

DEVELOPER TOLERANCE RESIST UNDERLAYER COMPOSITION
AND METHOD FOR MANUFACTURING RESIST PATTERN

BACKGROUND OF THE INVENTION

5

TECHNICAL FIELD

[0001] The present invention relates to a developer
tolerance resist underlayer composition. The present
invention also relates to a method for manufacturing a
10 resist pattern.

BACKGROUND ART

[0002] In a process of manufacturing devices such as
semiconductors, fine processing by lithographic
15 technology using a photoresist has generally been
employed. The wavelength used for exposure is
becoming shorter, and a lithographic technique using
extreme ultraviolet (EUV) with a wavelength of 13.5 nm
is under consideration.

20 Under conventional exposure conditions of
wavelengths of 248 nm and 193 nm, a chemically
amplified resist composition is used as the resist
material. When EUV is used, a variety of resist
materials are being considered, one of which is a metal-
25 containing resist (for example, Patent Document 1).

[0003] In the lithographic process, there is a problem that
the dimensional accuracy of the photoresist pattern
deteriorates due to the influence of standing waves
caused by the reflection of light from the substrate and
30 the influence of irregular reflection of the exposure light
due to the level difference of the substrate. Therefore,
in order to solve this problem, methods of providing a
resist underlayer have been widely studied. A resist
underlayer that can be developed with an alkaline
35 developer simultaneously with the resist film has also
been proposed (for example, Patent Document 2).

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

- 5 [0004] [Patent document 1] JP 2021-73367 A
[Patent document 2] WO 2011/086757

SUMMARY OF THE INVENTION

10 PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] The present inventors got an idea that a film formed from a metal-containing resist composition changes in physical properties of the film surface before and after exposure. In particular, in the exposed area, 15 the hydrophilicity changes before and after exposure.

The inventors have considered that there are one or more problems still need improvements. They include, for example, the followings:
The resist pattern tends to collapse; the resist 20 underlayer has low solvent resistance; the film thickness reduction of the resist underlayer occurs due to the resist composition; the resist underlayer is dissolved by a developer; adhesion to a substrate is reduced due to the change in the hydrophilicity of the resist film.

25 The present invention has been made based on the technical background as described above, and provides a resist underlayer composition.

MEANS FOR SOLVING THE PROBLEMS

30 [0006] The developer tolerance resist underlayer composition according to the present invention comprises a polymer (A), a cross-linking agent (B), a thermal acid generator (C) and a solvent (D), and the polymer (A) is one that comprises at least a unit 35 having a protective group that is deprotected by an acid, and the hydrophilicity of the portion where the

deprotected unit is present changes after exposure.

[0007] The method for manufacturing a resist pattern according to the present invention comprises the following steps:

- 5 (1) applying a resist underlayer composition above a substrate and heating the resist underlayer composition to form a resist underlayer;
- (2) applying a resist composition directly on the resist underlayer and heating the resist composition to form a resist film;
- 10 (3) exposing the resist film;
- (4) optionally, performing the post-exposure bake of the resist film; and
- (5) developing the resist film using a developer to form a resist pattern, provided that the resist underlayer is not developed by the developer:
- 15 wherein
- when the contact angle of the resist film before exposure is defined as θ_{PrR} , that of the resist film after exposure is defined as θ_{PeR} , that of the resist underlayer before exposure is defined as θ_{PrU} , and that of the resist underlayer after exposure is defined as θ_{PeU} ,
- 20 $\theta_{PeU}/\theta_{PrU} < 1.0$ when $\theta_{PeR}/\theta_{PrR} < 1.0$, and
- $\theta_{PeU}/\theta_{PrU} > 1.0$ when $\theta_{PeR}/\theta_{PrR} > 1.0$,
- 25 where the contact angle is measured using water.
- [0008] The method for manufacturing a device according to the present invention comprises the method above described.

30 EFFECTS OF THE INVENTION

[0009] According to the present invention, one or more of the following effects can be desired.

- The resist pattern collapse can be suppressed; the resist underlayer has sufficient solvent resistance; the film thickness reduction due to the resist composition is suppressed; the dissolution of the resist underlayer due
- 35

to the developer is suppressed; the acid generated from the thermal acid generator (C) accelerates the cross-linking reaction between the polymer (A) and the cross-linking agent (B) to impart developer tolerance to the resist underlayer; an acid generated by the photoacid generation part (E) with receipt of light selectively deprotects the polymer (A), thereby changing the hydrophilicity of the polymer (A); the acid generated from the photoacid generator present in the resist film moves to the resist underlayer film and selectively deprotects the polymer (A), thereby changing the hydrophilicity of the polymer (A); it is possible to match the change in the hydrophilicity of the resist underlayer with the change in the hydrophilicity of the resist film; and since the exposed area and the unexposed area of the resist underlayer are physically connected also after development, even if affinity with the substrate is decreased in a part of the resist underlayer, it is possible to maintain adhesion to the substrate as a whole resist underlayer film.

DETAILED DESCRIPTION OF THE INVENTION

MODE FOR CARRYING OUT THE INVENTION

25 [0010] [Definition]

Unless otherwise specified in the present specification, the definitions and examples described in this paragraph are followed.

30 The singular form includes the plural form and "one" or "that" means "at least one". An element of a concept can be expressed by a plurality of species, and when the amount (for example, mass % or mol %) is described, it means sum of the plurality of species.

35 "And/or" includes a combination of all elements and also includes single use of the element.

When a numerical range is indicated using "to" or

"-", it includes both endpoints and unit thereof are common. For example, 5 to 25 mol % means 5 mol % or more and 25 mol % or less.

5 The descriptions such as " C_{x-y} ", " C_x-C_y " and " C_x " mean the number of carbons in a molecule or substituent. For example, C_{1-6} alkyl means an alkyl chain having 1 or more and 6 or less carbons (methyl, ethyl, propyl, butyl, pentyl, hexyl etc.).

10 When polymer has a plural types of repeating unit, these repeating unit copolymerize. These copolymerization may be any of alternating copolymerization, random copolymerization, block copolymerization, graft copolymerization, or a mixture thereof. When polymer or resin is represented by a
15 structural formula, n, m or the like that is attached next to parentheses indicate the number of repetitions.

Celsius is used as the temperature unit. For example, 20 degrees means 20 degrees Celsius.

20 The additive refers to a compound itself having a function thereof (for example, in the case of a base generator, a compound itself that generates a base). An embodiment in which the compound is dissolved or dispersed in a solvent and added to a composition is also possible. As one embodiment of the present
25 invention, it is preferable that such a solvent is contained in the composition according to the present invention as the solvent (D) or another component.

BEST MODE FOR CARRYING OUT THE INVENTION

30 [0011] Hereinafter, embodiments of the present invention are described in detail.

<Developer tolerance resist underlayer composition>

35 The developer tolerance resist underlayer composition according to the present invention (hereinafter sometimes referred to as the composition) comprises a polymer (A), a cross-linking agent (B), a

thermal acid generator (C) and a solvent (D), and the polymer (A) is one that comprises at least a unit having a protective group that is deprotected by an acid, and the hydrophilicity of the portion where the deprotected unit is present changes after exposure.

In the present invention, the developer tolerance resist underlayer composition is a composition that forms a resist underlayer having tolerance to developer. The resist underlayer is formed above a substrate and immediately below a resist film. An interlayer may be interposed between the resist underlayer and the substrate. The resist underlayer of the present invention is preferably a substrate adhesion enhancing film. The resist underlayer of the present invention may have antireflection performance for light used in exposure. That is, the resist underlayer of the present invention may be an antireflection film.

The developer preferably comprises an organic solvent and more preferably consists of an organic solvent.

Preferably, the developer is one that develops a resist layer but does not develop any resist underlayer. As an embodiment of the present invention, when the developer is paddled on the resist underlayer for 30 seconds, the amount of decrease in the thickness of the resist underlayer is preferably 0 to 30% (more preferably 0 to 10%; further preferably 0.1 to 10%; further more preferably 0.1 to 5%), and/or preferably 5 nm or less (more preferably 0 to 5 nm; further preferably 0.1 to 3 nm; further more preferably 0.1 to 2 nm).

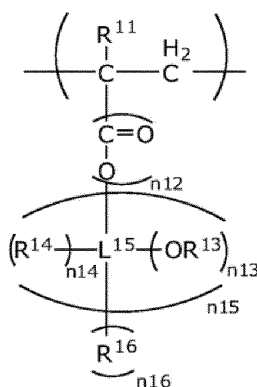
[0012] Polymer (A)

The composition according to the present invention comprises a polymer (A). The polymer (A) comprises at least a unit having a protective group that is deprotected by an acid, and the hydrophilicity of the portion where

the deprotected unit is present changes after exposure. In particular, the polymer (A) is hydrophobic before exposure and becomes hydrophilic after exposure, or is hydrophilic before exposure and becomes hydrophobic after exposure. Preferably, it is hydrophobic before exposure and changes to hydrophilic after exposure. The change in hydrophobicity or hydrophilicity can be measured by the contact angle of water dropped on the film. This is described later.

10 [0013] The polymer (A) preferably comprises the unit (A1) represented by the formula (a1).

The unit (A1) preferably has a protective group that is deprotected by an acid, and is deprotected after exposure.



(a1)

In the formula:

R^{11} is each independently H or methyl (preferably H).

L^{15} is each independently a C_{6-20} aromatic hydrocarbon group or a C_{1-6} saturated hydrocarbon group (preferably a C_{6-20} aromatic hydrocarbon group; more preferably cyclohexyl). As an embodiment of the present invention, L^{15} is each independently preferably phenyl or cyclohexyl.

R^{13} is each independently tert-butyl or C_{5-10} alkyl (where the methylene in the alkyl may be replaced with oxy and/or carbonyl). In this specification, tert-butyl is

sometimes described as t-Bu or tBu. R_{13} is preferably t-Bu or -C(=O)-O-tBu (more preferably t-Bu).

R^{14} is each independently C_{1-5} alkyl (preferably methyl, ethyl, i-propyl or n-propyl; more preferably methyl).

5 R^{16} is each independently t-Bu or C_{5-15} alkyl (preferably t-Bu, 1-methylcyclopentyl, 1-ethylcyclopentyl, 1-methyladamantyl, 1-ethyladamantyl or 1-ethylcyclohexyl; more preferably t-Bu, 1-ethylcyclopentyl, 1-ethyladamantyl or 1-ethylcyclohexyl; further preferably t-Bu or 1-ethylcyclopentyl; further more preferably t-Bu). R^{16} that is C_{5-15} alkyl may not be wound, or be wound to form a saturated hydrocarbon group.

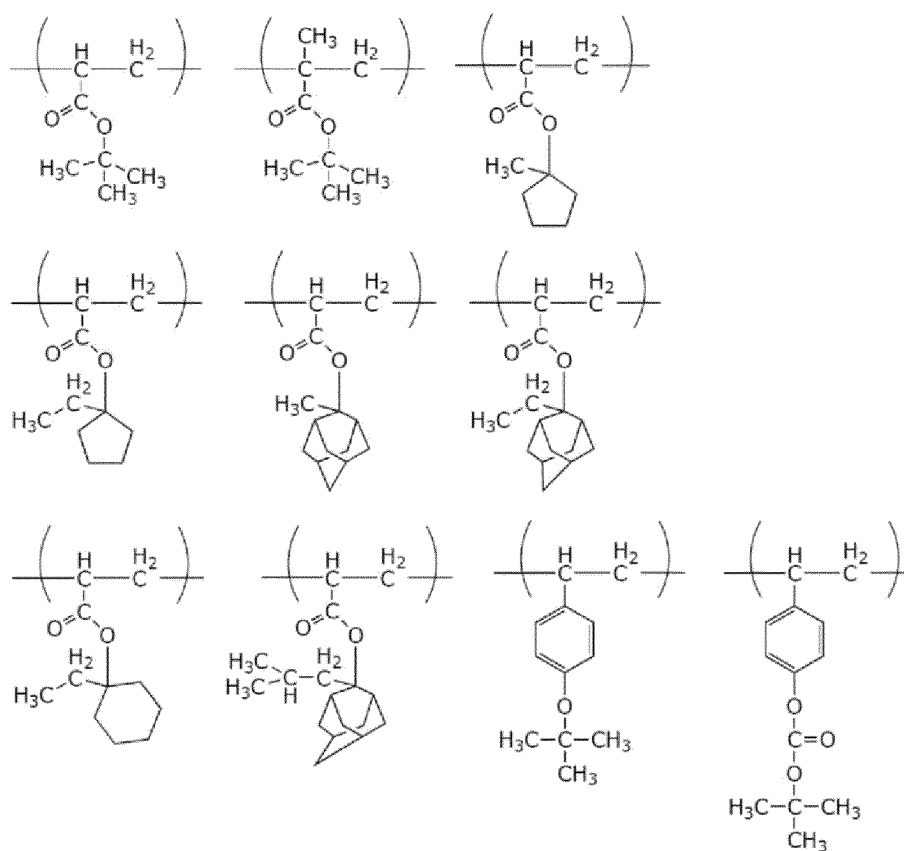
15 n_{12} , n_{15} and n_{16} are each independently a number of 0 to 1 (preferably each independently 0 or 1). n_{12} is more preferably 1. As another embodiment of the present invention, n_{12} is more preferably zero.

n_{13} is each independently a number of 1 to 3 (preferably 1, 2 or 3; more preferably 1).

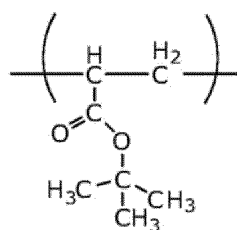
20 n_{14} is each independently a number of 0 to 4 (preferably 1, 2 or 3; more preferably 1).

Provided that $n_{12}=n_{16}=1$ when $n_{15}=0$, and $n_{16}=0$ when $n_{15}=1$. Preferably, $n_{15}=0$. It is also another preferred embodiment of the present invention that $n_{16}=0$.

25 [0014] Exemplified embodiments of the unit (A1) include the followings.

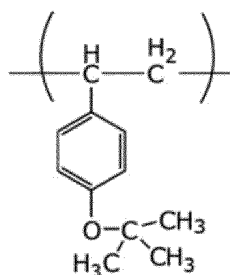


[0015] The structure below can be read in the unit (A1).
In the formula (a1), when $n_{12}=n_{16}=1$, $n_{15}=0$, $R^{11}=\text{H}$
and $R^{16}=\text{t-Bu}$, the following compound is obtained.



5

[0016] The structure below can be read in the unit (A1).
In formula (a1), when $n_{12}=n_{16}=0$, $n_{15}=1$, $R^{11}=\text{H}$,
 $L^{15}=\text{phenyl}$, $n_{14}=0$, $n_{13}=1$ and $R^{13}=\text{t-Bu}$, the following
compound is obtained.

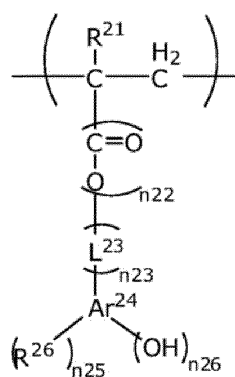


[0017] More preferably, the polymer (A) further comprises at least one of the unit (A2) represented by the formula (a2), the unit (A3) represented by the formula (a3), the unit (A4) represented by the formula (a4) and the unit (A5) represented by the formula (a5).

In a preferred embodiment, the polymer (A) comprises the unit (A1) represented by the formula (a1) and the unit (A2) represented by the formula (a2).

In a more preferred embodiment, the polymer (A) further comprises, in addition to the above, at least one of the unit (A3) represented by the formula (a3), the unit (A4) represented by the formula (a4) and the unit (A5) represented by the formula (a5).

[0018] The formula (a2) is as follows.



(a2)

In

the formula:

R^{21} is each independently H or methyl (preferably H).

L^{23} is each independently C_{1-10} alkylene (preferably methylene or ethylene).

Ar^{24} is each independently C_{6-20} aryl (preferably phenyl).

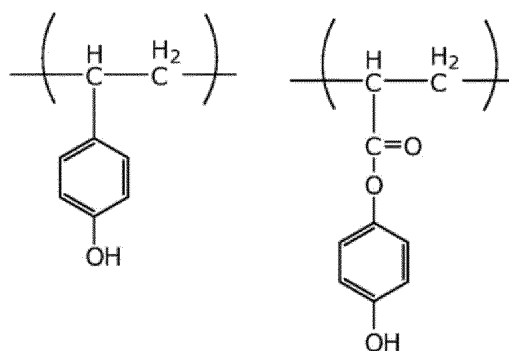
5 R^{26} is each independently C_{1-5} alkyl (preferably methyl or ethyl).

n_{22} and n_{23} are each independently a number of 0 to 1 (preferably 0 or 1; more preferably 0).

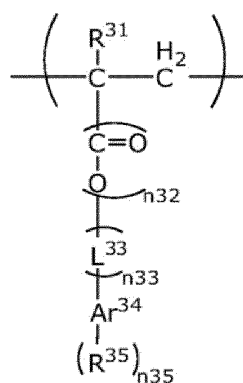
n_{25} is each independently a number of 0 to 4 (preferably 0 or 1; more preferably 0).

10 n_{26} is each independently a number of 1 to 3 (preferably 1 or 2; more preferably 1).

[0019] Exemplified embodiments of the unit (A2) include the followings.



15 [0020] The formula (a3) is as follows.



(a3)

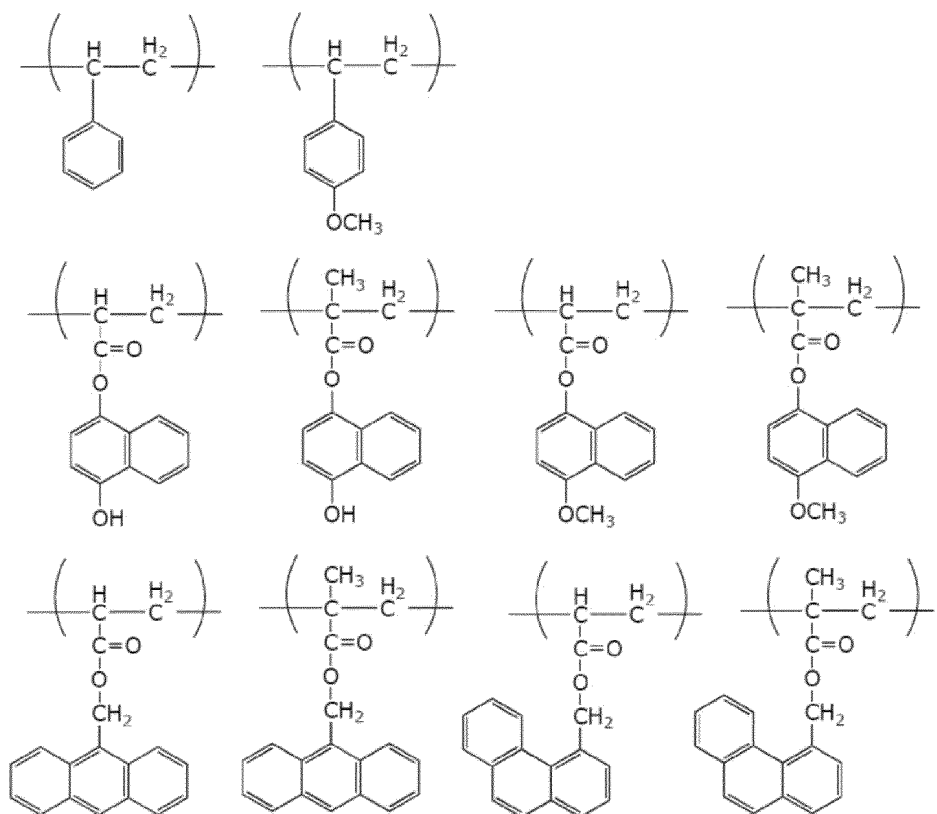
In the formula:

R^{31} is each independently H or methyl (preferably H).

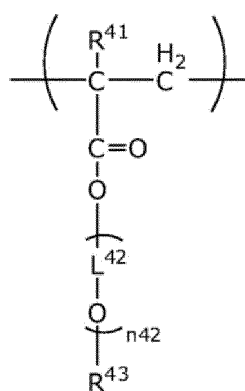
- L^{33} is each independently C_{1-10} alkylene (preferably methylene).
- Ar^{34} is each independently C_{6-20} aryl (preferably phenyl).
- R^{35} is each independently $-O-R^{35a}$, $-(C=O)-R^{35b}$, $-(C=O)-O-R^{35a}$, $-(C=O)-NR^{35c}R^{35d}$, $-O-(C=O)-R^{35e}$, $-NR^{35f}-(C=O)-R^{35g}$ or $-R^{35j}OH$ (preferably $-O-R^{35a}$; more preferably methoxy).
- n_{32} and n_{33} are each independently a number of 0 to 1 (preferably 0 or 1; more preferably 0).
- n_{35} is each independently a number of 0 to 3 (preferably 0 or 1; more preferably 1).
- R^{35a} is each independently C_{1-4} alkyl (excluding tBu).
 R^{35a} is preferably methyl or ethyl (more preferably methyl).
- R^{35b} is each independently H or C_{1-4} alkyl (preferably methyl, ethyl, n-propyl or i-propyl; more preferably methyl).
- R^{35c} and R^{35d} are each independently H or C_{1-4} alkyl (preferably H, methyl, ethyl, n-propyl or i-propyl; more preferably H or methyl). When both R^{35c} and R^{35d} are alkyl, these may be combined to form a ring.
- R^{35e} is each independently H, C_{1-4} alkyl or C_{1-4} alkoxy (excluding tert-butoxy) (preferably H, methyl, ethyl, n-propyl, i-propyl or methoxy; more preferably H, methyl or methoxy).
- R^{35f} is each independently H or C_{1-4} alkyl (preferably H, methyl, ethyl, n-propyl or i-propyl; more preferably H or methyl).
- R^{35g} is each independently H, C_{1-4} alkyl or $-NR^{35h}R^{35r}$ (preferably H, methyl, ethyl, n-propyl, i-propyl or $-NR^{35h}R^{35r}$; more preferably H, methyl or $-NR^{35h}R^{35r}$).
- R^{35h} and R^{35r} are each independently H or C_{1-4} alkyl (preferably H, methyl, ethyl, n-propyl or i-propyl; more preferably H or methyl). When both R^{35h} and R^{35r} are alkyl, these may be combined to form a ring.
- R^{35j} is each independently C_{1-4} alkylene (preferably

methylene or ethylene; more preferably methylene).

[0021] Exemplified embodiments of the unit (A3) include the followings.



5 [0022] The formula (a4) is as follows.



(a4)

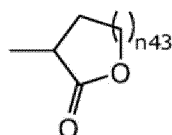
In the formula:

R^{41} is each independently H or methyl (preferably methyl).

L^{42} is C_{1-4} alkylene (preferably methylene).

5 n_{42} is a number of 0 to 1 (preferably 0 or 1; more preferably 0).

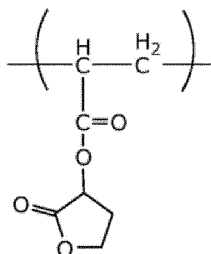
10 R^{43} is C_{1-4} alkyl (excluding tBu) or the following group (preferably methyl, ethyl, n-propyl, i-propyl or the following group; more preferably methyl or the following group; more preferably the following group):



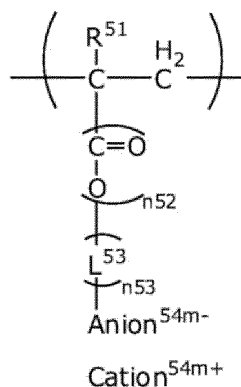
where

n_{43} is a number of 1 to 2 (preferably 1 or 2; more preferably 1).

15 [0023] Exemplified embodiments of the unit (A4) include the following.



[0024] The formula (a5) is as follows.



(a5)

In the formula:

R⁵¹ is each independently H or methyl (preferably methyl).

5 L⁵³ is each independently C₁₋₁₀ alkylene (preferably C₁₋₄ alkylene; more preferably linear C₁₋₄ alkylene; further preferably methylene or ethylene).

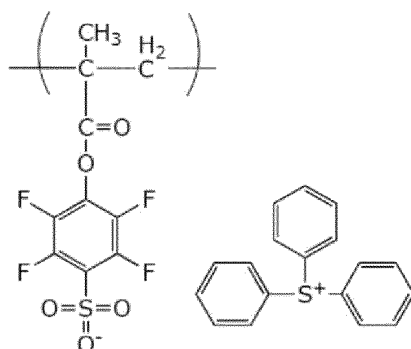
n52 and n53 are each independently a number of 0 to 1, n52 is preferably 0 or 1 (more preferably 1).

10 n53 is preferably 0 or 1 (more preferably 0).

Anion^{54m-} is an m-valent anion that is bonded upward in the formula, preferably an anion of the formula (E1) of the photoacid generator (E) described later.

15 Cation^{54m+} is an m-valent cation that is ionically bonded with Anion^{54m-}, preferably a cation of the formula (E1). m is a number of 1 to 2 (preferably 1 or 2; more preferably 1).

[0025] Exemplified embodiments of the unit (A5) include the followings.



[0026] The number of repetitions of the unit (A1), the unit (A2), the unit (A3), the unit (A4) and the unit (A5) are taken as $nA1$, $nA2$, $nA3$, $nA4$ and $nA5$, respectively.

5 $nA1/(nA1+nA2+nA3+nA4+nA5)$ is preferably 5 to 100% (more preferably 10 to 60%; further preferably 20 to 50%; further more preferably 25 to 45%).

10 $nA2/(nA1+nA2+nA3+nA4+nA5)$ is preferably 0 to 95% (more preferably 10 to 90%; further preferably 30 to 80%; further more preferably 40 to 75%).

15 $nA3/(nA1+nA2+nA3+nA4+nA5)$ is preferably 0 to 95% (more preferably 0 to 30%; further preferably 0 to 20%; further more preferably 5 to 20%). It is also a preferred embodiment of the present invention that $nA3/(nA1+nA2+nA3+nA4+nA5)$ is 0%.

20 $nA4/(nA1+nA2+nA3+nA4+nA5)$ is preferably 0 to 95% (more preferably 0 to 30%; further preferably 0 to 20%; further more preferably 5 to 20%). It is also a preferred embodiment of the present invention that $nA4/(nA1+nA2+nA3+nA4+nA5)$ is 0%.

25 $nA5/(nA1+nA2+nA3+nA4+nA5)$ is preferably 0 to 95% (more preferably 0 to 30%; further preferably 0 to 20%; further more preferably 1 to 10%). It is also a preferred embodiment of the present invention that $nA5/(nA1+nA2+nA3+nA4+nA5)$ is 0%.

As a preferred embodiment of the present invention, one that satisfies the followings is included:

$$5\% \leq nA1/(nA1+nA2+nA3+nA4+nA5) \leq 100\%,$$

$0\% \leq nA2/(nA1+nA2+nA3+nA4+nA5) \leq 95\%$,
 $0\% \leq nA3/(nA1+nA2+nA3+nA4+nA5) \leq 95\%$,
 $0\% \leq nA4/(nA1+nA2+nA3+nA4+nA5) \leq 95\%$, and
 $0\% \leq nA5/(nA1+nA2+nA3+nA4+nA5) \leq 95\%$.

5 [0027] The total number of all repeating units contained in the polymer (A) is taken as n_{total} .
 $(nA1+nA2+nA3+nA4+nA5)/n_{total}$ is preferably 80 to 100% (more preferably 90 to 100%; further preferably 95 to 100%).

10 Being $(nA1+nA2+nA3+nA4+nA5)/n_{total} = 100\%$, that is, not containing any repeating unit other than the unit (A1), the unit (A2), the unit (A3), the unit (A4) and the unit (A5) is also a preferred embodiment of the present invention.

15 A preferred embodiment of the present invention is that when any one of $nA3$, $nA4$ and $nA5$ is greater than 0, the other two are 0.

[0028] The mass average molecular weight (hereinafter sometimes referred to as M_w) of the polymer (A) is preferably 2,000 to 50,000 (more preferably 2,500 to 30,000; further preferably 3,000 to 20,000).

20 The polydispersity index M_w/M_n (PDI) of the polymer (A) is preferably 1.0 to 2.0 (more preferably 1.4 to 1.9).

25 In the present invention, M_w and M_n can be measured by gel permeation chromatography (GPC). In this measurement, it is a preferred example to use a GPC column at 40 degrees Celsius, an eluent that is tetrahydrofuran at 0.6 mL/min and monodispersed polystyrene as a standard.

30 [0029] The content of the polymer (A) is preferably 0.1 to 10 mass % based on the total mass of the composition (more preferably 0.1 to 2 mass %; further preferably 0.1 to 1 mass %; further more preferably 0.2 to 0.5 mass %).

35 The content of the polymer (A) is preferably 40 to

90 mass % (more preferably 50 to 80 mass %; further preferably 70 to 80 mass %) based on the sum of other components excluding the solvent (D).

5 [0030] The method for synthesizing the polymer (A) is not particularly limited, but exemplified embodiments are described later in Synthesis Examples of Examples. It is also possible to combine Synthesis Examples with any known synthesis method.

10 [0031] Cross-linking agent (B)
The composition according to the present invention comprises a cross-linking agent (B). Although not to be bound by theory, it can be thought that the cross-linking agent is useful for improving the film-forming properties of the composition when forming a film and prohibiting
15 intermixing with the resist film that is formed thereonto to prohibit the diffusion of low-molecular-weight components into the overlayer.

Examples of the cross-linking agent include melamine compounds, guanamine compounds, glycoluril
20 compounds or urea compounds substituted by at least one group selected from a methylol group, an alkoxymethyl group and an acyloxymethyl group; epoxy compounds; thioepoxy compounds; isocyanate compounds; azide compounds; and compounds
25 containing a double bond such as an alkenyl ether group. Compounds containing a hydroxy group can also be used as the cross-linking agent.

[0032] Examples of the epoxy compound include tris(2,3-epoxypropyl) isocyanurate, trimethylolmethane
30 triglycidyl ether, trimethylolpropane triglycidyl ether, triethylolethane triglycidyl ether, and the like.

Examples of the melamine compound include compounds derived by methoxymethylation of 1 to 6 methylol groups of hexamethylolmelamine,
35 hexamethoxymethylmelamine or hexamethylolmelamine, and mixtures thereof; and compounds derived by

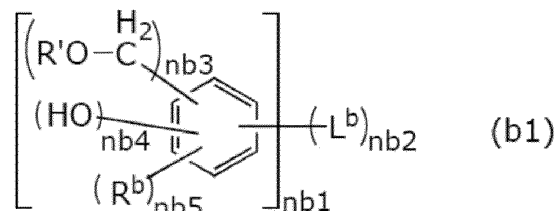
acyloxymethylation of 1 to 6 methylol groups of hexamethoxyethylmelamine, hexaacyloxymethylmelamine or hexamethylolmelamine, or mixtures thereof.

5 Examples of the guanamine compound include compounds derived by methoxymethylation of 1 to 4 methylol groups of tetramethylolguanamine, tetramethoxymethylguanamine or tetramethylolguanamine, and mixtures thereof; and
10 compounds derived by acyloxymethylation of 1 to 4 methylol groups of tetramethoxyethylguanamine, tetraacyloxyguanamine or tetramethylolguanamine, and mixtures thereof.

 Examples of the glycoluril compound include
15 compounds derived by methoxymethylation of 1 to 4 methylol groups of tetramethylolglycoluril, tetramethoxyglycoluril, tetramethoxymethylglycoluril or tetramethylolglycoluril, or mixtures thereof; and
 compounds derived by acyloxymethylation of 1 to 4
20 methylol groups of tetramethylolglycoluril, or mixtures thereof.

 Examples of the urea compound include
 compounds derived by methoxymethylation of 1 to 4 of
 methylol groups of tetramethylolurea,
25 tetramethoxymethylurea or tetramethylolurea, or mixtures thereof; tetramethoxyethylurea, and the like.
 Examples of the compound containing an alkenyl ether group include ethylene glycol divinyl ether, triethylene glycol divinyl ether, 1,2-propanediol divinyl ether, 1,4-
30 butanediol divinyl ether, tetramethylene glycol divinyl ether, neopentyl glycol divinyl ether, trimethylolpropane trivinyl ether, hexanediol divinyl ether, 1,4-
 cyclohexanediol divinyl ether, pentaerythritol trivinyl
 ether, pentaerythritol tetravinyl ether, sorbitol tetravinyl
35 ether, sorbitol pentavinyl ether, trimethylolpropane trivinyl ether, and the like.

[0033] In a preferred embodiment, the cross-linking agent (B) is represented by the formula (b1):

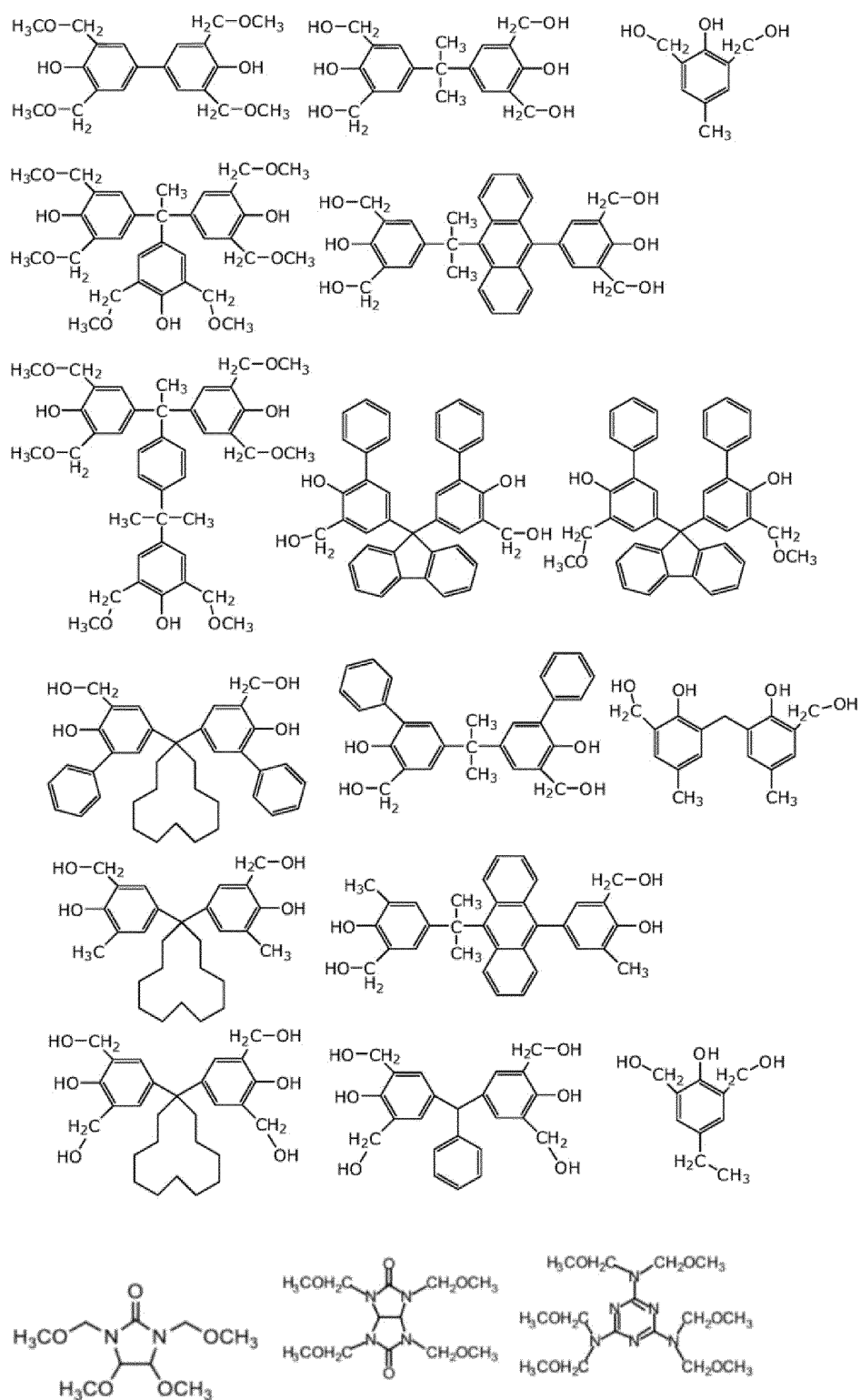


In

the formula:

- 5 nb1 is 1, 2, 3 or 4 (preferably 1, 2 or 3; more preferably 1 or 2; further preferably 1).
 nb2 is 0 when nc1 is 1, and 1 when nc1 is 2 or more.
 nb3 is 0, 1 or 2 (preferably 2).
 nb4 is 1 or 2 (preferably 1).
 10 nb5 is 0 or 1 (preferably 1).
 L^b is a single bond or a C₁₋₃₀ hydrocarbon group (preferably a single bond, C₁₋₂₀ alkylene or C₆₋₃₀ arylene; more preferably a single bond).
 R^b is each independently C₁₋₆ alkyl (where the methylene in the alkyl may be replaced with oxy) or C₆₋₁₀ aryl
 15 (preferably methyl or phenyl).
 R' is H or methyl (preferably methyl).

[0034] Examples of the cross-linking agent (B) include the followings.



[0035] The cross-linking agent (B) may be one type or two or more types (more preferably one type).

The content of the cross-linking agent (B) is preferably 5 to 100 mass % (more preferably 10 to 50 mass %; further preferably 20 to 40 mass %) based on the total mass of the polymer (A).

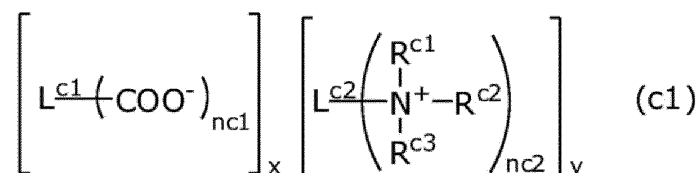
[0036] Thermal acid generator (C)

The composition according to the present invention comprises a thermal acid generator (C). The thermal acid generator generates an acid by heat. Preferably, the acid derived from (C) accelerates the cross-linking reaction of the polymer (A) and the cross-linking agent (B).

The pKa (H₂O) of the acid generated from the thermal acid generator (C) is preferably 1 to 8 (more preferably 2 to 6). In one preferred embodiment, the acid generated from the thermal acid generator (C) is a carboxylic acid. Although not to be bound by theory, it can be thought that the acid derived from (C) accelerates the cross-linking reaction of between (A) and (B), but does not deprotect the protective group of the polymer (A), thereby being able to control so as not all of the resist underlayer deprotected while maintaining developer tolerance.

[0037] Preferably, the thermal acid generator (C) is activated at a temperature above 80°C. Examples of the thermal acid generator (C) include metal-free, strongly non-nucleophilic alkylammoniums, dialkylammoniums and trialkylammoniums.

[0038] In a preferred embodiment, the thermal acid generator (C) is represented by the formula (c1).



In the formula:

nc1 is 1 or 2 (preferably 2).

L^{c1} is H or C_{1-6} alkyl when nc1 is 1, in which the alkyl may be substituted with halogen or hydroxy (preferably fluorine-substituted or unsubstituted C_{1-6} alkyl; more preferably fluorine-substituted C_{1-6} alkyl; further preferably fluorine-substituted ethyl). L^{c1} is C_{1-4} alkylene when nc1 is 2, in which the alkylene may be substituted by halogen or hydroxy, and the methylene in the alkylene may be replaced with carbonyl, oxy or amido (preferably C_{1-3} alkylene, in which the methylene in the alkylene may be replaced with carbonyl; more preferably methylene).

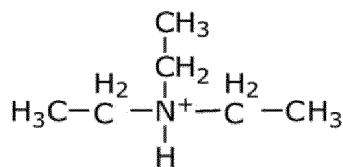
nc2 is 1 or 2 (preferably 1).

L^{c2} is C_{1-6} alkyl when nc2 is 1, in which the alkyl may be substituted with halogen or hydroxy (preferably methyl or ethyl). L^{c2} is C_{1-4} alkylene when nc2 is 1, in which the alkylene may be substituted with halogen or hydroxy, and the methylene in the alkylene may be replaced with carbonyl, oxy or amido (preferably methylene or ethylene).

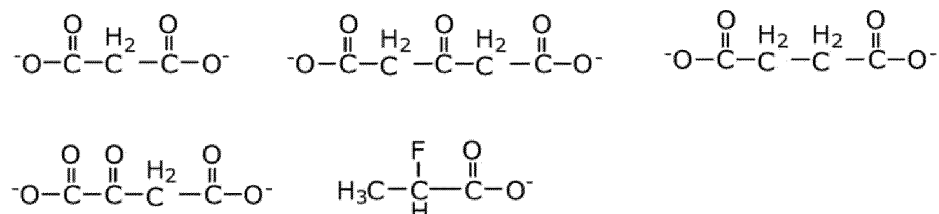
R^{c1} , R^{c2} and R^{c3} are each independently H or C_{1-10} alkyl, in which the alkyl may be substituted with halogen or hydroxy (preferably H, methyl or ethyl; more preferably methyl or ethyl; further preferably ethyl).

x and y are 1 or 2, provided that nc1 X = nc2 X y is satisfied. Preferably, x is 2 and y is 1.

[0039] Examples of the cation of the formula (c1) include the following.



[0040] Examples of the anion of the formula (c1) include the followings.



[0041] The thermal acid generator (C) may be one type or two or more types (more preferably one type).

5 The content of the thermal acid generator (C) is preferably 0.5 to 30 mass % (more preferably 1 to 15 mass %; further preferably 2 to 8 mass %) based on the total mass of the polymer (A).

[0042] Solvent (D)

10 The composition according to the present invention comprises a solvent (D). The solvent (D) is preferably water, hydrocarbon solvents, ether solvents, ester solvents, alcohol solvents, ketone solvents, or any combination of any of these.

15 Exemplified embodiments of the solvent (D) include water, n-pentane, i-pentane, n-hexane, i-hexane, n-heptane, i-heptane, 2,2,4-trimethylpentane, n-octane, i-octane, cyclohexane, methylcyclohexane, benzene, toluene, xylene, ethylbenzene, trimethylbenzene, methylethylbenzene, n-
 20 propylbenzene, i-propylbenzene, diethylbenzene, i-butylbenzene, triethylbenzene, di-i-propylbenzene, n-amylnaphthalene, trimethylbenzene, methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, sec-butanol, t-butanol, n-pentanol, i-pentanol, 2-
 25 methylbutanol, sec-pentanol, t-pentanol, 3-methoxybutanol, n-hexanol, 2-methylpentanol, sec-hexanol, 2-ethylbutanol, sec-heptanol, heptanol-3, n-octanol, 2-ethylhexanol, sec-octanol, n-nonyl alcohol, 2,6-dimethylheptanol-4, n-decanol, sec-undecyl alcohol, trimethyl nonyl alcohol, sec-tetradecyl alcohol, sec-
 30 heptadecyl alcohol, phenol, cyclohexanol,

methyleycyclohexanol, 3,3,5-trimethylcyclohexanol, benzyl alcohol, phenylmethyl carbinol, diacetone alcohol, cresol, ethylene glycol, propylene glycol, 1,3-butylene glycol, pentanediol-2,4, 2-methylpentanediol-2,4, hexanediol-2,5, heptanediol-2,4, 2-ethylhexanediol-1,3, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, glycerin, acetone, methyl ethyl ketone, methyl n-propyl ketone, methyl n-butyl ketone, diethyl ketone, methyl i-butyl ketone, methyl n-pentyl ketone, ethyl n-butyl ketone, methyl n-hexyl ketone, di-i-butyl ketone, trimethylnonanone, cyclohexanone, cyclopentanone, methylcyclohexanone, 2,4-pentanedione, acetonylacetone, diacetone alcohol, acetophenone, fenthion, ethyl ether, i-propyl ether, n-butyl ether, n-hexyl ether, 2-ethylhexyl ether, ethylene oxide, 1,2-propylene oxide, dioxolane, 4-methyl dioxolane, dioxane, dimethyl dioxane, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, ethylene glycol monophenyl ether, ethylene glycol mono-2-ethyl butyl ether, ethylene glycol dibutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol di-n-butyl ether, diethylene glycol mono-n-hexyl ether, ethoxytriglycol, tetraethylene glycol di-n-butyl ether, propylene glycol monomethyl ether (PGME), 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, tetrahydrofuran, 2-methyltetrahydrofuran; ester-based solvents, such as diethyl carbonate, methyl acetate, ethyl acetate, γ -butyrolactone, γ -valerolactone,

n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, sec-butyl acetate, n-pentyl acetate, sec-pentyl acetate, 3-methoxybutyl acetate, methylpentyl acetate, 2-ethylbutyl acetate, 2-ethylhexyl acetate, 5 benzyl acetate, cyclohexyl acetate, methyl cyclohexyl acetate, n-nonyl acetate, methyl acetoacetate, ethyl acetoacetate, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol 10 monoethyl acetate, diethylene glycol mono-n-butyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, propylene glycol monobutyl ether acetate, dipropylene glycol monomethyl 15 ether acetate, dipropylene glycol monoethyl ether acetate, glycol diacetate, methoxytriglycol acetate, ethyl propionate, n-butyl propionate, i-amyl propionate, diethyl oxalate, di-n-butyl oxalate, methyl lactate, ethyl lactate (EL), γ -butyrolactone, n-butyl lactate, n-amyl 20 lactate, diethyl malonate, dimethyl phthalate, diethyl phthalate, propylene glycol 1-monomethyl ether 2-acetate (PGMEA), propylene glycol monoethyl ether acetate and propylene glycol monopropyl ether acetate; N-methylformamide, N,N-dimethylformamide, N,N- 25 diethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, N-methylpropionamide, N-methyl pyrrolidone, dimethyl sulfide, diethyl sulfide, thiophene, tetrahydrothiophene, dimethyl sulfoxide, sulfolane, and 1,3-propane sultone. These solvents can be used alone 30 or in combination of any two or more of these.

The solvent (D) is further preferably PGMEA, PGME, EL or any mixture thereof (further more preferably any mixture of PGMEA, PGME and EL).

[0043] In relation to other layers or films, it is also one 35 embodiment that the solvent (D) does not contain water. For example, the amount of water in the whole solvent

(D) is preferably 0.1 mass % or less (more preferably 0.01 mass % or less; further preferably 0.001 mass % or less). It is also a preferable embodiment of the present invention that the solvent (D) contains no water (0.000 mass %).

[0044] The content of the solvent (D) is preferably 80 to 99.99 mass % based on the total mass of the composition (more preferably 90 to 99.9 mass %; further preferably 95 to 99.9 mass %; further more preferably 99.0 to 99.8 mass %).

[0045] Photoacid generation part (E)

The composition according to the present invention can further comprise a photoacid generation part (E). The photoacid generation part (E) is a part that generates an acid upon exposure. Preferably, the photoacid generation part (E) is a part of the polymer (A) or a component different from (A) to (D). More preferably, the photoacid generation part (E) is a part of the polymer (A), and (E) is incorporated into (A) as the unit (A5). In this specification, when (E) is incorporated into the unit (A5), it is calculated as the content of the polymer (A). That is, in this case, the content of (E) is 0 mass %.

The composition according to the present invention can further comprise a photoacid generator (F). The photoacid generator (F) is a component that generates an acid upon exposure. In one preferred embodiment, the photoacid generator (F) is a component different from (A) to (D). As one preferred embodiment, the photoacid generation part (E) is the photoacid generator (F).

Although not to be bound by theory, it can be thought that the photoacid generation part (E) generates an acid, which acts on the polymer (A) to deprotect, thereby the hydrophilicity of the polymer (A) easily changes.

The pKa (H₂O) of the acid generated from the photoacid generation part (E) is preferably -20 to 3 (more preferably -20 to 1).

5 The pKa (H₂O) of the acid generated from the thermal acid generator (C) is preferably greater than the pKa (H₂O) of the acid generated from the photoacid generation part (E). Although not to be bound by theory, it can be thought that the acid derived from (E) deprotects the protective group of the polymer (A),
10 thereby making it possible to selectively change the hydrophilicity of the exposed area or unexposed area of the resist underlayer.

[0046] The photoacid generation part (E) is preferably represented by the formula (E1).

15 Anion^{54m-} Cation^{54m+} (E1)

Provided that when the photoacid generation part (E) is a part of the polymer (A), H or F in Anion^{54m-} is substituted and such a part is bonded with other part of the polymer (A).

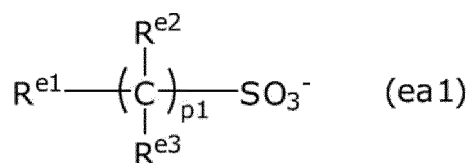
20 In the formula:

Anion^{54m-} is an anion selected from the group consisting of an anion represented by the formula (ea1) and an anion represented by the formula (ea2) (preferably an anion represented by the formula (ea1)).

25 Anion^{54m-} is m-valent as a whole.

Cation^{54m+} is a cation selected from the group consisting of a cation represented by the formula (ec1), a cation represented by the formula (ec2) and a cation represented by the formula (ec3) (preferably a cation represented by the formula (ec1)). Cation^{54m+} is m-valent as a whole.

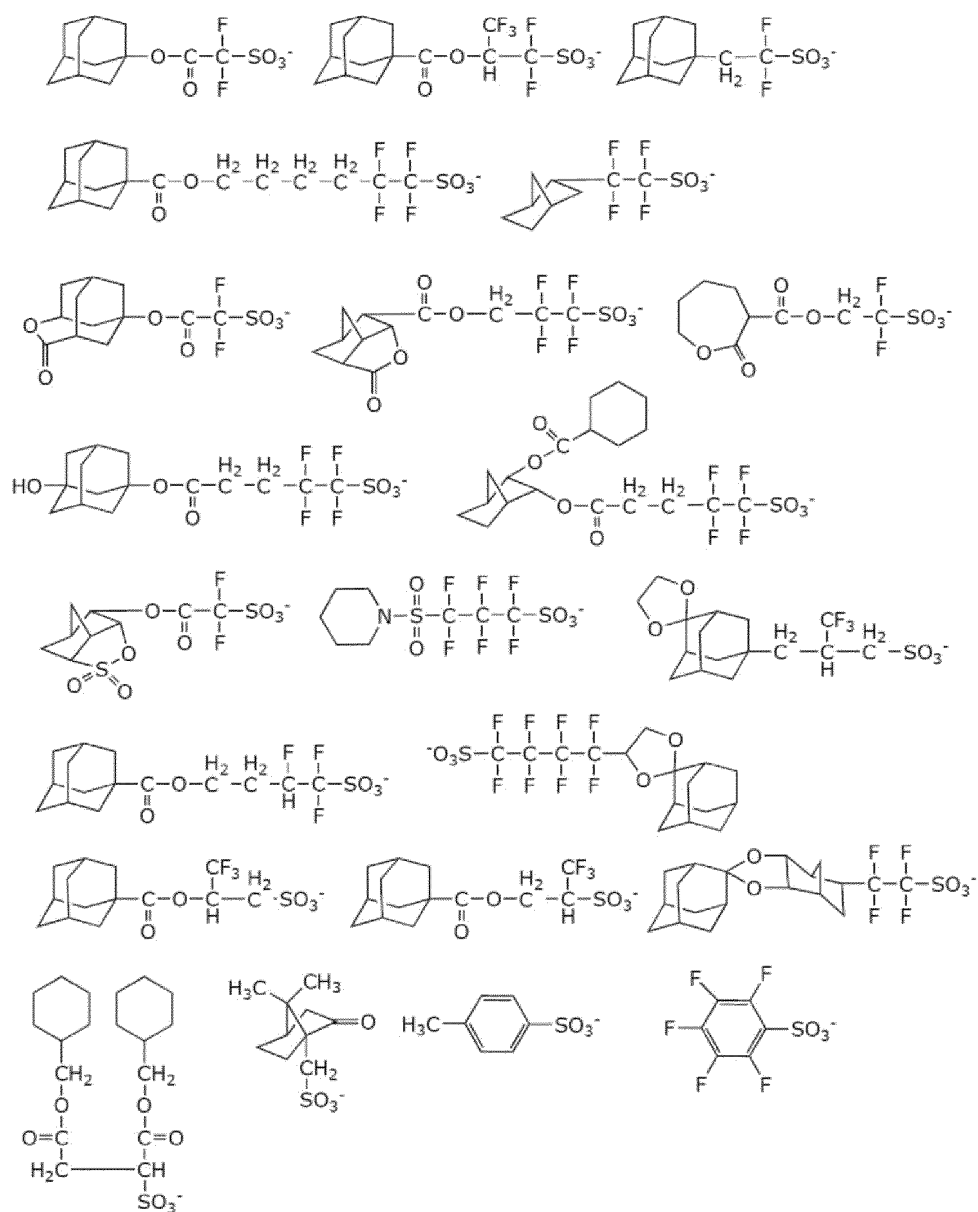
30 [0047] The formula (ea1) is as follows.



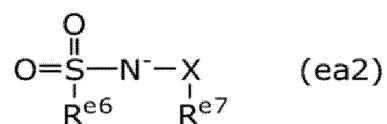
In the formula:

- 5 R^{e1} is a C_{4-30} hydrocarbon group containing a ring structure having 5 or more ring atoms, in which at least one of the ring atoms may be nitrogen, the hydrocarbon group may be substituted with nitro, hydroxy, halogen, -
10 OSO_2-R^{e4} , $-SO_2-R^{e4}$, $-OR^{e4}$, $-COOR^{e4}$, $-O-CO-R^{e4}$, $-O-R^{e5}-COOR^{e4}$, $-R^{e5}-CO-R^{e4}$ or $-S-R^{e5}$, and $-CH_2-$ in the hydrocarbon group may be replaced with carbonyl, ether, carbonyloxy, sulfide, thiocarbonyl or sulfonyl. R^{e1}
15 is preferably phenyl optionally substituted with C_{1-3} alkyl (more preferably phenyl or tolyl; further preferably tolyl).
 R^{e2} and R^{e3} are each independently H, fluorine, fluorine-substituted C_{1-5} alkyl or C_{1-5} alkyl (preferably H, fluorine,
20 trifluoromethyl or methyl; more preferably fluorine or trifluoro methyl).
 R^{e4} is each independently a C_{1-10} hydrocarbon group (preferably methyl, ethyl, i-propyl, n-propyl, tBu, cyclopentyl, cyclohexyl or adamantatyl).
25 R^{e5} is each independently a single bond or a C_{1-10} hydrocarbon group (preferably H, methyl, ethyl, i-propyl, n-propyl, tBu, cyclopentyl, cyclohexyl or adamantyl).
 $p1$ is each independently a number of 0 to 10 (preferably an integer of 0 to 4; more preferably an integer of 0 to 3; further preferably 0, 1 or 2; further more preferably 0).

[0048] Exemplified embodiments of the formula (ea1) include the followings.



[0049] The formula (ea2) is as follows.

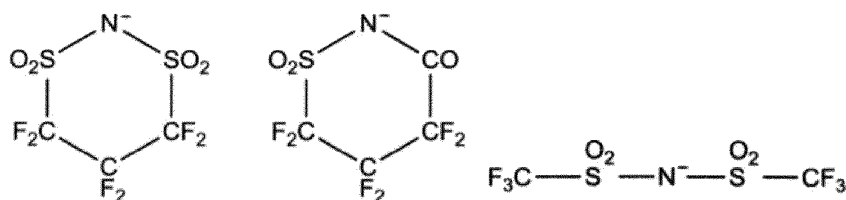


In the formula:

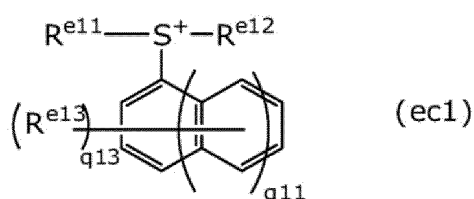
5 X is carbonyl or sulfonyl.

5 R^{e6} and R^{e7} are each independently C_{1-6} fluorine-substituted alkyl, C_{1-6} fluorine-substituted alkoxy, C_{6-12} fluorine-substituted aryl, C_{2-12} fluorine-substituted acyl or C_{6-12} fluorine-substituted alkoxyaryl, in which R^{e6} and R^{e7} may be bonded to each other to form a fluorine-substituted heterocyclic structure, preferably C_{1-3} fluorine-substituted alkyl. When forming a heterocyclic structure, it is preferably a 6-membered ring.

10 [0050] Exemplified embodiments of the formula (ea2) include the followings.



[0051] The formula (ec1) is as follows.



15 In the formula:
 R^{e11} and R^{e12} are each independently a C_{1-20} hydrocarbon group, and the hydrocarbon group may be substituted with $-OSO_2-R^{e14}$, $-SO_2-R^{e14}$, $-OR^{e14}$, $-COOR^{e14}$, $-O-CO-R^{e14}$, $-O-R^{e15}-COOR^{e14}$, $-R^{e15}-CO-R^{e14}$ or $-S-R^{e14}$ (more preferably phenyl, tolyl, trimethylphenyl or naphthyl;
 20 further preferably phenyl, tolyl or trimethylphenyl; further more preferably phenyl).

R^{e13} is each independently nitro, hydroxy, halogen, $-OSO_2-R^{e14}$, $-SO_2-R^{e14}$, $-OR^{e14}$, $-COOR^{e14}$, $-O-CO-R^{e14}$, $-O-R^{e15}-COOR^{e14}$, $-R^{e15}-CO-R^{e14}$, $-S-R^{e14}$ or a C_{1-20}
 25 hydrocarbon group, and the hydrocarbon group may be substituted with $-OSO_2-R^{e14}$, $-SO_2-R^{e14}$, $-OR^{e14}$, -

COOR^{e14}, -O-CO-R^{e14}, -O-R^{e15}-COOR^{e14}, -R^{e15}-CO-R^{e14} or -S-R^{e14}. R^{e13} is more preferably a C₁₋₂₀ hydrocarbon group (further preferably C₁₋₄ alkyl; further more preferably methyl).

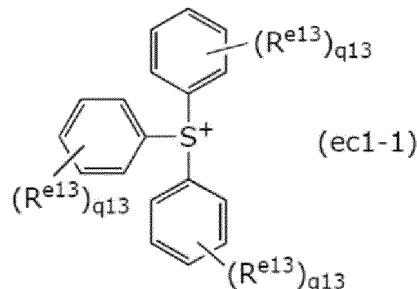
5 R^{e14} is each independently a C₁₋₁₀ hydrocarbon group (preferably methyl, ethyl, i-propyl, n-propyl, tBu, cyclopentyl or cyclohexyl; more preferably methyl or tBu).

10 R^{e15} is each independently a single bond or a C₁₋₁₀ hydrocarbon group (preferably methyl, ethyl, i-propyl, n-propyl, tBu, cyclopentyl or cyclohexyl; more preferably methyl or tBu).

q₁₁ is a number of 0 to 3 (preferably 0 or 1; more preferably 0).

15 q₁₃ is a number of 0 to 11 (preferably 0, 1, 2 or 3; more preferably 0, 1 or 3; more preferably 0 or 3).

[0052] The formula (ec1) is preferably represented by the following formula (ec1-1).



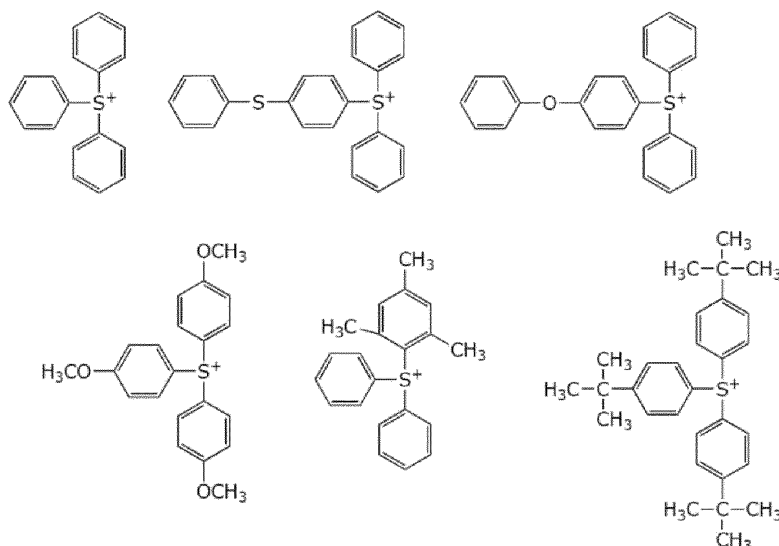
20 In the formula:

R^{e13} is each independently C₁₋₆ alkyl, C₁₋₆ alkoxy, C₆₋₁₂ aryl, C₆₋₁₂ arylthio or C₆₋₁₂ aryloxy; preferably methyl, ethyl, t-butyl, methoxy, ethoxy, phenylthio or phenyloxy; more preferably t-butyl, methoxy, ethoxy, phenylthio or phenyloxy.

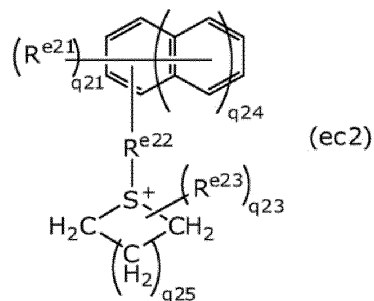
25 q₁₃ is each independently 0, 1, 2 or 3. It is also a preferred embodiment that all q₁₃ are 1 and all R^{e13} are identical. It is also a preferred embodiment that all q₁₃ are 0. It is also a preferred embodiment that one q₁₃

is 3 and the other two q13 are 0.

[0053] Exemplified embodiments of the formula (ec1) include the followings.



5 [0054] The formula (ec2) is as follows.



In

the formula:

10 R^{e21} and R^{e23} are each independently nitro, hydroxy, halogen, $-\text{OSO}_2\text{-}R^{e24}$, $-\text{SO}_2\text{-}R^{e24}$, $-\text{OR}^{e24}$, $-\text{COOR}^{e24}$, $-\text{O-CO-}R^{e24}$, $-\text{O-}R^{e25}\text{-COOR}^{e24}$, $-\text{R}^{e25}\text{-CO-}R^{e24}$, $-\text{S-}R^{e24}$ or a C_{1-20} hydrocarbon group, and the hydrocarbon group may be substituted with $-\text{OSO}_2\text{-}R^{e24}$, $-\text{SO}_2\text{-}R^{e24}$, $-\text{OR}^{e24}$, $-\text{COOR}^{e24}$, $-\text{O-CO-}R^{e24}$, $-\text{O-}R^{e25}\text{-COOR}^{e24}$, $-\text{R}^{e25}\text{-CO-}R^{e24}$ or $-\text{S-}R^{e24}$.

15 R^{e22} is a single bond or a C_{1-20} hydrocarbon group, and the hydrocarbon group may be substituted with $-\text{OSO}_2\text{-}$

Re^{24} , $-\text{SO}_2-\text{Re}^{24}$, $-\text{OR}^{24}$, $-\text{COOR}^{24}$, $-\text{O}-\text{CO}-\text{Re}^{24}$, $-\text{O}-\text{Re}^{25}-\text{COOR}^{24}$, $-\text{Re}^{25}-\text{CO}-\text{Re}^{24}$ or $-\text{S}-\text{Re}^{24}$.

Re^{24} is each independently a C_{1-10} hydrocarbon group,

Re^{25} is each independently a single bond or a C_{1-10} hydrocarbon group.

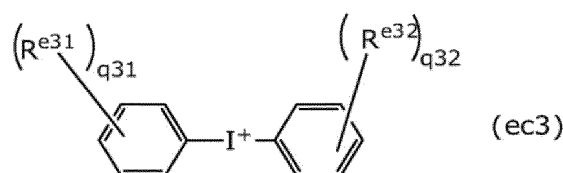
q_{21} is a number of 0 to 9.

q_{23} is a number of 0 to 10.

q_{24} is a number of 0 to 2.

q_{25} is a number of 0 to 3.

10 [0055] The formula (ec3) is as follows.



In the formula:

Re^{31} and Re^{32} are each independently nitro, hydroxy, halogen, $-\text{OSO}_2-\text{Re}^{33}$, $-\text{SO}_2-\text{Re}^{33}$, $-\text{OR}^{33}$, $-\text{COOR}^{33}$, $-\text{O}-\text{CO}-\text{Re}^{33}$, $-\text{O}-\text{Re}^{34}-\text{COOR}^{33}$, $-\text{Re}^{34}-\text{CO}-\text{Re}^{33}$, $-\text{S}-\text{Re}^{33}$ or a C_{1-20} hydrocarbon group, and the hydrocarbon group may be substituted with $-\text{OSO}_2-\text{Re}^{33}$, $-\text{SO}_2-\text{Re}^{33}$, $-\text{OR}^{33}$, $-\text{COOR}^{33}$, $-\text{O}-\text{CO}-\text{Re}^{33}$, $-\text{O}-\text{Re}^{34}-\text{COOR}^{33}$, $-\text{Re}^{34}-\text{CO}-\text{Re}^{33}$ or $-\text{S}-\text{Re}^{33}$. Re^{31} and Re^{32} are preferably C_{1-10} alkyl (more preferably C_{1-5} alkyl; further preferably C_{4-5} alkyl).

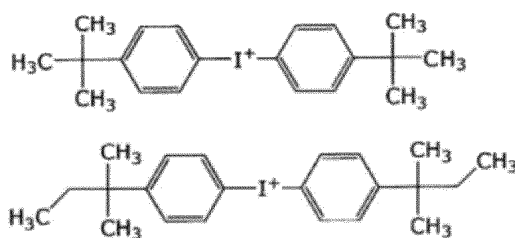
Re^{33} is each independently a C_{1-10} hydrocarbon group.

Re^{34} is each independently a single bond or a C_{1-10} hydrocarbon group.

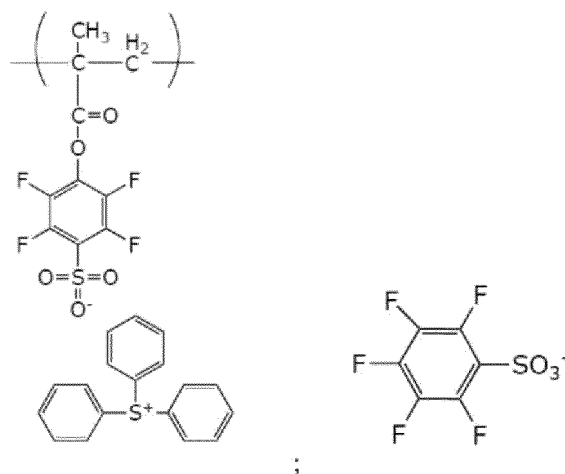
q_{31} is a number of 0 to 5 (preferably 0, 1 or 2; more preferably 1).

q_{32} is a number of 0 to 5 (preferably 0, 1 or 2; more preferably 1).

[0056] Exemplified embodiments of formula (ec3) include the followings.



[0057] When (E) is a part of the polymer (A), H or F in Anion^{54m-} is substituted and such a part is bonded with other part of the polymer (A). For clarity, explanation is provided using an example. The structure below left is the photoacid generation part (E) but is a part of the polymer (A) and can be read as the unit (A5). In particular, in the formula (a5), R⁵¹=methyl and n₅₂=1. Anion^{54m-} is originally a pentafluorosulfonate ion (the anion below right), then one F is substituted and such a part is bonded with the polymer (A). Cation^{54m+} is a triphenylsulfonium ion. m=1.



[0058] The photoacid generation part (E) may be one type or two or more types (more preferably one type). The content of the photoacid generation part (E) is preferably 0.5 to 20 mass % (more preferably 1 to 15 mass %; further preferably 2 to 10 mass %) based on the total mass of the polymer (A).

When the photoacid generation part (E) is a part of the polymer (A), the content of the photoacid generation part (E) in the composition is calculated as the content of the polymer (A). In this case, the content of the photoacid generation part (E) is 0 mass % based on the total mass of the polymer (A).

[0059] Photoacid generator (F)

The composition according to the present invention can further comprise a photoacid generator (F). As one preferred embodiment, the photoacid generation part (E) is a component different from (A) to (D) and is a photoacid generator (F). The photoacid generator (F) is preferably represented by the formula (E1) above, and its preferred embodiments are also the same as described above.

The photoacid generator (F) may be one type or two or more types (more preferably one type). The content of the photoacid generator (F) is preferably 0.5 to 20 mass % (more preferably 1 to 15 mass %; further preferably 2 to 10 mass %) based on the total mass of the polymer (A).

[0060] Surfactant (G)

The composition according to the present invention can further comprise a surfactant (G). Coatability can be improved by further comprising a surfactant (G).

[0061] Examples of the surfactant (G) that can be used in the present invention include (I) anionic surfactants, (II) cationic surfactants, and (III) nonionic surfactants. More particularly, (I) alkylsulfonates, alkylbenzenesulfonic acids and alkylbenzenesulfonates, (II) laurylpyridinium chloride and laurylmethylammonium chloride, and (III) polyoxyethylene octyl ether, polyoxyethylene lauryl ether and polyoxyethylene acetylenic glycol ether are preferred.

[0062] The surfactant (G) may be one type or two or

more types (more preferably one type). The content of the surfactant (G) is preferably 0 to 10 mass % (more preferably 0.5 to 8 mass %; further preferably 1 to 5 mass %) based on the total mass of the polymer (A). It is also a preferred embodiment that the composition of the present invention does not contain the surfactant (G) (0.0 mass %).

[0063] Additive (H)

The composition according to the present invention can further comprise other additive (H) than (A) to (G). The additive (H) is a dye, a lower alcohol, a surface smoothing agent, an acid, a base, a substrate adhesion enhancer, an antifoaming agent, an antiseptic, or any combination of any of these (preferably, a dye, an acid, a base, a substrate adhesion enhancer, or any combination of any of these). When an acid or a base is contained, it is also a preferred embodiment of the present invention to contain only either of them.

The content of the additive (H) is preferably 0 to 10 mass % (more preferably 0 to 5 mass %; further preferably 0.1 to 3 mass %) based on the total mass of the polymer (A). It is also a preferred example of the composition according to the present invention that the additive (H) is not contained (0.0 mass %).

[0064] <Method for manufacturing a resist pattern>

The method for manufacturing a resist pattern according to the present invention comprises the following steps:

- (1) applying a resist underlayer composition above a substrate and heating the resist underlayer composition to form a resist underlayer;
- (2) applying a resist composition directly on the resist underlayer and heating the resist composition to form a resist film;
- (3) exposing the resist film;
- (4) optionally, performing the post-exposure bake of the

resist film; and

(5) developing the resist film using a developer to form a resist pattern, provided that the resist underlayer is not developed by the developer.

5 In this specification, unless otherwise specified, the numbers in parentheses indicating the steps mean the order.

[0065] One embodiment of the manufacturing method according to the present invention is described below.

10 Step (1)

In the step (1), a resist underlayer composition is applied above a substrate, and the resist underlayer composition is heated to form a resist underlayer.

15 The resist underlayer composition is applied above a substrate (for example, a silicon/silicon dioxide-coated substrate, a silicon nitride substrate, a silicon wafer substrate, a glass substrate, an ITO substrate, etc.) by a suitable method.

20 The contact angle θ_s of the surface of the substrate is preferably less than 90° or greater than 90° (more preferably less than 90° ; further preferably less than 85°). The contact angle is measured using water as described later. In order to make the surface of the substrate hydrophobic as described above, a treatment
25 may be performed (for example, HMDS processing).

In the present invention, "above" includes the case of applying directly on a substrate and the case of applying via another layer. For example, a planarization film may be formed directly on a substrate, and the composition according to the present invention may be
30 applied directly on the planarization film. The application method is not particularly limited, but examples thereof include a method of coating with a spinner or coater. After coating, the resist underlayer is formed by heating. Preferably, in the step (1), the
35 resist underlayer composition is applied directly on the

substrate.

The resist underlayer composition is preferably the developer tolerance resist underlayer composition described above.

5 The heating in (1) is performed, for example, by a hot plate. The heating temperature is preferably 100 to 250°C (more preferably 125 to 225°C; further preferably 150 to 200°C). The temperature is the temperature of the heating atmosphere, for example, the temperature
10 of the heating surface of a hot plate. The heating time is preferably 30 to 300 seconds (more preferably 45 to 180 seconds; further preferably 60 to 120 seconds). Heating is preferably carried out in air or nitrogen gas atmosphere. Due to this heating, a cross-linking
15 reaction proceeds in the composition. Therefore, the resist underlayer is not easily dissolved in the subsequent steps.

 The film thickness of the resist underlayer is preferably 2 to 50 nm (more preferably 3 to 30 nm; further preferably 5 to 20 nm).

[0066] Step (2)

 In the step (2), a resist composition is applied directly on the resist underlayer, and the resist composition is heated to form a resist film.

25 The method of applying the resist composition is not particularly limited, but may be the same as the above application, and a vapor phase deposition method is also possible. As a more preferred embodiment, a coating method is included.

30 The resist composition is preferably a metal-containing resist, more preferably an organic metal oxide hydroxide-containing resist, and those described in JP 2021-73367 A can be used. The resist composition is preferably an EUV resist, and in one preferred
35 embodiment, it is a negative-type resist.

 The heating temperature in (2) is preferably 75 to

140°C (more preferably 80 to 130°C; further preferably 90 to 120°C). The heating time is preferably 30 to 240 seconds (more preferably 90 to 180 seconds). The heating is preferably carried out in air or nitrogen gas atmosphere.

The thickness of the resist film is preferably 20 to 70 nm (more preferably 25 to 50 nm). Although not to be bound by theory, it is more preferable that the resist underlayer is not dissolved by the resist composition. It can be confirmed that the resist composition is not dissolved by confirming whether or not film thickness reduction has occurred before and after the application of the resist composition.

[0067] Step (3)

In the step (3), the resist film is exposed through a predetermined mask. Although the wavelength of light to be used for exposure is not particularly limited, it is preferable to perform exposure with light having a wavelength of 13.5 to 248 nm. In particular, KrF excimer laser (wavelength: 248 nm), ArF excimer laser (wavelength: 193 nm), extreme ultraviolet ray (wavelength: 13.5 nm), or the like can be used, and extreme ultraviolet ray is preferred. These wavelengths accept a range of $\pm 1\%$.

It is a preferred embodiment of the present invention that the exposure wavelength passes through the resist film and reaches the resist underlayer. When the resist underlayer composition contains a photoacid generation part (E), it is a preferred embodiment of the present invention that an acid is generated from (E) by the exposure in the step (3).

[0068] Step (4)

After exposure, a post exposure bake (PEB) can be performed as needed. The PEB temperature is preferably 100 to 200°C (more preferably 150 to 190°C), and the heating time is preferably 30 to 240

seconds (more preferably 90 to 180 seconds).

Although not to be bound by theory, it is also a preferred embodiment of the present invention that the acid generated from the photoacid generator present in the resist film moves to the resist underlayer, and this acid deprotects the protective group of the polymer (A) in the resist underlayer. It can be thought that in this case, even if the resist underlayer composition of the present invention contains neither photoacid generation part (E) (for example, (E) incorporated in (A) as the unit (A5)) nor the photoacid generator (F), the hydrophilicity of the exposed area of the resist underlayer can be changed.

[0069] When the contact angle of the resist film before exposure is defined as θ_{PrR} , that of the resist film after exposure is defined as θ_{PeR} , that of the resist underlayer before exposure is defined as θ_{PrU} , and that of the resist underlayer after exposure is defined as θ_{PeU} ,

$\theta_{PeU}/\theta_{PrU} < 1.0$ when $\theta_{PeR}/\theta_{PrR} < 1.0$, and
 $\theta_{PeU}/\theta_{PrU} > 1.0$ when $\theta_{PeR}/\theta_{PrR} > 1.0$.

For example, when the hydrophilicity of the resist film is increased by exposure, the contact angle of the resist film becomes smaller. In this case, $\theta_{PeR}/\theta_{PrR} < 1.0$ because θ_{PeR} changes so as to be decreased from θ_{PrR} . It is preferable that in the manufacturing method of the present invention, the hydrophilicity of the resist underlayer changes so as to match the hydrophilicity of the resist film. That is, when the hydrophilicity of the resist film increases (θ_{PeR} changes so as to be decreased from θ_{PrR}), it is preferable that the hydrophilicity of the resist underlayer also increases (θ_{PeU} changes so as to be decreased from θ_{PrU}). Moreover, when the hydrophilicity of the resist film is decreased (the hydrophobicity is increased) by exposure, it is preferable that the hydrophilicity of the resist underlayer is also decreased. Since change of the hydrophilicity is

performed by deprotection of the protective group with acid, it is preferred that the hydrophilicity of the exposed area changes.

5 A more preferable embodiment of the present invention is that $\theta_{\text{PeR}}/\theta_{\text{PrR}} < 1.0$ and $\theta_{\text{PeU}}/\theta_{\text{PrU}} < 1.0$.

The contact angle is measured using water. Preferably, the contact angle is measured by dropping 2 μ L of water onto the resist film or the resist underlayer and using a contact angle meter.

10 [0070] Step (5)

Development of the exposed resist film is performed using a developer to form a resist pattern. Examples of the development include an alkali development and an organic solvent development or the like, and the organic solvent development is preferred. 15 The developer comprises an organic solvent, and more preferably it consists of an organic solvent. In the case of organic solvent development, the developer includes hydrocarbon solvents, ether solvents, ester solvents, 20 ketone solvents and alcohol solvents, preferably ester solvents or ketone solvents. Exemplified embodiments of the developer include 2-heptanone, butyl acetate, PGMEA and the like.

By means of using such a developer, the resist 25 layer can be developed. On the other hand, the developer does not develop the resist underlayer. Although not to be bound by theory, it can be thought that the resist underlayer is not developed because the cross-linking agent (B) and the polymer (A) are cross-linked. "Not developed" can be confirmed by the 30 following operation. The amount of decrease in the thickness of the resist underlayer is 0 to 30% and/or 5 nm or less when the developer is paddled on the resist underlayer for 30 seconds. "Developer tolerance" can 35 also be confirmed by the above-described operation.

Although not to be bound by theory, it can be

thought that by having the resist underlayer of the present invention, the hydrophilicity of the resist underlayer changes in accordance with the change in the hydrophilicity of the resist film, thereby preventing the collapse of the resist pattern due to the decrease in affinity with the substrate. Although not to be bound by theory, it can be thought that the hydrophilicity of the resist underlayer in the exposed area or unexposed area changes in accordance with the resist film, so that the sufficient affinity of the resist pattern and the resist underlayer can be maintained. Although not to be bound by theory, it can be thought that the exposed area and unexposed area of the resist underlayer are physically connected even after development, so even if the affinity in a part of the resist underlayer with the substrate is reduced, the resist underlayer can entirely maintain the adhesion to the substrate as a whole resist underlayer.

[0071] The method for manufacturing a resist pattern can further comprises a following step:
(6) washing the resist pattern with a cleaning liquid and removing the cleaning liquid from between the patterns.

A cleaning liquid can be used to clean the resist pattern in order to remove localized film residues. As the cleaning liquid, water or organic solvents (for example, IPA, PGME, PGMEA, PGEE, nBA are included) are included. In a preferred embodiment of the present invention, the cleaning liquid is a rinse liquid, and cleaning is performed by replacing the developer with the rinse liquid. Examples of the rinse liquid include those described in JP 2019-519804 A and WO 2021/204651 A1.

[0072] The method for manufacturing a processed substrate according to the present invention comprises the following steps:
forming a resist pattern by the above-described method;

and

(7) processing using the resist pattern as a mask.

Preferably, in the step (7), the resist underlayer and/or the substrate is processed. It is also possible to

5 process the substrate by etching the resist underlayer and the substrate at once, or to process the substrate stepwise by etching the resist underlayer and then etching the substrate using it as a mask. More

preferably, the resist underlayer and the substrate are
10 etched at once. Etching may be either dry etching or wet etching. This allows a gap to be formed on the substrate or a layer on the substrate. After forming the gap, the resist pattern can be removed by contacting with water, a mixture of a water-soluble organic solvent
15 and water, or an alkaline aqueous solution. It is also possible to process the substrate by methods other than etching.

[0073] After that, if necessary, the substrate is further processed to form a device. These further processing
20 can be performed by applying well-known methods. Preferably, the method further comprises a step of forming a wiring on the processed substrate. If necessary, the substrate is cut into chips, connected to lead frames, and packaged with resin. In the present
25 invention, this packaged product is called a device. Preferably, the device is a semiconductor device.

[0074] [Example]

The present invention is described below with reference to various examples. The embodiments of the
30 present invention are not limited only to these examples.

[0075] In the following Examples, the mass average molecular weight (Mw) is measured by gel permeation chromatography (GPC) using polystyrene as a standard.
35 GPC is measured using alliance™ e2695 type high-speed GPC system (Nihon Waters) and organic solvent-based

GPC column Shodex KF-805L (Showa Denko). The measurement is performed using monodispersed polystyrene as a standard sample and chloroform as an eluent, under the measuring conditions of a flow rate of 0.6 ml/min and a column temperature of 40°C, and Mw is calculated as a relative molecular weight to the standard sample.

[0076] <Synthesis of Polymer 2>

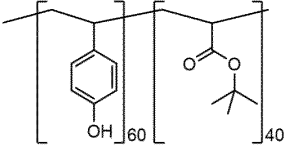
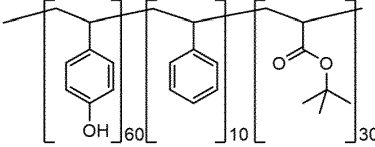
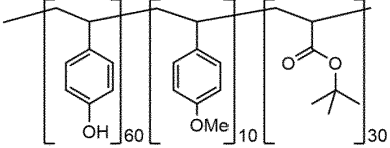
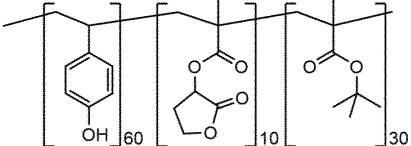
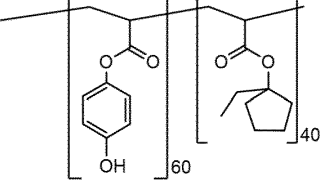
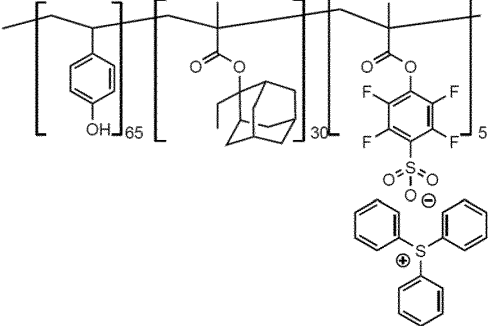
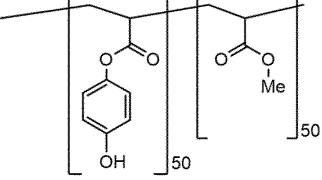
95.8 g of p-acetoxystyrene as a monomer that derives the unit (A2) after being deprotected, 37.8 g of t-butyl acrylate as a monomer that derives the unit (A1), and 10.3 g of styrene as a monomer that derives the unit (A3), as well as 6 g of azobisisobutyronitrile (AIBN) and 1 g of t-dodecylmercaptan as polymerization initiators are dissolved in 230 g of PGME, and the polymerization is conducted at 70°C for 16 hours in a nitrogen atmosphere. After the polymerization is completed, the reaction solution is added dropwise to a large amount of hexane to solidify/purify the formed polymer. Next, 150 g of PGME is added to the polymer thus purified, and then 300 g of methanol, 80 g of triethylamine and 15 g of water are further added, and the hydrolysis reaction is carried out for 8 hours while heating under reflux. After the reaction is completed, the solvent and triethylamine are evaporated under reduced pressure. The polymer obtained is then dissolved in acetone. This solution is added dropwise to a large amount of distilled water with stirring to solidify. The white solid formed is filtered and then dried under reduced pressure at 50°C overnight. Polymer 2 thus obtained is a random copolymer with a mass average molecular weight (Mw) of 12,000 and a polydispersity index (PDI) of 1.6, and its ¹³C-NMR analysis indicates that a molar ratio of vinylphenol-derived unit, t-butyl acrylate-derived unit and styrene-derived unit is 60 : 30 : 10.

[0077] <Synthesis of Polymer 6>

16.7 g of 4-vinylphenol as a monomer that derives the unit (A2), 3.0 g of triphenylsulfonium 2,3,5,6-tetrafluoro-4-(methacryloyloxy)benzenesulfonic acid as a monomer that derives the unit (A5), 27.9 g of 2-ethyl-2-adamantyl methacrylate as a monomer that derives the unit (A1) and 2.1 g of AIBN as a polymerization initiator are dissolved in 76 g of anhydrous tetrahydrofuran and acetonitrile (volume ratio = 1 : 1), and the polymerization is conducted at 65°C for 24 hours in a closed pressure vessel. After the polymerization is completed, the reaction solution is added dropwise to a large amount of diethyl ether with stirring to solidify the polymer. The white solid formed is filtered and then dried under reduced pressure at 50°C overnight. The dried white solid is then dissolved in tetrahydrofuran and the solution is added dropwise with stirring to a large amount of diethyl ether to solidify the polymer again, which is filtered. The resulting white solid is dissolved in tetrahydrofuran and the solution is added dropwise with stirring to a large amount of diethyl ether to solidify the polymer again, which is filtered. The solid obtained is dried under reduced pressure at 50°C overnight. Polymer 6 thus obtained is a random copolymer of $M_w = 4,000$ and $PDI = 1.6$, and its ^{13}C -NMR analysis indicates that a molar ratio of 4-vinylphenol-derived unit, 2-ethyl-2-adamantyl methacrylate-derived unit and triphenylsulfonium 2,3,5,6-tetrafluoro-4-(methacryloyloxy)benzenesulfonic acid-derived unit is 65 : 30 : 5.

[0078] <Synthesis of Polymers 1, 3 to 5 and 7>

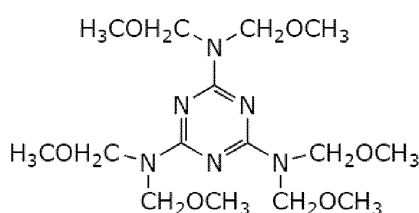
Polymers 1, 3 to 5 and 7 are synthesized in the same manner as the synthesis of Polymer 2 above, except that the monomers and molar ratios are changed. The polymers after synthesis are described in Table 1. [Table 1]

Table	Structure	Mw	PDI
Polymer 1		13,000	1.7
Polymer 2		12,000	1.6
Polymer 3		12,500	1.7
Polymer 4		15,000	1.8
Polymer 5		18,000	1.6
Polymer 6		4,000	1.6
Polymer 7		19,500	1.8

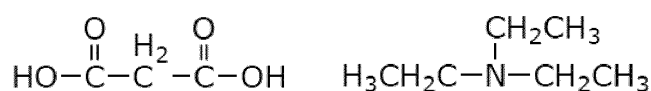
[0079] <Preparation of the composition of Example 1>

By mixing so as to make a mass ratio of PGMEA :
 PGME : EL is 30 : 40 : 30, Solvent 1 is obtained. 100
 mass parts of the above Polymer 1, 30 mass parts of
 5 Cross-linking agent 1, 5 mass parts of Thermal acid
 generator 1 and 5 mass parts of Photoacid generator 1
 are added to Solvent 1, and the solid component
 concentration is adjusted to become 0.385 mass %.
 Components other than the solvent are solid
 10 components. This is stirred at room temperature for 30
 minutes. It is visually confirmed that the solid
 components are completely dissolved. Filtration is
 carried out through a 0.2 μm pore size filter. This gives
 the composition of Example 1.

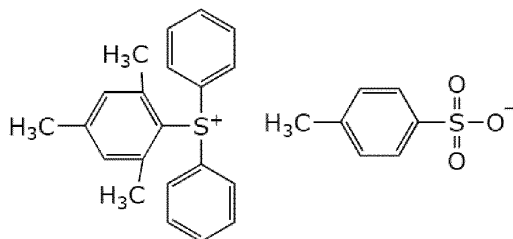
15 Cross-linking agent 1 is as follows.



Thermal acid generator 1 is a mixture of malonic
 acid : triethylamine = 1 : 2.



20 Photoacid generator 1 is diphenyl-2,4,6-trimethyl-
 phenylsulfonium p-toluenesulfonic acid.



[0080] <Preparation of the compositions of Examples 2 to 6 and

Comparative Example 1>

5 The compositions of Examples 2 to 6 and Comparative Example 1 are prepared in the same manner as the composition of Example 1, except that each component and its compounding ratio are changed as described in Table 2. The solid component concentration is 0.385 mass % as in Example 1 for all compositions.

[Table 2]

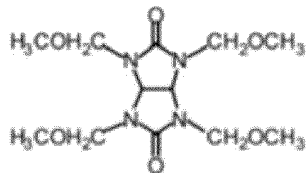
Table 2

		Composition										Evaluation		
		(A)		(B)		(C)		(D)	(F)		(G)		Pattern collapse	Solvent resistance
Example	1	Polym er 1	100	Cross-linking agent 1	30	Thermal acid generator 1	5	Solve nt 1	Photoacid generator 1	5	—		A	A
	2	Polym er 2	100	Cross-linking agent 2	30	Thermal acid generator 1	5	Solve nt 1	Photoacid generator 1	5	Surfac tant 1	0.0005	A	A
	3	Polym er 3	100	Cross-linking agent 3	30	Thermal acid generator 1	5	Solve nt 1	Photoacid generator 1	5	—		A	A
	4	Polym er 4	100	Cross-linking agent 4	30	Thermal acid generator 1	5	Solve nt 1	Photoacid generator 1	5	—		A	B
	5	Polym er 5	100	Cross-linking agent 1	30	Thermal acid generator 1	5	Solve nt 1	Photoacid generator 1	5	—		A	B
	6	Polym er 6	100	Cross-linking agent 1	30	Thermal acid generator 1	5	Solve nt 2	—		—		A	A
Comparative Example	1	Polym er 7	100	Cross-linking agent 1	30	Thermal acid generator 1	5	Solve nt 1	Photoacid generator 2	5	—		B	B

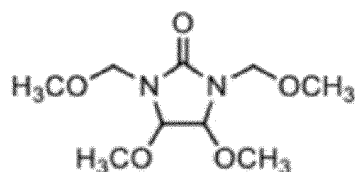
In the table:

Polymers 1 to 7, Cross-linking agent 1, Thermal acid generator 1, Photoacid generator 1 and Solvent 1 are as described above.

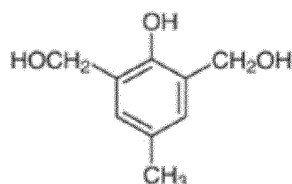
15 Cross-linking agent 2 is as follows.



Cross-linking agent 3 is as follows.

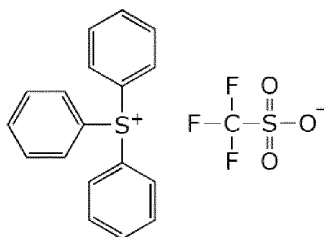


Cross-linking agent 4 is as follows.

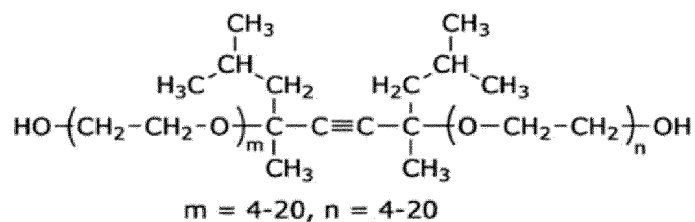


Solvent 2 is a mixed solvent mixed so as to the mass ratio of PGMEA : PGME : EL becomes 20 : 50 : 30.

Photoacid generator 2 is triphenylsulfonium trifluoromethanesulfonate.



Surfactant 1 is an acetylenic diol polyoxyalkylene ether and represented by the following.



[0081] <Evaluation of pattern collapse>

Each composition prepared above is applied onto a silicon substrate by spin coating. This is heated on a hot plate at 170°C for 90 seconds for cross-linking reaction to obtain a resist underlayer (thickness: 10 nm). Then, a solution of 4-methyl-2-pentanol and an organometal tin oxy hydroxide resist composition is

spin-coated on the resist underlayer and heated at 100°C for 2 minutes to form a Sn resist film (thickness: 35 nm). This substrate is exposed to extreme ultraviolet ray having a wavelength of 13.5 nm so as to form a pattern of lines of 16 nm and spaces of 16 nm. This substrate is subjected to PEB at 170°C for 2 minutes in an air atmosphere using a hot plate. The resist film on the substrate is paddle-developed using 2-heptanone for 30 seconds. The wafer is spined at high speed and dried. A SEM (0.5 μm × 0.5 μm) photograph of the resist pattern is taken. The space size of the resist pattern is 16 nm. Pattern collapse prevention performance is evaluated using CG4000 (Hitachi High Technologies). Evaluation criteria are as described below. The results obtained are as described in Table 2.

A: No pattern collapse is observed.
B: Pattern collapse is observed.

Although not to be bound by theory, it can be thought that since Polymer 7 of Comparative Example 1 has no unit having a protective group that is deprotected by an acid, the hydrophilicity does not change even if an acid is generated from the photoacid generator.

[0082] <Evaluation of solvent resistance>

Each composition prepared above is applied onto a silicon substrate by spin coating. This is heated on a hot plate at 170°C for 90 seconds for cross-linking reaction to obtain a resist underlayer (thickness: 10 nm). The insolubility of this underlayer in 4-methyl-2-pentanol and 2-heptanone is confirmed by the following test.

4-methyl-2-pentanol is filled up on the resist underlayer and left to stand for 30 seconds. This is spin-dried and an SEM section is formed. Film thickness measurement is performed using an ellipsometer. The same test is performed by changing the liquid from 4-methyl-2-pentanol to 2-heptanone. Evaluation criteria

for solvent resistance are as follows. The results obtained are listed in Table 2.

A: With any liquid, film thickness reduction of the resist underlayer is not observed or is less than 1 nm.

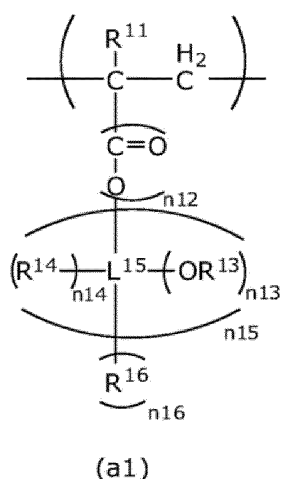
5 B: With at least one of the liquids, film thickness reduction of 1 to 2 nm is observed.

C: With at least one of the liquids, film thickness reduction larger than 2 nm is observed.

10 Although not to be bound by theory, it can be thought that using the resist underlayer of the present invention, the film thickness reduction due to the resist composition and developer can be suppressed.

Patent Claims

1. A developer tolerance resist underlayer composition comprising a polymer (A), a cross-linking agent (B), a thermal acid generator (C) and a solvent (D):
wherein the polymer (A) comprises at least a unit having a protective group that is deprotected by an acid, and the hydrophilicity of the portion where the deprotected unit is present changes after exposure.
2. The composition according to claim 1, wherein the polymer (A) comprises the unit (A1) represented by the formula (a1):



where

R^{11} is each independently H or methyl,

L^{15} is each independently a C_{6-20} aromatic hydrocarbon group or a C_{1-6} saturated hydrocarbon group,

R^{13} is each independently tert-butyl or C_{5-10} alkyl (where the methylene in the alkyl may be replaced with oxy and/or carbonyl),

R^{14} is each independently C_{1-5} alkyl,

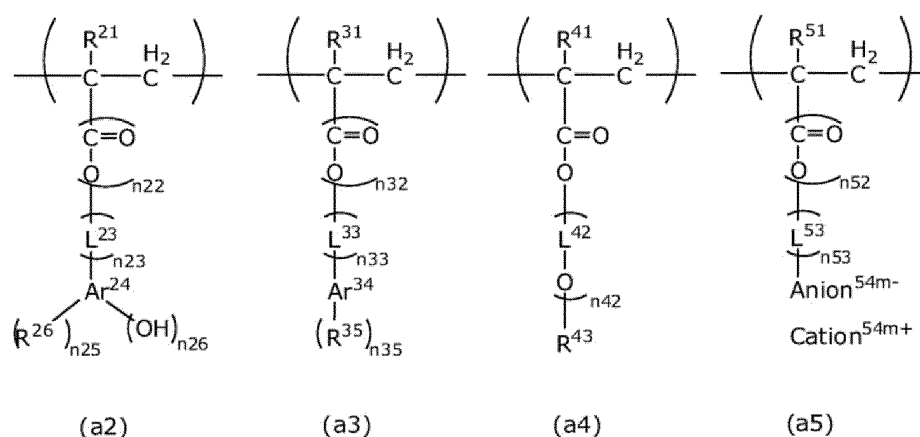
R^{16} is each independently tert-butyl or C_{5-15} alkyl, and

n_{12} , n_{15} and n_{16} are each independently a number of 0 to 1,

n_{13} is each independently a number of 1 to 3,

n_{14} is each independently a number of 0 to 4,
provided that $n_{12}=n_{16}=1$ when $n_{15}=0$, and $n_{16}=0$ when
 $n_{15}=1$.

3. The composition according to claim 1 or 2, wherein the
polymer (A) further comprises at least one of the unit (A2)
represented by the formula (a2), the unit (A3) represented by
the formula (a3), the unit (A4) represented by the formula (a4)
and the unit (A5) represented by the formula (a5):



where

in the formula (a2):

R^{21} is each independently H or methyl,

L^{23} is each independently C_{1-10} alkylene,

Ar^{24} is each independently C_{6-20} aryl,

R^{26} is each independently C_{1-5} alkyl,

n_{22} and n_{23} are each independently a number of 0 to 1,

n_{25} is each independently a number of 0 to 4, and

n_{26} is each independently a number of 1 to 3;

in the formula (a3):

R^{31} is each independently H or methyl,

L^{33} is each independently C_{1-10} alkylene,

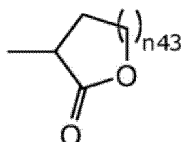
Ar^{34} is each independently C_{6-20} aryl,

R^{35} is each independently $-\text{O}-\text{R}^{35a}$, $-(\text{C}=\text{O})-\text{R}^{35b}$, $-(\text{C}=\text{O})-\text{O}-\text{R}^{35a}$,

$-(\text{C}=\text{O})-\text{NR}^{35c}\text{R}^{35d}$, $-\text{O}-(\text{C}=\text{O})-\text{R}^{35e}$, $-\text{NR}^{35f}-(\text{C}=\text{O})-\text{R}^{35g}$ or -

R^{35j}OH ,

n_{32} and n_{33} are each independently a number of 0 to 1,
 n_{35} is each independently a number of 0 to 3,
 R^{35a} is each independently C_{1-4} alkyl (excluding tert-butyl),
 R^{35b} is each independently H or C_{1-4} alkyl,
 R^{35c} and R^{35d} are each independently H or C_{1-4} alkyl, and when both R^{35c} and R^{35d} are alkyl, these may be combined to form a ring,
 R^{35e} is each independently H, C_{1-4} alkyl or C_{1-4} alkoxy (excluding tert-butoxy),
 R^{35f} is each independently H or C_{1-4} alkyl,
 R^{35g} is each independently H, C_{1-4} alkyl or $-NR^{35h}R^{35r}$,
 R^{35h} and R^{35r} are each independently H or C_{1-4} alkyl, and when both R^{35h} and R^{35r} are alkyl, these may be combined to form a ring, and
 R^{35j} is each independently C_{1-4} alkylene;
 in the formula (a4):
 R^{41} is each independently H or methyl,
 L^{42} is C_{1-4} alkylene,
 n_{42} is a number of 0 to 1,
 R^{43} is C_{1-4} alkyl (excluding tert-butyl) or the following group:



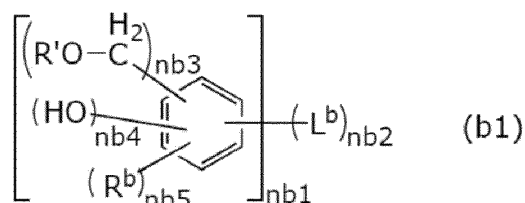
where
 n_{43} is a number of 1 to 2; and
 in the formula (a5):
 R^{51} is each independently H or methyl,
 L^{53} is each independently C_{1-10} alkylene,
 n_{52} and n_{53} are each independently a number of 0 to 1,
 $Anion^{54m-}$ is an m-valent anion that is bonded upward in the formula,
 $Cation^{54m+}$ is an m-valent cation that is ionically bonded with $Anion^{54m-}$, and
 m is a number of 1 to 2.

4. The composition according to one or more of claims 1 to 3, which satisfies, when the number of repetitions of the unit (A1), the unit (A2), the unit (A3), the unit (A4) and the unit (A5) are respectively $nA1$, $nA2$, $nA3$, $nA4$ and $nA5$, the followings:

$$\begin{aligned} 5\% \leq nA1/(nA1+nA2+nA3+nA4+nA5) \leq 100\%, \\ 0\% \leq nA2/(nA1+nA2+nA3+nA4+nA5) \leq 95\%, \\ 0\% \leq nA3/(nA1+nA2+nA3+nA4+nA5) \leq 95\%, \\ 0\% \leq nA4/(nA1+nA2+nA3+nA4+nA5) \leq 95\%, \text{ and} \\ 0\% \leq nA5/(nA1+nA2+nA3+nA4+nA5) \leq 95\%. \end{aligned}$$

5. The composition according to one or more of claims 2 to 4, wherein the unit (A1) has a protective group that is deprotected by an acid and is deprotected after exposure.

6. The composition according to one or more of claims 1 to 5, wherein the cross-linking agent (B) is represented by the formula (b1):



where

$nb1$ is 1, 2, 3 or 4,

$nb2$ is 0 when $nb1$ is 1, and 1 when $nb1$ is 2 or more,

$nb3$ is 0, 1 or 2,

$nb4$ is 1 or 2,

$nb5$ is 0 or 1,

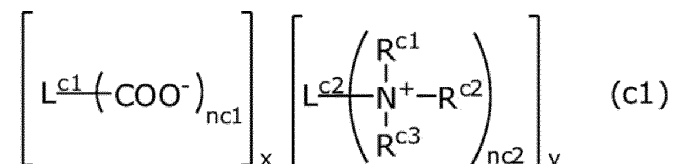
L^b is a single bond or a C_{1-30} hydrocarbon group,

R^b is each independently C_{1-6} alkyl (where the methylene in the alkyl may be replaced with oxy) or C_{6-10} aryl, and

R' is H or methyl.

7. The composition according to one or more of claims 1 to

6, wherein the thermal acid generator (C) is represented by the formula (c1):



where

nc1 is 1 or 2,

L^{c1} is H or C_{1-6} alkyl when nc1 is 1, in which the alkyl may be substituted with halogen or hydroxy, and C_{1-4} alkylene when nc1 is 2, in which the alkylene may be substituted by halogen or hydroxy, and the methylene in the alkylene may be replaced with carbonyl, oxy or amido,

nc2 is 1 or 2,

L^{c2} is C_{1-6} alkyl when nc2 is 1, in which the alkyl may be substituted with halogen or hydroxy, and C_{1-4} alkylene when nc2 is 1, in which the alkylene may be substituted with halogen or hydroxy, and the methylene in the alkylene may be replaced with carbonyl, oxy or amido;

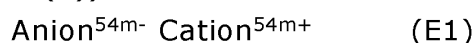
R^{c1} , R^{c2} and R^{c3} are each independently H or C_{1-10} alkyl, in which the alkyl may be substituted with halogen or hydroxy, and x and y are 1 or 2, provided that $nc1 \times x = nc2 \times y$ is satisfied.

8. The composition according to one or more of claims 1 to 7, wherein the solvent (D) is water, a hydrocarbon solvent, an ether solvent, an ester solvent, an alcohol solvent, a ketone solvent, or any combination of any of these.

9. The composition according to one or more of claims 1 to 8, comprising a photoacid generation part (E):
preferably, the photoacid generation part (E) is a part of the polymer (A) or a component different from (A) to (D), or preferably, the photoacid generation part (E) is a photoacid generator (F).

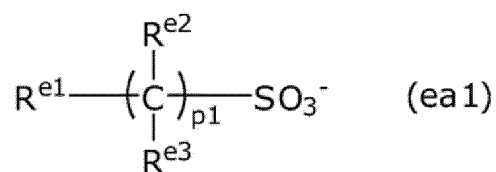
10. The composition according to one or more of claims 1 to 9, wherein the pKa (H₂O) of the acid generated from the thermal acid generator (C) is greater than that of the acid generated from the photoacid generation part (E): preferably, the pKa (H₂O) of the acid generated from the thermal acid generator (C) is 1 to 8 (more preferably 2 to 6), or preferably, the pKa (H₂O) of the acid generated from the photoacid generation part (E) is -20 to 3 (more preferably -20 to 1).

11. The composition according to one or more of claims 1 to 10, wherein the photoacid generation part (E) is represented by the formula (E1) (provided that when the photoacid generation part (E) is a part of the polymer (A), H or F in Anion^{54m-} is substituted and such a part is bonded with other part of the polymer (A)):



wherein

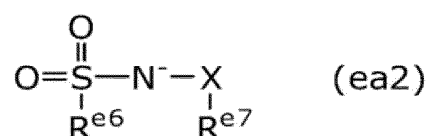
Anion^{54m-} is an anion selected from the group consisting of an anion represented by the formula (ea1) and an anion represented by the formula (ea2), and is m-valent as a whole, Cation^{54m+} is a cation selected from the group consisting of a cation represented by the formula (ec1), a cation represented by the formula (ec2) and a cation represented by the formula (ec3), and is m-valent as a whole:



where

R^{e1} is a C₄₋₃₀ hydrocarbon group containing a ring structure having 5 or more ring atoms, in which at least one of the ring atoms may be nitrogen, the hydrocarbon group may be substituted with nitro, hydroxy, halogen, -OSO₂-R^{e4}, -SO₂-R^{e4}, -OR^{e4}, -COOR^{e4}, -O-CO-R^{e4}, -O-R^{e5}-COOR^{e4}, -R^{e5}-CO-R^{e4} or -S-

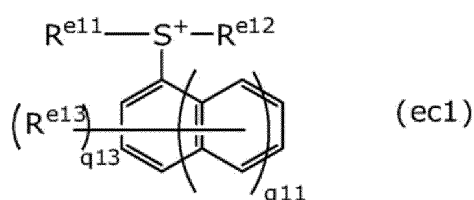
R^{e5} , and $-CH_2-$ in the hydrocarbon group may be replaced with carbonyl, ether, carbonyloxy, sulfide, thiocarbonyl or sulfonyl, R^{e2} and R^{e3} are each independently H, fluorine, fluorine-substituted C_{1-5} alkyl or C_{1-5} alkyl, R^{e4} is each independently a C_{1-10} hydrocarbon group, R^{e5} is each independently a single bond or a C_{1-10} hydrocarbon group, and p_1 is each independently a number of 0 to 10;



where

X is carbonyl or sulfonyl, and

R^{e6} and R^{e7} are each independently C_{1-6} fluorine-substituted alkyl, C_{1-6} fluorine-substituted alkoxy, C_{6-12} fluorine-substituted aryl, C_{2-12} fluorine-substituted acyl or C_{6-12} fluorine-substituted alkoxyaryl, in which R^{e6} and R^{e7} may be bonded to each other to form a fluorine-substituted heterocyclic structure;

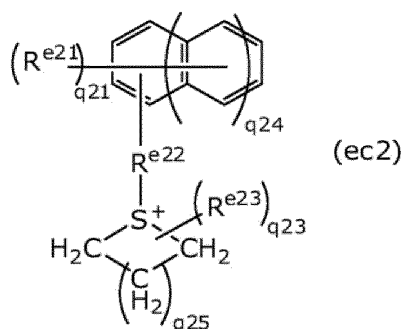


where

R^{e11} and R^{e12} are each independently a C_{1-20} hydrocarbon group, and the hydrocarbon group may be substituted with $-\text{OSO}_2-\text{R}^{e14}$, $-\text{SO}_2-\text{R}^{e14}$, $-\text{OR}^{e14}$, $-\text{COOR}^{e14}$, $-\text{O}-\text{CO}-\text{R}^{e14}$, $-\text{O}-\text{R}^{e15}-\text{COOR}^{e14}$, $-\text{R}^{e15}-\text{CO}-\text{R}^{e14}$ or $-\text{S}-\text{R}^{e14}$,

R^{e13} is each independently nitro, hydroxy, halogen, $-\text{OSO}_2-\text{R}^{e14}$, $-\text{SO}_2-\text{R}^{e14}$, $-\text{OR}^{e14}$, $-\text{COOR}^{e14}$, $-\text{O}-\text{CO}-\text{R}^{e14}$, $-\text{O}-\text{R}^{e15}-\text{COOR}^{e14}$, $-\text{R}^{e15}-\text{CO}-\text{R}^{e14}$, $-\text{S}-\text{R}^{e14}$ or a C_{1-20} hydrocarbon group, and the hydrocarbon group may be substituted with $-\text{OSO}_2-\text{R}^{e14}$, $-\text{SO}_2-\text{R}^{e14}$, $-\text{OR}^{e14}$, $-\text{COOR}^{e14}$, $-\text{O}-\text{CO}-\text{R}^{e14}$, $-\text{O}-\text{R}^{e15}-\text{COOR}^{e14}$, $-\text{R}^{e15}-\text{CO}-\text{R}^{e14}$ or $-\text{S}-\text{R}^{e14}$,

R^{e14} is each independently a C_{1-10} hydrocarbon group,
 R^{e15} is each independently a single bond or a C_{1-10} hydrocarbon group,
 $q11$ is a number of 0 to 3, and
 $q13$ is a number of 0 to 11;



where

R^{e21} and R^{e23} are each independently nitro, hydroxy, halogen, -OSO₂- R^{e24} , -SO₂- R^{e24} , -OR^{e24}, -COOR^{e24}, -O-CO- R^{e24} , -O- R^{e25} -COOR^{e24}, - R^{e25} -CO- R^{e24} , -S- R^{e24} or a C_{1-20} hydrocarbon group, and the hydrocarbon group may be substituted with -OSO₂- R^{e24} , -SO₂- R^{e24} , -OR^{e24}, -COOR^{e24}, -O-CO- R^{e24} , -O- R^{e25} -COOR^{e24}, - R^{e25} -CO- R^{e24} or -S- R^{e24} ,

R^{e22} is a single bond or a C_{1-20} hydrocarbon group, and the hydrocarbon group may be substituted with -OSO₂- R^{e24} , -SO₂- R^{e24} , -OR^{e24}, -COOR^{e24}, -O-CO- R^{e24} , -O- R^{e25} -COOR^{e24}, - R^{e25} -CO- R^{e24} or -S- R^{e24} ,

R^{e24} is each independently a C_{1-10} hydrocarbon group,

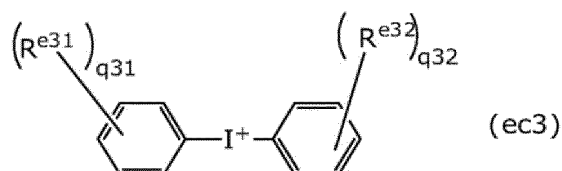
R^{e25} is each independently a single bond or a C_{1-10} hydrocarbon group,

$q21$ is a number of 0 to 9,

$q23$ is a number of 0 to 10,

$q24$ is a number of 0 to 2, and

$q25$ is a number of 0 to 3; and



where

R^{e31} and R^{e32} are each independently nitro, hydroxy, halogen, -OSO₂- R^{e33} , -SO₂- R^{e33} , -OR^{e33}, -COOR^{e33}, -O-CO- R^{e33} , -O- R^{e34} -COOR^{e33}, - R^{e34} -CO- R^{e33} , -S- R^{e33} or a C₁₋₂₀ hydrocarbon group, and the hydrocarbon group may be substituted with -OSO₂- R^{e33} , -SO₂- R^{e33} , -OR^{e33}, -COOR^{e33}, -O-CO- R^{e33} , -O- R^{e34} -COOR^{e33}, - R^{e34} -CO- R^{e33} or -S- R^{e33} ,

R^{e33} is each independently a C₁₋₁₀ hydrocarbon group,

R^{e34} is each independently a single bond or a C₁₋₁₀ hydrocarbon group,

q31 is a number of 0 to 5, and

q32 is a number of 0 to 5.

12. The composition according to one or more of claims 1 to 11, further comprising a surfactant (G).

13. The composition according to one or more of claims 1 to 12, further comprising other additive (H):

wherein the additive (H) is a dye, a lower alcohol, a surface smoothing agent, an acid, a base, a substrate adhesion enhancer, an antifoaming agent, an antiseptic, or any combination of any of these.

14. The composition according to one or more of claims 1 to 13,

wherein

the content of the polymer (A) is 0.1 to 10 mass % based on the total mass of the composition,

the content of the cross-linking agent (B) is 5 to 100 mass % based on the total mass of the polymer (A),

the content of the thermal acid generator (C) is 0.5 to 30 mass % based on the total mass of the polymer (A), or

the content of the solvent (D) is 80 to 99.99 mass % based on the total mass of the composition:

preferably, the content of the photoacid generation part (E) is 0.5 to 20 mass % based on the total mass of the polymer (A),

preferably, the content of the photoacid generator (F) is 0.5 to 20 mass % based on the total mass of the polymer (A),
preferably, the content of the surfactant (G) is 0 to 10 mass % based on the total mass of the polymer (A), or
preferably, the content of the additive (H) is 0 to 10 mass % based on the total mass of the polymer (A).

15. The composition according to one or more of claims 1 to 14, wherein the developer comprises an organic solvent:
preferably, the developer is one that develops a resist layer but does not develop any resist underlayer,
preferably, the amount of decrease in the thickness of the resist underlayer is 0 to 30% when the developer is paddled on the resist underlayer for 30 seconds, or
preferably, the amount of decrease in the thickness of the resist underlayer is 5 nm or less when the developer is puddled on the resist underlayer for 30 seconds.

16. The composition according to one or more of claims 1 to 15, wherein the resist is a metal-containing resist:
preferably, the resist is an organometal oxide hydroxide-containing resist,
preferably the resist is an EUV resist, or
preferably, the resist is a negative-type resist.

17. A method for manufacturing a resist pattern comprising the following steps:

- (1) applying a resist underlayer composition above a substrate and heating the resist underlayer composition to form a resist underlayer;
- (2) applying a resist composition directly on the resist underlayer and heating the resist composition to form a resist film;
- (3) exposing the resist film;
- (4) optionally, performing the post-exposure bake of the resist film; and

(5) developing the resist film using a developer to form a resist pattern, provided that the resist underlayer is not developed by the developer:

wherein

when the contact angle of the resist film before exposure is defined as θ_{PrR} , that of the resist film after exposure is defined as θ_{PeR} , that of the resist underlayer before exposure is defined as θ_{PrU} , and that of the resist underlayer after exposure is defined as θ_{PeU} ,

$\theta_{PeU}/\theta_{PrU} < 1.0$ when $\theta_{PeR}/\theta_{PrR} < 1.0$, and

$\theta_{PeU}/\theta_{PrU} > 1.0$ when $\theta_{PeR}/\theta_{PrR} > 1.0$,

where the contact angle is measured using water.

18. The method according to claim 17, wherein the resist underlayer composition is the developer tolerance resist underlayer composition according to one or more of claims 1 to 16.

19. The method according to claim 17 or 18, wherein the contact angle is measured by dropping 2 μ L of water onto the resist film or the resist underlayer and using a contact angle meter.

20. The method according to one or more of claims 17 to 19, wherein the contact angle θ_s of the surface of the substrate is less than 90° or greater than 90°.

21. The method according to one or more of claims 17 to 20, wherein the acid generated in the steps (3) and (4) moves to the resist underlayer to cause a change from θ_{PrU} to θ_{PeU} .

22. The method according to one or more of claims 17 to 21, further comprising a step (6):

(6) washing the resist pattern with a cleaning liquid and removing the cleaning liquid from between the patterns.

23. A method for manufacturing a processed substrate comprising the following steps:
forming a resist pattern by the method according to one or more of claims 17 to 22; and
(7) processing using the resist pattern as a mask:
preferably, in the step (7), the resist underlayer and/or the substrate is processed.

24. A method for manufacturing a device comprising the method according to one or more of claims 17 to 23:
preferably, a step of forming a wiring on the processed substrate is further comprised, or
preferably the device is a semiconductor device.