) was performed after exposure, for 60 seconds at 110°C, and development was carried out for 60 seconds with a 2.38 wt% TMAH developer solution.

On the other hand, a process of performing exposure, rinsing with pure water, PEB, and development without forming a resist protective film, and a conventional process of omitting the rinsing with pure water after exposure were also carried out (Comparative Example 3).

The silicon substrates thus produced were cut, and a comparison was made on the 80-nm L/S pattern shape and the sensitivity. The amount of exposure needed for performing resolution of 80-nm L/S at 1:1 was defined as the sensitivity. The measurement results are presented in the following Table 2.

[Table 2]

Resist protective film	Polymer for resist protective film	Sensitivity (mJ/cm ²)	80-nm pattern shape
Example 5	Formula 9	25	Rectangular shape
Example 6	Formula 10	24	Rectangular shape
Example 7	Formula 11	25	Rectangular shape
Example 8	Formula 12	26	Rectangular shape
Comparative Example 2	Formula 13	25	Film-diminishing shape
Comparative Example 3	No protective film	28	T-top shape

From the results of Table 2, when the substrate without a protective film was rinsed with pure water after exposure as in the case of Comparative Example 3, the pattern shape became a T-top shape. This is thought to be because the acid generated was dissolved in water. Furthermore, in the case of Comparative Example 2, a film-diminishing shape was exhibited, but in the case of Examples 5 and 6, there was no change in the shape.

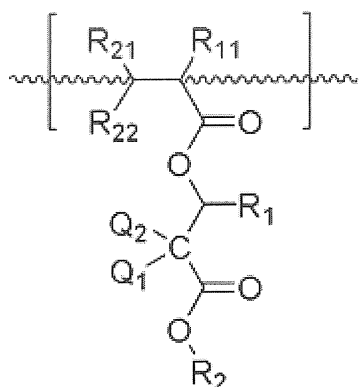
As such, preferred embodiments of the present invention have been described in

detail, but the scope of the present invention is not intended to be limited thereto, and various modifications and improvements that can be made by an ordinarily skilled person using the fundamental concept of the present invention as defined in the following claims are also included in the scope of the present invention.

CLAIMS

1. A resist protective film composition comprising a copolymer, wherein the
5 copolymer comprises a repeating unit represented by the following formula (1-a); and a
repeating unit represented by any one selected from the group consisting of the following
formula (4-a), formula (5-a), formula (6-a), formula (7-a), and combinations thereof:

[Formula 1-a]



- 10 wherein R₁₁, R₂₁ and R₂₂ each independently represent any one selected from the group
consisting of a hydrogen atom, a halogen atom, an alkyl group having 1 to 8 carbon atoms,
and a halogenated alkyl group having 1 to 5 carbon atoms;

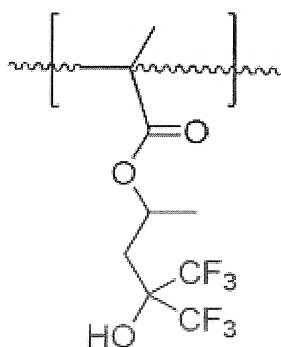
R₁ represents an alkyl group;

- R₂ represents any one selected from the group consisting of a hydrogen atom and
15 an alkyl group having 1 to 5 carbon atoms; and

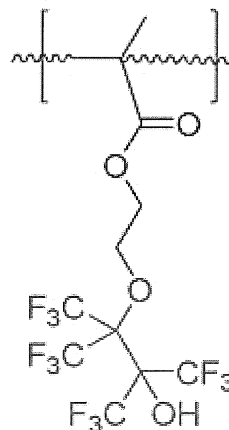
Q₁ and Q₂ each independently represent a halogen atom;

[Formula 4-a]

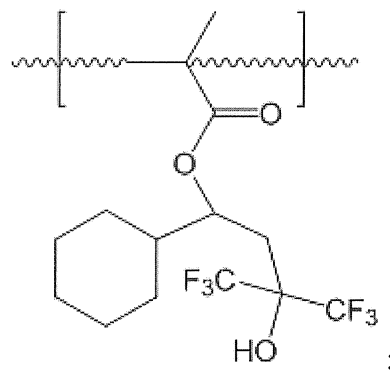
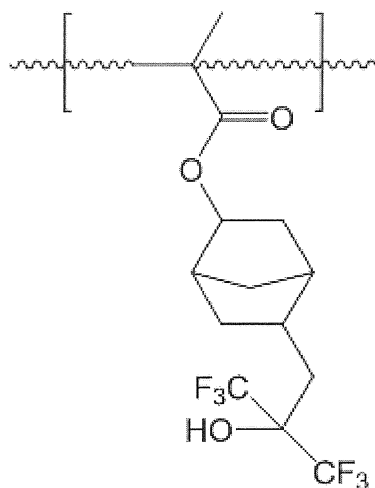
[Formula 5-a]



[Formula 6-a]



[Formula 7-a]



wherein the molar proportion m of the repeating unit represented by the formula (1-
5 a) is $0.01 \leq m \leq 0.6$, the molar proportion l of the repeating unit selected from the group
consisting of the following formula (4-a), formula (5-a), formula (6-a), formula (7-a), and
combinations thereof is $0.4 \leq l \leq 0.99$, and the sum of m and l is 1.

2. The resist protective film composition according to claim 1, wherein the
10 copolymer has a weight average molecular weight as measured by gel permeation
chromatography of 1,000 to 500,000 g/mol.

3. The resist protective film composition according to claim 1, further comprising an alcohol solvent having 4 to 8 carbon atoms.