

[DESCRIPTION]

[Title of Invention]

RESIST COMPOSITION AND METHOD FOR PRODUCING RESIST FILM
USING THE SAME

5

[Technical Field]

[0001]

The present invention relates to a resist composition to be used for producing a semiconductor element, a semiconductor integrated circuit, or the like, and a method for producing a resist film using the resist composition.

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[Background Art]

[0002]

In the process of producing devices such as semiconductors, microfabrication by a lithography technique with the use of a resist composition has been commonly performed. In recent years, the need for higher integration of LSIs has been increased. This higher integration has achieved reduced sizes and higher speeds, which greatly contributed to improvements in performance of electronic devices such as computers, smartphones, and network devices.

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[0003]

In order to achieve higher integration, finer resist patterns are required. Lithography processes with the use of a KrF excimer laser, an ArF excimer laser, an extreme ultraviolet ray, an X-ray, an electron beam, or the like are performed as microscopic techniques. As for finer resist patterns, photosensitive resist compositions are required, from which resist patterns closer to rectangles can be formed.

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Blending an anthracene derivative that has a specific structure in a resist composition is proposed for preventing halation and obtaining a good shape for a resist pattern (PTL 1).

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[Citation List]

[Patent Literature]

[0004]

[PTL 1] Japanese Patent Application Publication No. 2004-310121

[Summary of Invention]

[Technical Problem]

[0005]

5 In the case of forming a pattern with high rectangularity, irradiation light may be reflected and diffused at the interface between a substrate and a resist, and for example, in the case of a positive resist, a phenomenon (undercut) may occur in which a lower part of the resist is scraped in a
10 scooped fashion, thereby making it impossible to obtain a pattern with high rectangularity. While a bottom anti-reflective coating (BARC) is formed on the substrate for suppressing the undercut, the inventors have focused on the fact that techniques for reducing the undercut without using any BARC and obtaining highly rectangular patterns have been required in order to improve production volumes per unit time and reducing production costs.

15 [0006]

 The inventors have considered that there are still one or more problems for which improvement is still required regarding the resist composition and the use thereof. The problems include: a sufficiently rectangular resist
20 pattern cannot be obtained; undercuts occur at the resist pattern and the substrate surface; footing occurs at the interface between the resist pattern and the substrate; the resist pattern has insufficient resistance (for example, against dry etching) in subsequent steps; the resist composition has insufficient coatability; the resist pattern has insufficient resolution; the resist pattern has insufficient LWR; the optimum exposure is large; the
25 resist pattern has insufficient etching resistance; the resist pattern largely varies in pattern width; the resist pattern has a low aspect ratio; the process window is narrow; and the manufacturing yield is poor.

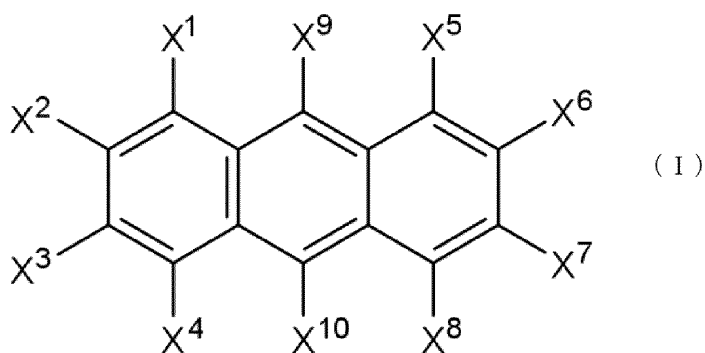
 The present invention has been made based on the technical background as described above, and provides a resist composition and a method for
30 producing a resist film using the resist composition.

[Solution to Problem]

[0007]

A resist composition according to the present invention comprises an acid dissociable group-containing polymer (A) and a compound (B) represented by formula (I).

[C1]



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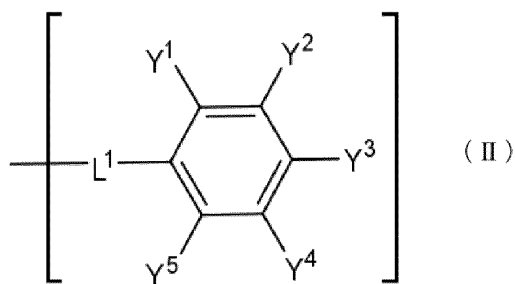
(where:

X¹ to X¹⁰ are each independently H, OH, NH₂, halogen, C₁₋₁₀ alkyl, C₁₋₁₀ alkoxy, or R represented by formula (II);

10

when X¹ to X¹⁰ are each independently alkyl, one or more non-adjacent methylene (-CH₂-) groups of the alkyl may each independently be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CH=CH-, or -C≡C-; and at least one of X¹ to X¹⁰ is R.)

[C2]



15

(where:

Y¹ to Y⁵ are each independently H, OH, NH₂, halogen, C₁₋₁₀ alkyl, or C₁₋₁₀ alkoxy;

when Y¹ to Y⁵ are each independently alkyl, one or more non-adjacent methylene (-CH₂-) groups of the alkyl may each independently be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CH=CH-, or -C≡C-; and when Y¹ to Y⁵ are each independently alkyl, one or more H atoms of the

5 alkyl may be replaced with OH, NH₂, or halogen;
at least one of Y¹ to Y⁵ is or comprises OH;

L¹ is a single bond or C₁₋₁₀ alkylene; and;

when L¹ is alkylene, one or more non-adjacent methylene (-CH₂-) groups in L¹ may each independently be replaced with -O-, -S-, -CO-, -CO-O-, -O-
10 CO-, -O-CO-O-, -CH=CH-, or -C≡C-.)

[0008]

A method for producing a resist film according to the present invention comprises a step of applying the above-mentioned resist composition above a substrate to form a coating film.

15 [0009]

A method for producing a resist pattern according to the present invention comprises the following steps:

producing a resist film by the method mentioned above;

exposing the resist film to light; and

20 developing the resist film.

[0010]

A method for producing a processed substrate according to the present invention comprises the following steps:

producing a resist pattern by the method mentioned above; and

25 performing a processing treatment with the resist pattern as a mask.

[0011]

A method for producing a device according to the present invention comprises the method described above.

[0012]

30 The present invention relates to use of the above-mentioned resist composition for forming a resist film on a substrate.

[Advantageous Effects of Invention]

[0013]

According to the present invention, it is possible to desire one or more of the following effects:

a resist pattern with rectangularity improved can be obtained; undercuts
5 can be suppressed at the resist pattern and the substrate surface; the
occurrence of footing can be suppressed at the interface between the resist
pattern and the substrate; the resist pattern has sufficient resistance (for
example, against dry etching) in subsequent steps; the resist composition
has sufficient coatability; the resist pattern has sufficient resolution; the
10 resist pattern has sufficiently low LWR; the optimal exposure is sufficiently
small; the resist pattern has sufficient etching resistance; the variation of
the resist pattern in pattern width can be suppressed; the resist pattern has
a sufficiently high aspect ratio; the process window is sufficiently wide; and
the manufacturing yield is improved.

15 [Description of Embodiments]

[0014]

[Definitions]

In the present specification, the definitions and examples provided in this
paragraph are used unless specifically stated otherwise.

20 The singular shall include the plural, and “a” or “the” means “at least
one”. An element of a concept can be expressed by a plurality of types, and
when an amount (e.g., % by mass or mol%) thereof is described, the
amount thereof means a sum of the plurality of types thereof.

25 “And/or” includes all combinations of elements, and also includes use of
either one of the elements.

When a numerical range is indicated using “to” or “-”, both end points are
included in the range, and the units are common. For example, 5 to 25
mol% means 5 mol% or more and 25 mol% or less.

30 Descriptions such as “C_{x-y}”, “C_x-C_y”, and “C_x” mean the number of
carbons in a molecule or a substituent. For example, C₁₋₆ alkyl means an
alkyl chain (such as methyl, ethyl, propyl, butyl, pentyl, or hexyl) having
from 1 to 6 carbons.

The group such as alkyl, alkylene, or alkoxy may have any of structures including a linear, branched, or cyclic structure. The alkyl means a group obtained by removing any one hydrogen atom from a saturated hydrocarbon, and the alkylene means a group obtained by removing any two hydrogen atoms from a saturated hydrocarbon.

When the polymer includes multiple types of repeating units, these repeating units create a copolymer. The copolymer may be any of an alternating copolymer, a random copolymer, a block copolymer, a graft copolymer, or a mixture thereof. When a polymer or a resin is represented by a structural formula, n, m, or the like written in parentheses represents the number of repetitions.

The unit of temperature used is Celsius temperature (degree Celsius). For example, 20 degrees means 20 degrees Celsius.

An additive refers to a compound itself that has that function (e.g., a base generator refers to a compound itself that generates a base). There may also be an embodiment in which the compound is dissolved or dispersed in a solvent and is added to a composition. As an embodiment of the present invention, such a solvent is preferably contained as the solvent (G) or other component in the composition according to the present invention.

[0015]

Hereinafter, embodiments of the present invention will be described in detail.

[0016]

<Resist Composition>

A resist composition (hereinafter, referred to as a composition in some cases) according to the present invention comprises an acid dissociable group-containing polymer (A) and a compound (B) represented by formula (I).

The composition according to the present invention is preferably a thin-film chemically amplified resist composition.

In this regard, in the present invention, the thin film means a film of 1200 nm or less in thickness, and is preferably a film of 50 to 1100 nm, more preferably 80 to 1000 nm in thickness. The kinematic viscosity of the composition according to the present invention is preferably 0.5 to 5 mm²/s, more preferably 1.5 to 4 mm²/s. In this regard, the viscosity is measured at 25°C with a capillary viscometer.

The composition according to the present invention is, as a preferred embodiment, a thin-film KrF chemically amplified resist composition. The composition according to the present invention is, as another embodiment, preferably a positive resist composition, more preferably a thin-film positive chemically amplified resist composition, still more preferably a thin-film KrF positive chemically amplified resist composition.

[0017]

Acid Dissociable Group-containing Polymer (A)

The acid dissociable group-containing polymer (A) (hereinafter, referred to as a component (A) in some cases, the same applies to other components) to be used for the present invention reacts with an acid to increase the solubility in an alkaline aqueous solution. Such a polymer has, for example, an acid group protected by a protecting group, and when an acid is added thereto from the outside, the protecting group is eliminated in order to increase the solubility in an alkaline aqueous solution.

[0018]

In a preferred embodiment, the component (A) comprises:

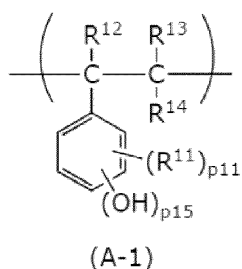
a repeating unit represented by formula (A-1), and

at least one repeating unit selected from the group consisting of repeating units represented by formulas (A-2) to (A-4).

[0019]

Formula (A-1) is as follows.

[C3]



where:

Groups R^{11} are each independently C_{1-5} alkyl (where $-CH_2-$ of the alkyl may be replaced with $-O-$), preferably methyl or ethyl, more preferably methyl.

5 R^{12} , R^{13} , and R^{14} are each independently H, C_{1-5} alkyl, C_{1-5} alkoxy or $-COOH$, preferably H or methyl, more preferably H.

p_{11} is 0 to 4, preferably 0 or 1, more preferably 0.

p_{15} is 1 to 2, preferably 0 or 1, more preferably 1.

$p_{11} + p_{15} \leq 5$.

10 The component (A) can comprise multiple types of units represented by formula (A-1). The component (A) can have, for example, a unit with $p_{15} = 1$ and a unit with $p_{15} = 2$ at a ratio of 1:1.

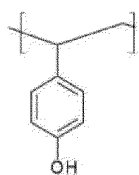
In this case, $p_{15} = 1.5$ as a whole. Hereinafter, unless otherwise specified, the same applies to numbers that express resins or polymers in the present

15 invention.

[0020]

Specific examples of formula (A-1) include the following.

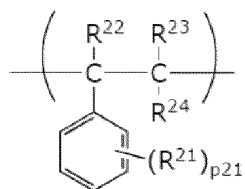
[C4]



20 [0021]

Formula (A-2) is as follows.

[C5]



(A-2)

where:

Groups R^{21} are each independently C_{1-5} alkyl (where $-\text{CH}_2-$ of the alkyl may be replaced with $-\text{O}-$), preferably methyl, ethyl, t-butyl, or t-butoxy, more preferably methyl or ethyl, still more preferably methyl.

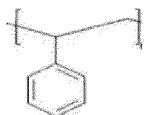
R^{22} , R^{23} , and R^{24} are each independently H, C_{1-5} alkyl, C_{1-5} alkoxy, or $-\text{COOH}$, preferably H or methyl, more preferably H.

p_{21} is 0 to 5, preferably 0, 1, 2, 3, 4, or 5, more preferably 0 or 1, still more preferably 0.

[0022]

Specific examples of formula (A-2) include the following.

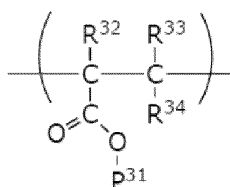
[C6]



[0023]

Formula (A-3) is as follows.

[C7]



(A-3)

where:

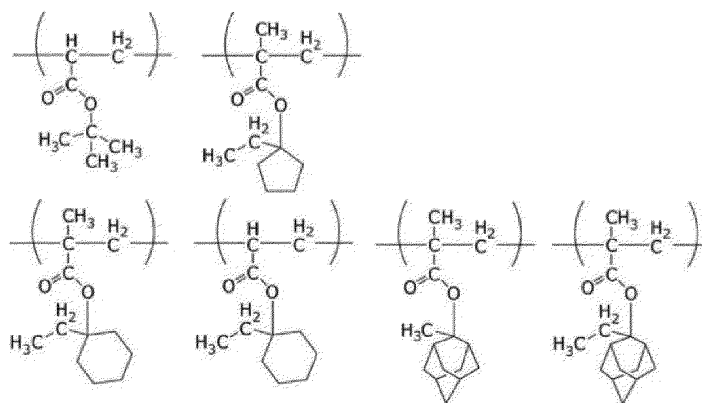
R^{32} , R^{33} , and R^{34} are each independently H, C_{1-5} alkyl, C_{1-5} alkoxy, or -COOH, preferably H, methyl, ethyl, t-butyl, methoxy, t-butoxy, or -COOH, more preferably H or methyl, still more preferably H.

P^{31} is C_{4-20} alkyl. In this regard, the alkyl may partially or entirely form a ring, and part or all of H of the alkyl may be substituted with halogen. The alkyl moiety of P^{31} is preferably branched or cyclic. In the case of substituting H of the C_{4-20} alkyl of P^{31} with halogen, all of H atoms are preferably substituted, and the substituent halogen is preferably F or Cl; more preferably F. Substituting H of the C_{4-20} alkyl of P^{31} with no halogen is a preferred embodiment of the present invention. P^{31} is preferably methyl, isopropyl, t-butyl, cyclopentyl, methylcyclopentyl, ethylcyclopentyl, cyclohexyl, methylcyclohexyl, ethylcyclohexyl, adamantyl, methyladamantyl, or ethyladamantyl, more preferably t-butyl, ethylcyclopentyl, ethylcyclohexyl, or ethyladamantyl, still more preferably t-butyl, ethylcyclopentyl, or ethyladamantyl, even more preferably t-butyl.

[0024]

Specific examples of formula (A-3) include the following.

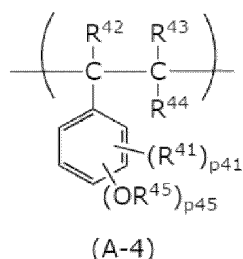
[C8]



[0025]

Formula (A-4) is as follows.

[C9]



where:

R^{41} and R^{45} are each independently C_{1-5} alkyl (where $-CH_2-$ of the alkyl may be replaced with $-O-$). R^{45} is preferably methyl, t-butyl, or $-CH(CH_3)-O-$

CH_2CH_3 . R^{41} is preferably methyl, ethyl, or t-butyl, more preferably methyl.

R^{42} , R^{43} , and R^{44} are each independently H, C_{1-5} alkyl, C_{1-5} alkoxy, or $-COOH$, preferably H or methyl, more preferably H.

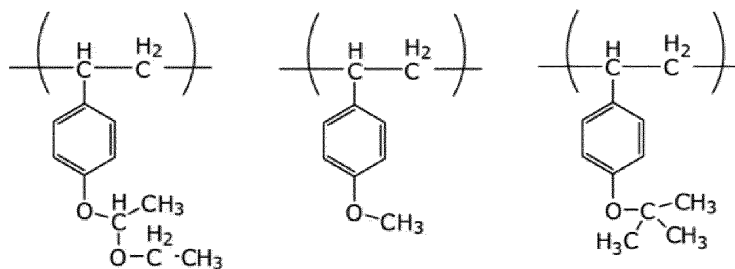
p_{41} is 0 to 4, p_{45} is 1 to 2, and $p_{41} + p_{45} \leq 5$. p_{41} is preferably 0, 1, 2, 3, or 4, more preferably 0 or 1, still more preferably 0. p_{45} is preferably 1 or 2,

more preferably 1.

[0026]

Specific examples of formula (A-4) include the following.

[C10]



[0027]

The number of repeating units n_{A-1} , n_{A-2} , n_{A-3} , and n_{A-4} of the repeating units (A-1), (A-2), (A-3), and (A-4) in the component (A) are described below.

$n_{A-1}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 40% to 80%; more preferably 50% to 80%; still more preferably 55% to 75%; even more preferably 60% to 70%.

$n_{A-2}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 0% to 40%; more preferably 5% to 35%; still more preferably 5% to 25%; even more preferably 10% to 20%.

$n_{A-3}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 0% to 40%; more preferably 10% to 35%; still more preferably 15% to 35%; even more preferably 20% to 30%.

$n_{A-4}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})$ is preferably 0% to 40%; more preferably 10% to 35%; still more preferably 15% to 35%; even more preferably 20% to 30%.

Preferred embodiments include $n_{A-1}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 40\%$ to 80%, $n_{A-2}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 0\%$ to 40%, $n_{A-3}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 0\%$ to 40%, and $n_{A-4}/(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4}) = 0\%$ to 40%.

As an embodiment of the present invention, $n_{A-3} > 0$ and $n_{A-4} = 0$, or $n_{A-3} = 0$ and $n_{A-4} > 0$ are preferred, and $n_{A-3} > 0$ and $n_{A-4} = 0$ are more preferred.

[0028]

The component (A) can also comprise a repeating unit other than the repeating units represented by (A-1), (A-2), (A-3), and (A-4). When the total number of all the repeating units comprised in the component (A) is defined as n_{total} , $(n_{A-1} + n_{A-2} + n_{A-3} + n_{A-4})/n_{total}$ is preferably 80% to 100%; more preferably 90% to 100%, still more preferably 95% to 100%, even more preferably 100%.

More specifically, including no unit other than the repeating units represented by (A-1), (A-2), (A-3), and (A-4) is also a preferred embodiment of the present invention.

[0029]

The mass average molecular weight (hereinafter, referred to as M_w in some cases) of the component (A) is preferably 1,000 to 50,000, more preferably 2,000 to 30,000, still more preferably 5,000 to 20,000, even more preferably 8,000 to 15,000.

The number average molecular weight (hereinafter, referred to as M_n in some cases) of the component (A) is preferably 1,000 to 50,000; more preferably 2,000 to 30,000.

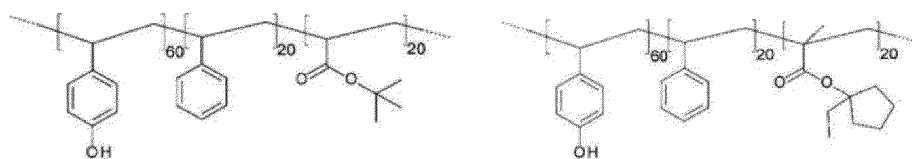
In the present invention, Mw and Mn can be measured by gel permeation chromatography (GPC).

For the measurement, it is a preferred example to use a GPC column at 40°C, an elution solvent of tetrahydrofuran at 0.6 mL/min, and monodisperse polystyrene as a standard.

[0030]

A description is given for the sake of explanation. In the composition according to the present invention, two or more components (A) can be used in combination, as long as the components (A) are represented by the formula mentioned above. For example, a composition comprising the following two polymers as the components (A) is also an embodiment of the present invention.

[C11]



The component (A) preferably comprises one or two polymers, more preferably comprises two polymers. Mw distribution and polymerization may vary.

[0031]

The content of the component (A) is preferably 1 to 15% by mass, more preferably 1.5 to 12% by mass, still more preferably 2 to 10% by mass, based on the total mass of the composition.

The composition according to the present invention may comprise polymers other than the component (A). The content of the polymer (if more than one, the sum thereof) excluding the component (A) is, based on the total mass of the component (A), preferably 0 to 20% by mass, more preferably 0 to 10% by mass, still more preferably 0 to 5% by mass, and even more preferably, the composition according to the present invention comprises no polymer (0% by mass), other than the component (A).

[0032]

Compound (B) represented by Formula (I)

The composition according to the present invention comprises the compound (B) represented by formula (I).

5 Including the component (B) allows a resist pattern with sufficient rectangularity to be obtained. This is, while not bound by any theory, considered to be due to the following reason.

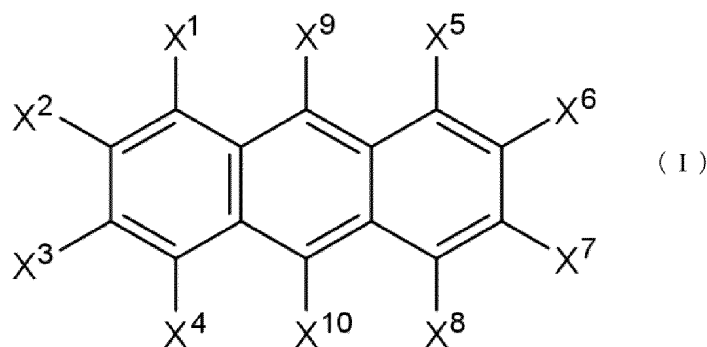
For example, when the resist composition is positive, the component (B) absorbs excessive light reaching the vicinity of the substrate at the time of exposure, and thus, the resist pattern is considered capable of being kept
10 from undergoing undercuts due to reflection of irradiation light.

Furthermore, the component (B) has good solubility in a developer, the resist pattern can also be kept from undergoing footing after development due to defective development, and as a result, the resist pattern is
15 considered capable of being kept from being tapered.

[0033]

Formula (I) is as follows.

[C12]



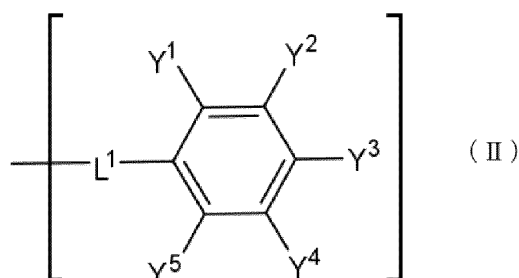
20 where:

X¹ to X¹⁰ are each independently H, OH, NH₂, halogen, C₁₋₁₀ alkyl, C₁₋₁₀ alkoxy, or R represented by formula (II);

when X¹ to X¹⁰ are each independently alkyl, one or more non-adjacent methylene (-CH₂-) groups of the alkyl may each independently be replaced
25 with -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CH=CH-, or -C≡C-; and

at least one of X^1 to X^{10} is R.

[C13]



where:

5 Y^1 to Y^5 are each independently H, OH, NH_2 , halogen, C_{1-10} alkyl, or C_{1-10} alkoxy, preferably H, OH, C_{1-10} alkyl, or C_{1-10} alkoxy, more preferably H, OH, or C_{1-5} alkyl.

When Y^1 to Y^5 are each independently alkyl, one or more non-adjacent methylene ($-CH_2-$) groups of the alkyl may be each independently replaced with $-O-$, $-S-$, $-CO-$, $-CO-O-$, $-O-CO-$, $-O-CO-O-$, $-CH=CH-$, or $-C\equiv C-$, preferably unsubstituted.

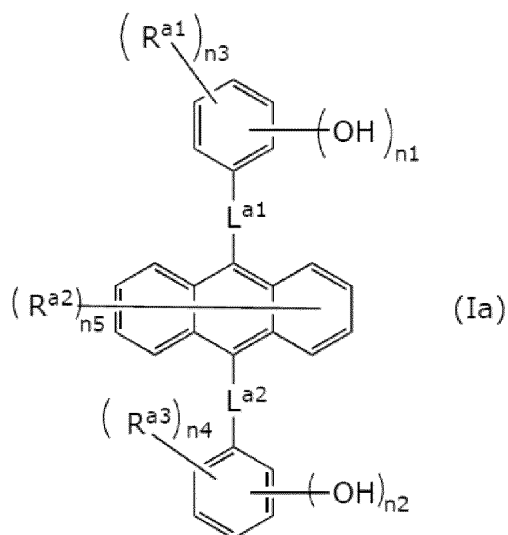
When Y^1 to Y^5 are each independently alkyl, one or more H atoms of the alkyl may be replaced with OH, NH_2 , or halogen, preferably unsubstituted. At least one of Y^1 to Y^5 is or comprises OH, preferably, at least one thereof is OH. The number of OH per aromatic ring is preferably 3 or less, more preferably 2 or less, still more preferably 1. While not bound by any theory, the above-mentioned number of OH per aromatic ring is considered to allow the progress of a crosslinking reaction and the occurrence of interaction between the compounds to be more effectively inhibited.

20 L^1 is a single bond or C_{1-10} alkylene, preferably a single bond, methylene ($-CH_2-$) or ethylene ($-CH_2-CH_2-$), more preferably a single bond or methylene. When L^1 is alkylene, one or more non-adjacent methylene ($-CH_2-$) groups of L^1 may be each independently replaced with $-O-$, $-S-$, $-CO-$, $-CO-O-$, $-O-CO-$, $-O-CO-O-$, $-CH=CH-$, or $-C\equiv C-$, preferably unsubstituted.

25 [0034]

In a preferred embodiment, the component (B) is represented by formula (Ia).

[C14]



5 where:

n1 is 1, 2, 3, 4, or 5, preferably 1, 2, or 3, more preferably 1 or 2, still more preferably 1.

n2 is 1, 2, 3, 4, or 5, preferably 1, 2, or 3, more preferably 1 or 2, still more preferably 1.

10 R^{a1} , R^{a2} and R^{a3} are each independently halogen, C_{1-10} alkyl, or C_{1-10} alkoxy, preferably C_{1-5} alkyl or C_{1-5} alkoxy.

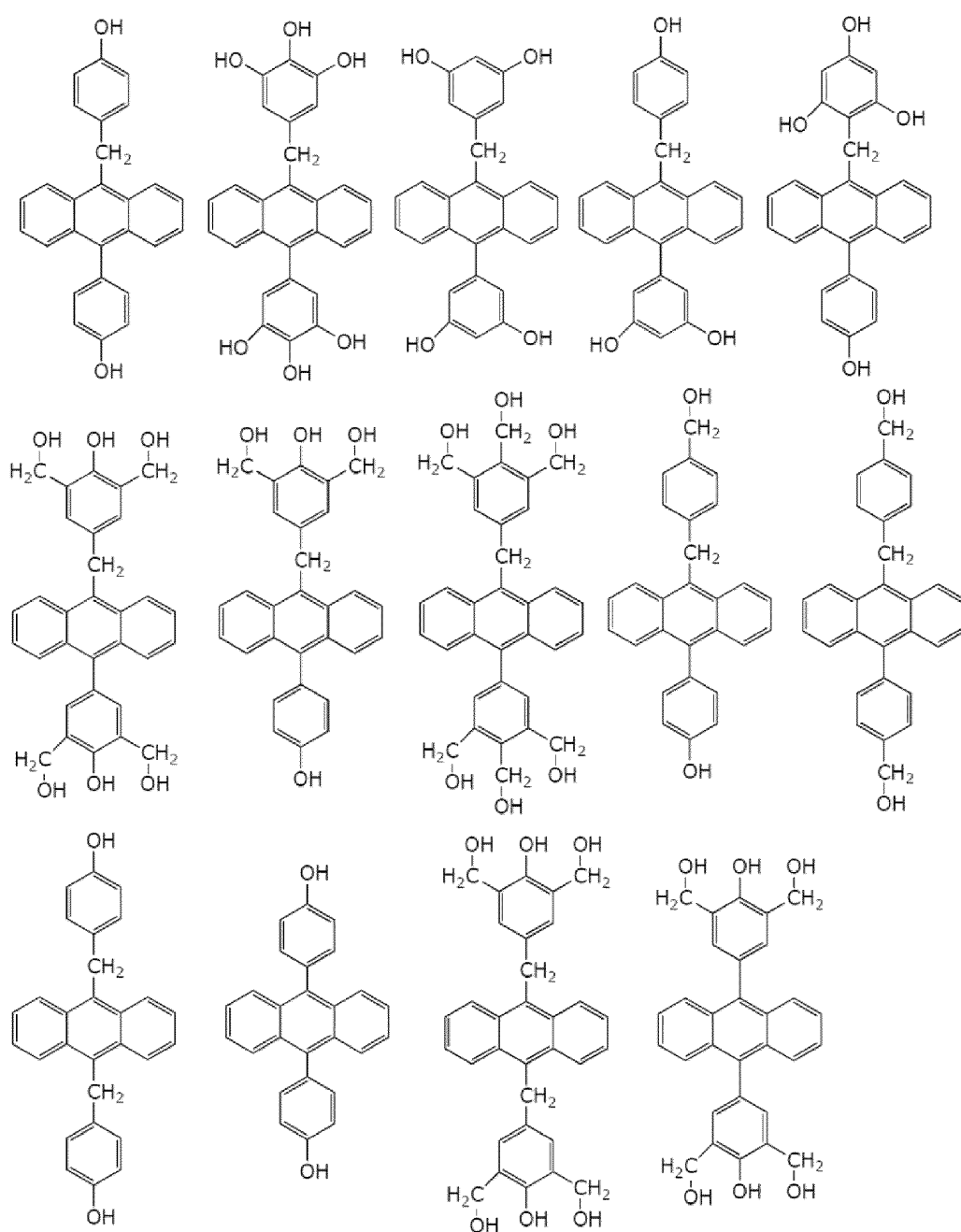
n3, n4, and n5 are each independently 0, 1, 2, 3, or 4, preferably 0 or 1, still more preferably 0.

15 L^{a1} and L^{a2} are each independently a single bond or C_{1-10} alkylene, preferably a single bond, methylene ($-CH_2-$), or ethylene ($-CH_2-CH_2-$), more preferably a single bond or methylene.

[0035]

Specific examples of the component (B) include the following.

[C15]



[0036]

The content of the component (B) is preferably 0.01 to 0.1% by mass, more preferably 0.02 to 0.09% by mass, still more preferably 0.03 to 0.08% by mass, based on the total mass of the composition.

[0037]

Specific examples of compounds that can be read from formula (I) and formula (II) are described below in detail.

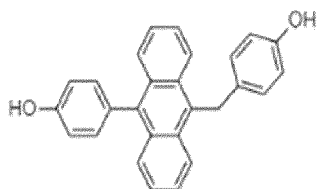
The following compounds can be read from formula (I) and formula (II).

5 In formula (I), X^1 to X^8 are H, and X^9 and X^{10} are R.

In formula (II), for R corresponding to X^9 , L^1 is a single bond, Y^1 , Y^2 , Y^4 , and Y^5 are H, and Y^3 is OH.

For R corresponding to X^{10} , L^1 is C_1 alkylene, that is, methylene, Y^1 , Y^2 , Y^4 , and Y^5 are H, and Y^3 is OH.

10 [C16]



[0038]

The following compounds can also be read from formula (I) and formula (II).

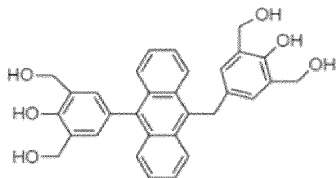
15 In formula (I), X^1 to X^8 are H, and X^9 and X^{10} are R.

In formula (II), for R corresponding to X^9 , L^1 is a single bond, Y^1 and Y^5 are H, Y^2 and Y^4 are C_1 alkyl with one H replaced with OH, that is, hydroxymethyl, and Y^3 is OH.

For R corresponding to X^{10} , L^1 is C_1 alkylene, that is, methylene, Y^1 and Y^5 are H, Y^2 and Y^4 are C_1 alkyl with one H replaced with OH, that is, hydroxymethyl, and Y^3 is OH.

20

[C17]



[0039]

As in the two examples mentioned above, when multiple groups of X^1 to X^{10} are R in formula (I), L^1 and Y^1 to Y^5 of formula (II) may be different from or identical with each other in the multiple groups R.

[0040]

5 First Acid Generator (C)

The composition according to the present invention preferably further comprises a first acid generator (C). The first acid generator (C) has a -SO₂- structure.

10 The component (C) is preferably a photoacid generator that releases an acid upon irradiation with light. Preferably, an acid derived from the component (C) acts on the component (A) to play a role of increasing the solubility of the component (A) in an alkaline aqueous solution. For example, the component (A) causes its acid-dissociable group to be eliminated with the acid. The component (C) to be used for the composition

15 according to the present invention can be selected from conventionally known components.

[0041]

The component (C) releases, on exposure to light, an acid with an acid dissociation constant pK_a (H₂O) of preferably -20 to 1.4; more preferably, -

20 16 to 1.4; still more preferably, -16 to 1.2; even more preferably, -16 to 1.1.

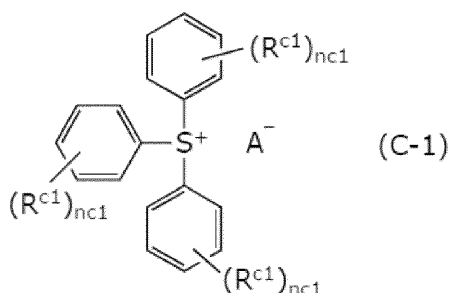
[0042]

The component (C) is preferably represented by the following formula (C-1) or formula (C-2).

[0043]

25 Formula (C-1) is as follows.

[C18]



where:

Groups R^{c1} are each independently C_{1-6} alkyl, C_{1-6} alkoxy, C_{6-12} aryl, C_{6-12} arylthio, or C_{6-12} aryloxy, preferably methyl, ethyl, t-butyl, methoxy, ethoxy, phenylthio, or phenyloxy, more preferably t-butyl, methoxy, ethoxy, phenylthio, or phenyloxy.

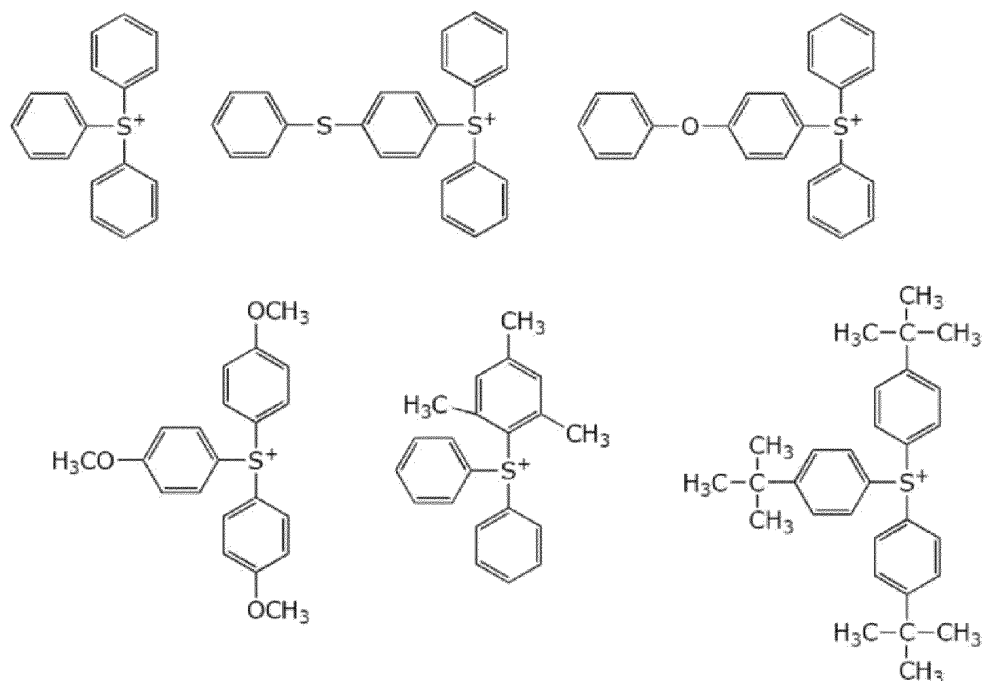
Numbers $nc1$ are each independently 0, 1, 2, or 3. A preferred embodiment is one wherein all of the numbers $nc1$ are 1. Another preferred embodiment is one wherein all of the numbers $nc1$ are equal. Another preferred embodiment is one wherein all of the numbers $nc1$ are 0. Another preferred embodiment is one wherein one of the numbers $nc1$ is 3, whereas the other two numbers $nc1$ are 0.

A^- is a monovalent anion.

[0044]

Specific examples of the cation of formula (C-1) include the following.

[C19]

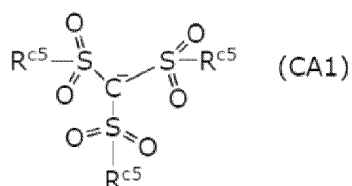


[0045]

Examples of A^- include a halide ion, a hexafluoroantimonate ion, a hexafluorophosphate ion, and ions represented by one of the following formulas (CA1) to (CA4), and A^- is preferably a hexafluoroantimonate ion, an ion represented by formula (CA1), or an ion represented by formula (CA2).

Formula (CA1) is as follows.

[C20]



where groups R^{c5} are each independently C_{1-6} fluorine-substituted alkyl, C_{1-6} fluorine-substituted alkoxy, or C_{1-6} alkyl. For example, $-CF_3$ means methyl (C_1) that has hydrogen entirely substituted with fluorine. In the present invention, fluorine substitution means that hydrogen that is present in an

alkyl moiety of alkyl or alkoxy is partially or entirely substituted with fluorine, and more preferably, the hydrogen is entirely substituted with fluorine.

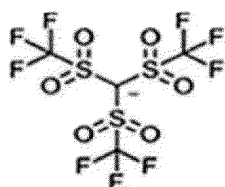
R^{c5} is preferably fluorine-substituted or -unsubstituted methyl, ethyl, t-butyl, methoxy, ethoxy, or t-butoxy, more preferably fluorine-substituted or -unsubstituted methyl.

R^{c5} is preferably fluorine-substituted alkyl; more preferably, $-CF_3$.

[0046]

Specific examples of formula (CA1) include the following.

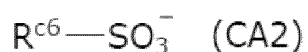
[C21]



[0047]

Formula (CA2) is as follows.

[C22]

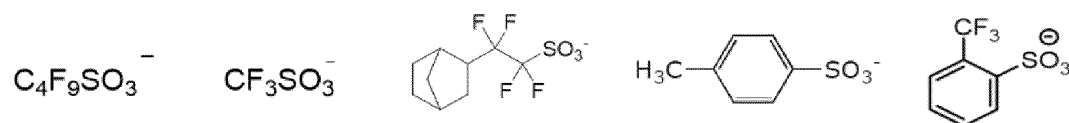


wherein R^{c6} is C_{1-10} fluorine-substituted alkyl, C_{1-6} fluorine-substituted alkoxy, C_{6-12} fluorine-substituted aryl, C_{2-12} fluorine-substituted acyl, C_{6-12} fluorine-substituted alkoxyaryl, or C_{6-12} alkyl-substituted aryl; preferably C_{1-10} fluorine-substituted alkyl, C_{6-12} fluorine-substituted aryl, or C_{6-12} alkyl-substituted aryl, more preferably C_{1-6} fluorine-substituted alkyl, or C_{6-10} fluorine-substituted aryl. The alkyl or alkyl moiety of R^{c6} is preferably linear or cyclic.

[0048]

Specific examples of formula (CA2) include the following.

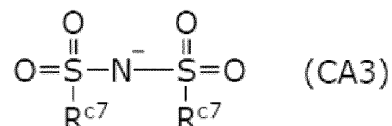
[C23]



[0049]

Formula (CA3) is as follows.

[C24]



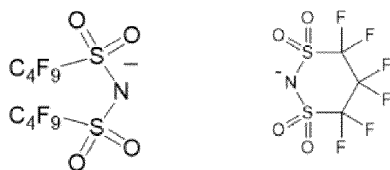
5 where:

Groups $\text{R}^{\text{c}7}$ 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; preferably C_{2-6} fluorine-substituted alkyl. Two groups $\text{R}^{\text{c}7}$ may be bonded to each other to form a fluorine-substituted heterocyclic structure. The heterocyclic structure is preferably a saturated ring. The heterocyclic structure is preferably a five to eight-membered monocyclic structure including N and S; more preferably a five-membered ring or a six-membered ring; still more preferably a six-membered ring.

15 [0050]

Specific examples of formula (CA3) include the following.

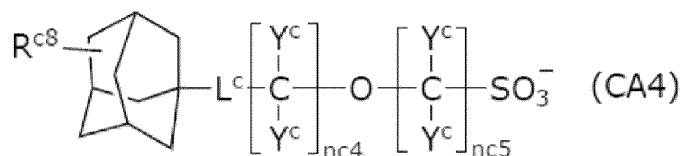
[C25]



[0051]

20 Formula (CA4) is as follows.

[C26]



where:

R^{c8} is H, C₁₋₆ alkyl, C₁₋₆ alkoxy, or OH; preferably H, methyl, ethyl, methoxy, or OH; more preferably, H or OH.

L^c is methylene, ethylene, carbonyl, oxy, or carbonyloxy; preferably ethylene or carbonyl.

Groups Y^c are each independently H or fluorine; preferably, one or more thereof are fluorine.

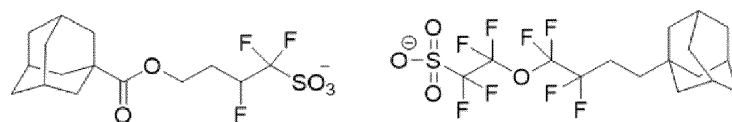
nc₄ is an integer of 0 to 10; preferably 0, 1, or 2.

nc₅ is an integer of 0 to 21; preferably 4, 5, or 6.

[0052]

Specific examples of formula (CA4) include the following.

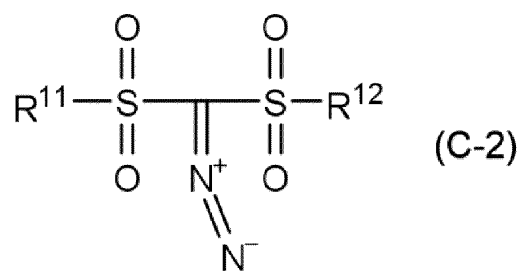
[C27]



[0053]

Formula (C-2) is as follows.

[C28]



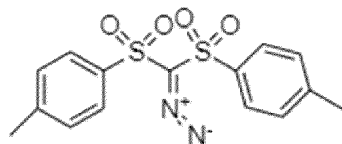
where:

R¹¹ is C₁₋₁₀ alkyl or C₆₋₁₂ aryl, preferably tolyl, C₁₋₆ alkyl or C₆₋₁₀ aryl, more preferably p-tolyl.

[0054]

Specific examples of formula (C-2) include the following.

[C29]



[0055]

The molecular weight of the component (C) is preferably 400 to 2,500, more preferably 400 to 1,500.

5

[0056]

The component (C) may have one, or two or more, preferably two or more, more preferably three or more, still more preferably three components.

10

The content of the component (C) is preferably 1 to 15% by mass, more preferably 1.5 to 10% by mass, still more preferably 2 to 6% by mass, based on the total mass of the component (A).

[0057]

Second Acid Generator (D)

15

The composition according to the present invention preferably further comprises a second acid generator (D). The component (D) is different from the component (C).

The component (D) is preferably a photoacid generator that generates an acid with light.

[0058]

20

As a preferred embodiment of the present invention, a cation derived from the component (D) reacts with an anion moiety derived from the component (C), and functions as a quencher. In this case, the component (D) can serve a function as a quencher that inhibits the diffusion of an acid derived from the component (C) produced in an exposed part. This is considered, while not bound by any theory, as the following mechanism.

25

When exposure causes an acid to be released from the component (C), and the acid diffuses into an unexposed part, salt exchange with the component (D) occurs. More specifically, the anion of the component (C)

and the cation of the component (D) form a salt. Thus, the diffusion of the acid is inhibited. In this case, it is considered that while the anion of the component (D) is released, this anion is a weak acid, and not capable of deprotecting the polymer, and thus, the unexposed part is not affected.

5 [0059]

Furthermore, the component (D) has the effect of keeping the acid on the surface of the resist film from being deactivated due to a component such as an amine included in the air. This is considered, while not bound by any theory, as the following mechanism. In the exposed part, the acids (the
10 weak acid derived from the component (D) and the acid derived from component (C)) are generated by the exposure. The amine in the air permeates the surface of the resist film, thereby neutralizing the acids present therein. The presence of the weak acid released from the component (D), however, reduces the frequency of neutralization of the
15 acid released from the component (C). Increasing the acid in the exposed part as described above is considered to keep the acid from being deactivated.

[0060]

The component (D) is preferably represented by formula (D-1).

20 D^{m+} cation D^{m-} anion (D-1)

where:

The D^{m+} cation is a cation represented by formula (DC1) or a cation represented by formula (DC2); preferably a cation represented by formula (DC1).

25 The D^{m+} cation is m-valent as a whole, and m is 1 to 3.

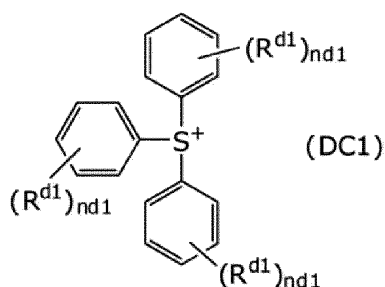
The D^{m-} anion is an anion represented by formula (DA1) or an anion represented by formula (DA2); preferably an anion represented by formula (DA1). The D^{m-} anion is m-valent as a whole.

m is preferably 1 or 2; more preferably 1.

30 [0061]

Formula (DC1) is as follows.

[C30]



where:

Groups R^{d1} are each independently C_{1-6} alkyl, C_{1-6} alkoxy, or C_{6-12} aryl; and numbers $nd1$ are each independently 0, 1, 2, or 3.

5 [0062]

R^{d1} is preferably methyl, ethyl, t-butyl, methoxy, ethoxy, phenylthio, or phenyloxy; more preferably t-butyl, methoxy, ethoxy, phenylthio, or phenyloxy; still more preferably t-butyl or methoxy.

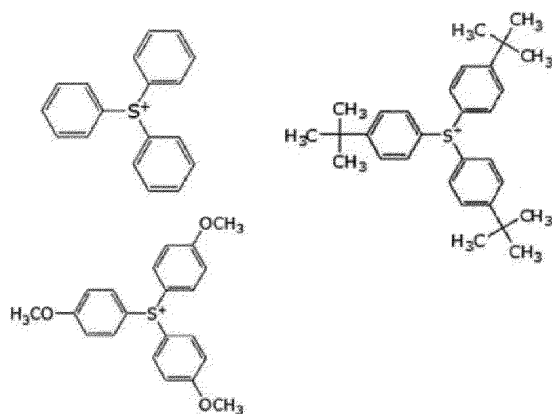
$nd1$ is preferably 0 or 1; more preferably 0.

10 Another preferred embodiment is one wherein all of the numbers $nd1$ are 1, while all of the groups R^{d1} are identical.

[0063]

Specific examples of formula (DC1) include the following.

[C31]

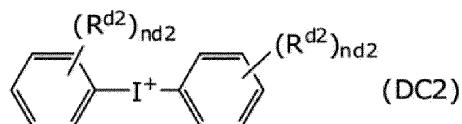


15

[0064]

Formula (DC2) is as follows.

[C32]



where:

Groups R^{d2} are each independently C_{1-6} alkyl, C_{1-6} alkoxy, or C_{6-12} aryl;5 Numbers $nd2$ are each independently 0, 1, 2, or 3.

[0065]

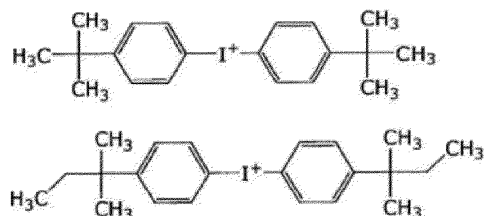
R^{d2} is preferably alkyl that has a C_{4-6} branched structure. Each R^{d2} in the formula may be identical or different, more preferably identical. R^{d2} is still more preferably t-butyl or 1,1-dimethylpropyl; even more preferably t-butyl.

10 Each $nd2$ is preferably 1.

[0066]

Specific examples of formula (DC2) include the following.

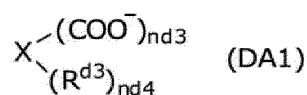
[C33]



15 [0067]

Formula (DA1) is as follows.

[C34]



where:

20 X is a C_{1-20} hydrocarbon group or a single bond;Groups R^{d3} are each independently H, OH, C_{1-6} alkyl, or C_{6-10} aryl; $nd3$ is 1, 2, or 3; and

nd4 is 0, 1, or 2.

[0068]

When X is a hydrocarbon group, X may be linear, branched, or cyclic, preferably linear or cyclic. When X is linear, X is preferably C₁₋₄ (more preferably C₁₋₂), and preferably has one double bond in the chain, or is saturated. When X is cyclic, X may be a monocyclic ring of an aromatic ring, or a saturated monocyclic ring or polycyclic ring, and when X is a monocyclic ring, the ring is preferably a six-membered ring, and when X is a polycyclic ring, the ring is preferably an adamantane ring.

X is preferably methyl, ethyl, propyl, butyl, ethane, phenyl, cyclohexane, adamantane, or a single bond; more preferably methyl, phenyl, cyclohexane, or a single bond; still more preferably phenyl or a single bond; even more preferably phenyl.

nd3 is preferably 1 or 2; more preferably 1.

nd4 is preferably 0 or 1; more preferably 1.

R^{d3} is preferably OH, methyl, ethyl, 1-propyl, 2-propyl, t-butyl, or phenyl; more preferably, OH.

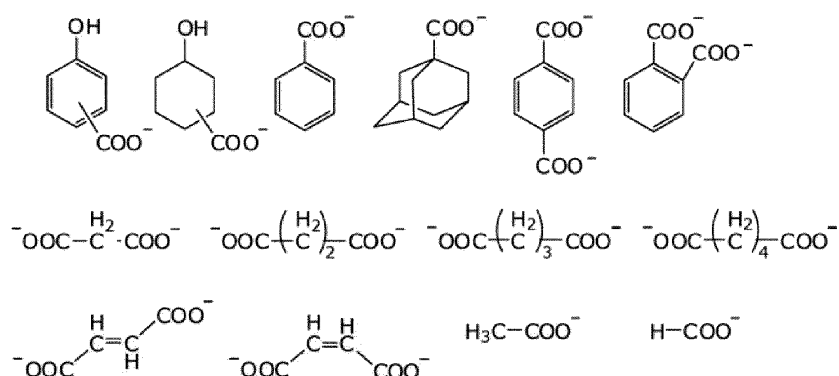
[0069]

When X is a single bond, R^{d3} is preferably H. X represents a single bond, R^{d3} represents H, and (DA1) with nd3 = nd4 = 1 represents an anion of H-COO⁻.

[0070]

Specific examples of formula (DA1) include the following.

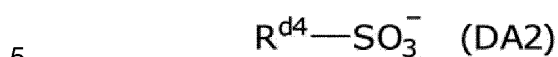
[C35]



[0071]

Formula (DA2) is as follows.

[C36]



where:

R^{d4} is C_{1-15} alkyl (where the alkyl may partially or entirely form a ring, and $-CH_2-$ of the alkyl may be replaced with $-C(=O)-$). R^{d4} is preferably C_{3-13} alkyl; more preferably C_{5-12} alkyl; still more preferably C_{8-12} alkyl; even more preferably, C_{10} alkyl. The alkyl of R^{d4} preferably partially or entirely forms a ring; more preferably, partially forms a ring. Preferably, one or more (more preferably one) $-CH_2-$ groups of the alkyl of R^{d4} are replaced with $-C(=O)-$.

[0072]

Specific examples of formula (DA2) include the following.

15 [C37]



[0073]

The component (D) releases, on exposure to light, an acid with an acid dissociation constant pK_a (H_2O) of preferably 1.5 to 8, more preferably 1.5 to 5.

20

[0074]

The molecular weight of the component (D) is preferably 300 to 1,400; more preferably, 300 to 1,200.

[0075]

5 The component (D) may have one, or two or more components.
The content of the component (D) is preferably 0.005 to 0.3% by mass, more preferably 0.01 to 0.2% by mass, still more preferably 0.03% to 1% by mass, based on the total mass of the component (A).

[0076]

10 Photobase Generator (E)

The composition according to the present invention preferably further comprises a photobase generator (E). The component (E) can serve a function as a quencher that inhibits the diffusion of the acid derived from the component (C) produced in the exposed part.

15 Examples of the component (E) include a Co-amine complex-based, oxime carboxylic acid ester-based, carbamic acid ester-based, or quaternary ammonium salt-based photobase generator can be used. Specific examples thereof include 2-nitrobenzylcyclohexylcarbamate, triphenylmethanol, O-carbamoylhydroxylamide, O-carbamoyloxime, [[[2,6-dinitrobenzyl)oxy]carbonyl]cyclohexylamine, bis[[[2-nitrobenzyl)oxy]carbonyl]hexane -1,6-diamine, 4-(methylthiobenzoyl)-1-methyl-1-morpholinoethane, (4-morpholinobenzoyl)-1-benzyl-1-dimethylaminopropane, N-(2-nitrobenzyloxycarbonyl)pyrrolidine, hexaamminecobalt (III) tris(triphenylmethylborate), 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone, 2,6-dimethyl-3,5-diacetyl-4-(2'-nitrophenyl)-1,4-dihydropyridine, and 2,6-dimethyl-3,5-diacetyl-4-(2',4'-dinitrophenyl)-1,4-dihydropyridine.

[0077]

30 The component (E) may have one, or two or more components.
The content of the component (E) is preferably 0.1 to 10% by mass, more preferably 0.2% to 7% by mass, still more preferably 0.3 to 4% by mass, based on the total mass of the component (A).

[0078]

Amine Compound (F)

The composition according to the present invention can preferably further comprise an amine compound (F). The component (F) has the effect of inhibiting the diffusion of the acid generated in the exposed part and the effect of keeping the acid on the surface of the resist film from being deactivated due to an amine component included in the air.

[0079]

Examples of the component (F) preferably comprises C₁₋₁₆ primary aliphatic amine compounds, C₂₋₃₂ secondary aliphatic amine compounds, C₃₋₄₈ tertiary aliphatic amine compounds, C₆₋₃₀ aromatic amine compounds, or C₅₋₃₀ heterocyclic amine compounds.

[0080]

Examples of the component (F) include ethylamine, n-octylamine, n-heptylamine, ethylenediamine, triethylamine, tri-n-octylamine, diethylamine, triethanolamine, tris[2-(2-methoxyethoxy)ethyl]amine, 1,8-diazabicyclo[5.4.0]-7-undecene, 1,5-diazabicyclo[4.3.0]-5-nonene, 7-methyl-1,5,7-triazabicyclo[4.4.0]deca-5-ene, and 1,5,7-triazabicyclo[4.4.0]deca-5-ene.

[0081]

The base dissociation constant pK_b (H₂O) of the component (F) is preferably -12 to 5, more preferably 1 to 4.

[0082]

The molecular weight of the component (F) is preferably 17 to 500; more preferably 60 to 400.

[0083]

The component (F) may have one, or two or more components. The content of the component (F) is preferably 0.1 to 10% by mass, more preferably 0.15 to 7% by mass, still more preferably 0.2 to 4% by mass, based on the total mass of the component (A).

[0084]

Solvent (G)

The composition according to the present invention preferably further comprises a solvent (G). The solvent is not particularly limited as long as the solvent is capable of dissolving each of components to be blended. The component (G) is preferably water, a hydrocarbon solvent, an ether solvent,
5 an ester solvent, an alcohol solvent, a ketone solvent, or a combination of any of these solvents.

Examples of the solvent 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,
10 trimethylbenzene, methylethylbenzene, n-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-methylbutanol, sec-pentanol, t-pentanol, 3-methoxybutanol, n-
15 hexanol, 2-methylpentanol, sec-hexanol, 2-ethylbutanol, sec-heptanol, 3-heptanol, n-octanol, 2-ethylhexanol, sec-octanol, n-nonyl alcohol, 2,6-dimethylheptan-4-ol, n-decanol, sec-undecyl alcohol, trimethylnonyl alcohol, sec-tetradecyl alcohol, sec-heptadecyl alcohol, phenol, cyclohexanol, methylcyclohexanol, 3,3,5-trimethylcyclohexanol, benzyl alcohol,
20 phenylmethyl carbinol, diacetone alcohol, cresol, ethylene glycol, propylene glycol, 1,3-butylene glycol, 2,4-pentanediol, 2-methylpentane-2,4-diol, 2,5-hexanediol, 2,4-heptanediol, 2-ethylhexane-1,3-diol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, glycerin, acetone, methyl ethyl ketone, methyl-n-propyl ketone, methyl-n-butyl ketone, diethyl
25 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, fenchone, ethyl ether, i-propyl ether, n-butyl ether (di-n-butyl ether, DBE), n-hexyl ether, 2-
30 ethylhexyl ether, ethylene oxide, 1,2-propylene oxide, dioxolane, 4-methyldioxolane, 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-ethylbutyl ether,
ethylene glycol dibutyl ether, diethylene glycol monomethyl ether,
diethylene glycol monoethyl ether, diethylene glycol diethyl ether,
5 diethylene glycol mono-n-butyl ether, diethylene glycol di-n-butyl ether,
diethylene glycol mono-n-hexyl ether, ethoxy triglycol, 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
10 glycol monoethyl ether, dipropylene glycol monopropyl ether, dipropylene
glycol monobutyl ether, tripropylene glycol monomethyl ether,
tetrahydrofuran, 2-methyltetrahydrofuran, diethyl carbonate, methyl acetate,
ethyl acetate, γ -butyrolactone, γ -valerolactone, n-propyl acetate, i-propyl
acetate, n-butyl acetate (normal butyl acetate, nBA), i-butyl acetate, sec-
15 butyl acetate, n-pentyl acetate, sec-pentyl acetate, 3-methoxybutyl acetate,
methylpentyl acetate, 2-ethylbutyl acetate, 2-ethylhexyl acetate, benzyl
acetate, cyclohexyl acetate, methylcyclohexyl acetate, n-nonyl acetate,
methyl acetoacetate, ethyl acetoacetate, ethylene glycol monomethyl ether
acetate, ethylene glycol monoethyl ether acetate, diethylene glycol
20 monomethyl ether acetate, diethylene glycol monoethyl ether acetate,
diethylene glycol mono-n-butyl ether acetate, propylene glycol monomethyl
ether acetate (PGMEA), propylene glycol monoethyl ether acetate,
propylene glycol monopropyl ether acetate, propylene glycol monobutyl
ether acetate, dipropylene glycol monomethyl ether acetate, dipropylene
25 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), n-butyl lactate, n-amyl
lactate, diethyl malonate, dimethyl phthalate, diethyl phthalate, N-
methylformamide, N,N-dimethylformamide, N,N-diethylformamide,
30 acetamide, N-methylacetamide, N,N-dimethylacetamide, N-
methylpropionamide, N-methylpyrrolidone, dimethyl sulfide, diethyl sulfide,
thiophene, tetrahydrothiophene, dimethyl sulfoxide, sulfolane, and 1,3-

propanesultone. These solvents can be used alone, or two or more thereof can be used in mixture.

The component (G) is preferably PGME, PGMEA, EL, nBA, DBE, or a mixture of any of these solvents; more preferably PGME, PGMEA, EL, nBA, DBE, or a mixture of any of these solvents; still more preferably PGME, PGMEA, EL or a mixture thereof; even more preferably a mixture of PGME, PGMEA and EL.

[0085]

Another embodiment is one wherein the component (G) contains substantially no water in relation to the other layers and membranes. For example, the amount of water in the whole component (G) is preferably 0.1% by mass or less, more preferably 0.01% by mass or less, still more preferably 0.001% by mass or less. Another preferred embodiment is one wherein the solvent (G) contains no water (0% by mass).

[0086]

The content of (G) is preferably 50 to 99% by mass, more preferably 70 to 98% by mass, still more preferably 80 to 95% by mass, based on the total mass of the composition.

[0087]

Surfactant (H)

The composition according to the present invention preferably comprises a surfactant (H). Including a surfactant allows the coatability to be improved. Surfactants that can be used in the present invention may include (I) anionic surfactants, (II) cationic surfactants, or (III) nonionic surfactants, and more specifically include (I) alkyl sulfonates, alkyl benzene sulfonic acids, and alkyl benzene sulfonates, (II) lauryl pyridinium chlorides and lauryl methyl ammonium chlorides, and (III) polyoxyethylene octyl ethers, polyoxyethylene lauryl ethers, polyoxyethylene acetylenic glycol ethers, fluorine-containing surfactants (for example, Fluorad (3M), MEGAFACE (DIC), Surflon (AGC Inc.), and organosiloxane surfactants (for example, KF-53 and KP341 (Shin-Etsu Chemical Co., Ltd.)).

[0088]

The component (H) may have one, or two or more components.
The content of the component (H) is preferably 0.0005 to 0.01% by mass,
more preferably 0.001 to 0.009% by mass, still more preferably 0.002 to
0.007% by mass, based on the total mass of the composition.

5 [0089]

Additive (I)

The composition according to the present invention can comprise an
additive (I) besides the components mentioned above. The component (I) is
preferably selected from at least one of the group consisting of a surface
10 smoothing agent, a plasticizer, a dye, a contrast enhancer, an acid, a
radical generator, a substrate adhesion enhancer, and a defoaming agent.

The content (if more than one, the sum thereof) of the component (I) is
preferably 0 to 20% by mass, more preferably 0 to 10% by mass, still more
preferably 0 to 5% by mass, based on the total mass of the component (A).

15 Another embodiment of the present invention is one wherein the
composition according to the present invention comprises no component (I)
(0% by mass).

[0090]

The acid can be used to adjust the pH value of the composition or to
20 improve the solubility of the additive component. The acid to be used is not
particularly limited, and examples thereof include formic acid, acetic acid,
propionic acid, benzoic acid, phthalic acid, salicylic acid, lactic acid, malic
acid, citric acid, oxalic acid, malonic acid, succinic acid, fumaric acid, maleic
acid, aconitic acid, glutaric acid, adipic acid, p-toluenesulfonic acid,
25 camphorsulfonic acid, hydrates of any of these acids, and combinations
thereof. The content of the acid is preferably 0.005 to 0.1% by mass (more
preferably 0.01 to 0.1% by mass), based on the total mass of the
composition.

[0091]

30 <Method for Producing Resist Film>

A method for producing a resist film according to the present invention
comprises:

applying the above-mentioned resist composition above a substrate to form a coating film.

[0092]

Hereinafter, an embodiment of the production method according to the present invention will be described.

The composition according to the present invention is applied by an appropriate method above the substrate (for example, a silicon/silicon dioxide coated substrate, a silicon nitride substrate, a silicon wafer substrate, a glass substrate, an ITO substrate, and the like). In this regard, in the present invention, the term of above includes a case of being formed directly on and a case of being formed with another layer interposed. For example, a planarization film or a resist lower layer film may be formed directly on the substrate, and the composition according to the present invention may be applied directly on the planarization film or the resist lower layer film. Preferably, no anti-reflective coating is formed as the resist lower layer film. The method for the application is not particularly limited, and examples thereof include a method by application with a spinner or a coater. A film according to the present invention is formed by heating after the application. The coating film is preferably heated, and this heating is performed, for example, with a hot plate. The heating temperature is preferably 30 to 200°C, more preferably 50 to 150°C. The temperature herein is in a heating atmosphere, for example, a heating surface temperature of a hot plate. The heating time is preferably 30 to 300 seconds; more preferably 30 to 120 seconds. The heating is preferably performed in the atmosphere or a nitrogen gas atmosphere.

[0093]

The film thickness of the resist film is selected depending on the purpose. In the case of using the composition according to the present invention, a pattern having a more excellent shape can be formed when a coating film of a thin film is formed. The thickness of the resist film is preferably 1200 nm or less, more preferably 50 to 1100 nm, still more preferably 80 to 1000 nm.

[0094]

A method for producing a resist pattern according to the present invention comprises the following steps:

producing a resist film by the method mentioned above;

5 exposing the resist film to light; and

developing the resist film.

[0095]

The resist film is exposed to light through a predetermined mask. The wavelength of the light for use in the exposure is not particularly limited.

10 The exposure is preferably performed with light of 13.5 to 248 nm in wavelength. Specifically, a KrF excimer laser (wavelength: 248 nm), an ArF excimer laser (wavelength: 193 nm), an extreme ultraviolet ray (wavelength: 13.5 nm), and the like can be used, and a KrF excimer laser is preferred. These wavelengths may fall within a range of $\pm 1\%$. After the

15 exposure, post-exposure bake (post exposure bake, PEB) can also be performed, if necessary. The temperature of the PEB is preferably 80 to 160°C; more preferably 100 to 150°C, and the heating time is 0.3 to 5 minutes; preferably 0.5 to 2 minutes.

[0096]

20 The exposed resist film is developed with the use of a developer. As a method for the development, a method conventionally for use in developing a photoresist can be used, such as a paddle development method, an immersion development method, or a swing immersion development method. As the developer, an aqueous solution is used, which contains an

25 inorganic alkali such as sodium hydroxide, potassium hydroxide, sodium carbonate, or sodium silicate, ammonia, an organic amine such as ethylamine, propylamine, diethylamine, diethylaminoethanol, or triethylamine, a quaternary amine such as tetramethylammonium hydroxide (TMAH), or the like, and an aqueous solution of 2.38% by mass TMAH is

30 preferred. A surfactant can also be further added to the developer. The temperature of the developer is preferably 5 to 50°C; more preferably 25 to 40°C, and the developing time is preferably 10 to 300 seconds. After the

development, water washing or rinsing can also be performed, if necessary. When a positive resist composition is used, the exposed part is removed by the development to form a resist pattern. This resist pattern can also be further made finer with the use of, for example, a shrink material.

5 [0097]

A method for producing a processed substrate according to the present invention comprises the following steps:
producing a resist pattern by the method mentioned above; and
performing a processing treatment with the resist pattern as a mask.

10 [0098]

The formed resist pattern is preferably used for processing a lower layer film or a substrate (more preferably a substrate). Specifically, with the resist pattern as a mask, various substrates to serve as bases can be processed by using a dry etching method, a wet etching method, an ion implantation method, a metal plating method, or the like.

15 [0099]

Thereafter, if necessary, the substrate is further processed to form a device. Known methods can be applied to these steps of further processing, and the processing preferably comprises forming a wiring on the processed substrate. Thereafter, if necessary, the substrate is cut into chips, connected to a lead frame, and packaged with a resin. In the present invention, this packaged product is referred to as a device. Examples of the device include a semiconductor element, a liquid crystal display element, an organic EL display element, a plasma display element, and a solar cell element. The device is preferably a semiconductor element.

20 [0100]

The present invention relates to use of the resist composition for forming a resist film on a substrate. Preferably, the resist film is used as a mask in a step of ion implantation into the substrate, and more preferably, the step of ion implantation is intended for fabricating a logic gate.

30 [0101]

[Examples]

The present invention is described by way of examples as follows. It is to be noted that the embodiment of the present invention is not limited to only these examples.

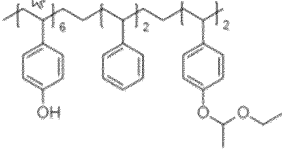
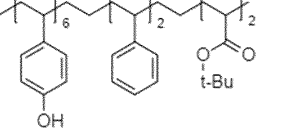
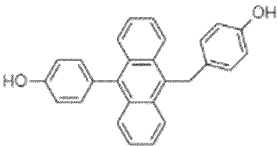
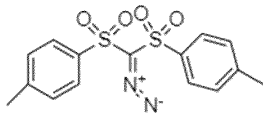
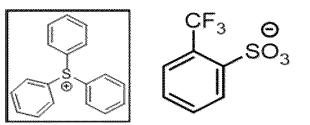
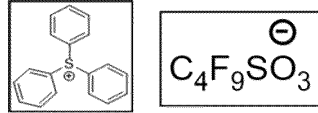
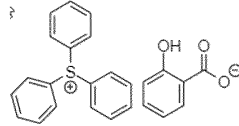
[0102]

5 [Preparation of Composition of Example 1]

The components listed in Table 1 are mixed in parts by mass as listed in Table 1, and a container containing the mixture is stirred overnight, thereby providing a uniformly dissolved composition. This is filtered through a 0.05 μm filter. Thereby, a composition of Example 1 is obtained. Each of the
10 components is weighed with the use of an analytical balance with 0.1 mg precision.

[Table 1]

Table 1

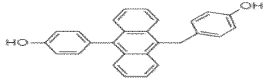
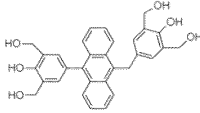
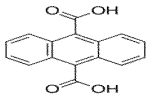
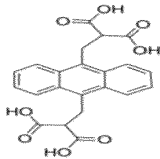
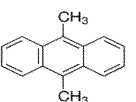
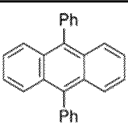
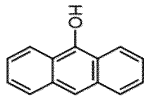
Component		Chemical Structure	CAS NO.	Parts by mass
(A)	A-1	 Mw=12,000	200808-68-0	2.925
	A-2	 Mw=13,000	177034-67-2	3.575
(B)	B-1	9-(4-hydroxybenzyl)-1-(4-hydroxyphenyl)anthracene 	1291058-46-2	0.054
(C)	C-1		14159-45-6	0.13
	C-2		425670-97-9	0.077
	C-3		144317-44-2	0.036
(D)	D-1		345580-99-6	0.005
(E)	E-1	triphenylmethanol	76-84-6	0.063
(F)	F-1	tri-n-octylamine	1116-76-3	0.042
(G)	G-1	PGMEA	108-65-6	51.52
	G-2	PGME	108-65-6	20.738
	G-3	EL	97-64-3	20.759
(H)	H-1	polyether modified polysiloxane	64365-23-7	0.004

[0103]

[Preparation of Compositions of Example 2, Comparative Example 1 to 6]

Compositions of Example 2 and Comparative Examples 1 to 6 are prepared in the same manner as in the preparation of the composition of Example 1, except that the component (B) is changed to the compounds listed in Table 2. Comparative Example 6 contains no component (B).

5 [Table 2]

Table 2		(B)	Coatability	Rectangularity
Example	1		A	A
	2		A	B
Comparative Example	1		B	—
	2		B	—
	3		A	C
	4		A	C
	5		A	C
	6	None	A	D

[0104]

<Formation of Resist Pattern>

10 An 8-inch silicon wafer is pretreated with hexamethyldisilazane. The composition prepared as mentioned above is added to the wafer in a dropwise manner. The wafer is subjected to spin coating at about 1200rpm,

and then to heating (prebake) on a hot plate at 90°C for 35 seconds to form a resist film. The film thickness at the time is 310 nm. On the resist film, an anti-reflective coating (TARC) of 43 nm in film thickness is formed.

5 The resist film is exposed to light with the use of a KrF stepper (FPA 300-EX5, CANON, numerical aperture 0.63, sigma value 0.65). The exposure at the center of the wafer is 190 J/nm². For the wafer mask pattern, Dense Line L:S 1:1 180 nm is used.

10 Thereafter, the wafer is baked (PEB) on a hot plate at 135°C for 90 seconds. This is subjected to paddle development with a 2.38% by mass aqueous TMAH solution for 30 seconds. Thus, a resist pattern is obtained.
[0105]

[Evaluation of Coatability]

15 In the process of forming the resist film, the coatability of the composition is evaluated in accordance with the following criteria, and the results are listed in Table 2.

A: The coatability is good, and a resist film can be formed.

B: The coatability is defective, and no resist film can be formed.

According to Comparative Examples 1 and 2, no resist film can be formed, the subsequent evaluation is not made.

20 [0106]

[Evaluation of Rectangularity]

25 A cross section of the resist pattern formed as mentioned above is observed with the use of a SEM apparatus (SU8230, Hitachi High-Tech Corporation), evaluated in accordance with the following criteria, and the results are listed in Table 2.

A: The resist pattern is rectangular or substantially rectangular.

B: The resist pattern is rectangular or substantially rectangular, but a scum is slightly observed on the pattern. The quality of the resist pattern falls within an acceptable range.

30 C: The interface between the resist pattern and the substrate has footing, and the resist pattern has a tapered shape.

D: The resist pattern has a reversely tapered shape.

[CLAIMS]

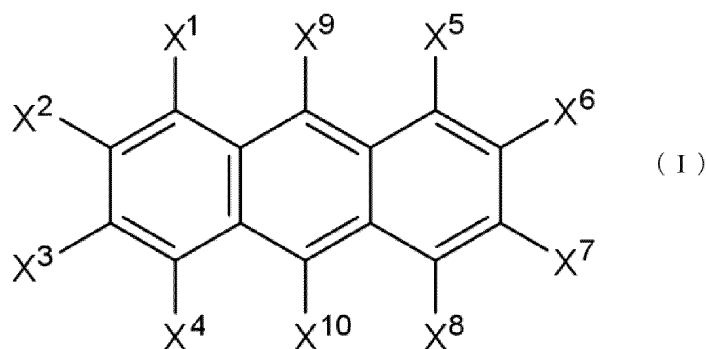
[Claim 1]

A resist composition comprising:

an acid dissociable group-containing polymer (A); and

5 a compound (B) represented by formula (I):

[C1]



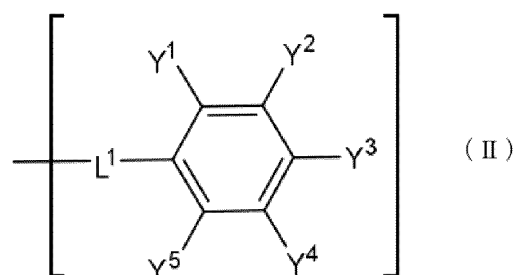
where:

10 X¹ to X¹⁰ are each independently H, OH, NH₂, halogen, C₁₋₁₀ alkyl, C₁₋₁₀ alkoxy, or R represented by formula (II);

when X¹ to X¹⁰ are each independently alkyl, one or more non-adjacent methylene (-CH₂-) groups of the alkyl may each independently be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CH=CH-, or -C≡C-; and

at least one of X¹ to X¹⁰ is R;

15 [C2]



where:

Y¹ to Y⁵ are each independently H, OH, NH₂, halogen, C₁₋₁₀ alkyl, or C₁₋₁₀ alkoxy;

when Y¹ to Y⁵ are each independently alkyl, one or more non-adjacent methylene (-CH₂-) groups of the alkyl may each independently be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CH=CH-, or -C≡C-;

when Y¹ to Y⁵ are each independently alkyl, one or more H atoms of the alkyl may be replaced with OH, NH₂, or halogen;

at least one of Y¹ to Y⁵ is or comprises OH;

L¹ is a single bond or C₁₋₁₀ alkylene; and;

when L¹ is alkylene, one or more non-adjacent methylene (-CH₂-) groups of L¹ may each independently be replaced with -O-, -S-, -CO-, -CO-O-, -O-CO-, -O-CO-O-, -CH=CH-, or -C≡C-.

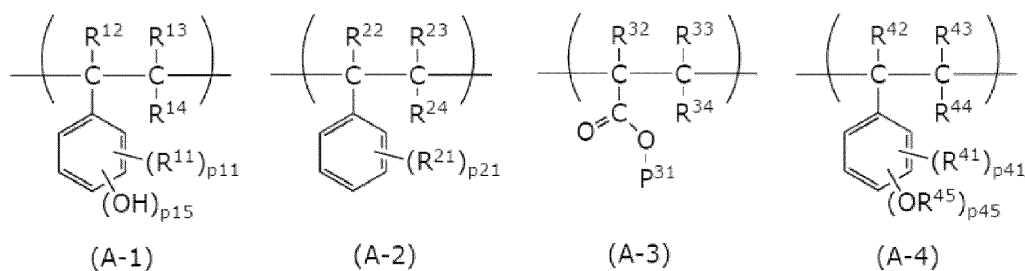
[Claim 2]

The resist composition according to claim 1, wherein the polymer (A) comprises:

a repeating unit represented by formula (A-1); and

at least one repeating unit selected from the group consisting of repeating units represented by formulas (A-2) to (A-4).

[C3]



where:

R¹¹, R²¹, R⁴¹, and R⁴⁵ are each independently C₁₋₅ alkyl, where -CH₂- of the alkyl may be replaced with -O-; and

R¹², R¹³, R¹⁴, R²², R²³, R²⁴, R³², R³³, R³⁴, R⁴², R⁴³, and R⁴⁴ are each independently H, C₁₋₅ alkyl, C₁₋₅ alkoxy, or -COOH;

p₁₁ is 0 to 4, p₁₅ is 1 to 2, and p₁₁ + p₁₅ ≤ 5;

p21 is 0 to 5;

p41 is 0 to 4, p45 is 1 to 2, and $p41 + p45 \leq 5$; and

P³¹ is C₄₋₂₀ alkyl, where the alkyl may partially or entirely form a ring, and part or all of H of the alkyl may be substituted with halogen.

5 [Claim 3]

The resist composition according to claim 1 or 2, further comprising a first acid generator (C), wherein the first acid generator (C) has a -SO₂- structure.

[Claim 4]

10 The resist composition according to claim 3, wherein the first acid generator (C) is a photoacid generator.

[Claim 5]

The resist composition according to any one of claims 1 to 4, further comprising a solvent (G).

15 [Claim 6]

The resist composition according to any one of claims 1 to 5, wherein the content of the acid dissociable group-containing polymer (A) is 1 to 15% by mass, based on the total mass of the resist composition, and

20 the content of the compound (B) represented by formula (I) is 0.01 to 0.1% by mass, based on the total mass of the resist composition.

[Claim 7]

The resist composition according to any one of claims 1 to 6, wherein the resist composition is a positive resist composition.

[Claim 8]

25 A method for producing a resist film, comprising the steps of:

applying the resist composition according to any one of claims 1 to 7 above a substrate to form a coating film; and

preferably, forming no anti-reflective coating on the substrate before the formation of the coating film; or

30 optionally heating the coating film.

[Claim 9]

A resist film of 1200 nm or less in film thickness, produced by the method according to claim 8.

[Claim 10]

5 A method for producing a resist pattern, comprising the steps of:
producing a resist film by the method according to claim 8;
exposing the resist film to light;
optionally heating the resist film after the exposure; and
developing the exposed resist film.

[Claim 11]

10 A method for producing a processed substrate, comprising the steps of:
producing a resist pattern by the method according to claim 10; and
performing a processing treatment with the resist pattern as a mask.

[Claim 12]

15 A method for producing a device, comprising the method according to
claim 11;
preferably, further comprising a step of forming a wiring on the
processed substrate; and
preferably, wherein the device is a semiconductor device.

[Claim 13]

20 Use of the resist composition according to claim 1 for forming a resist
film on a substrate.

[Claim 14]

25 The use according to claim 13, wherein the resist film is used as a mask
in a step of ion implantation into a substrate, and
preferably, the step of ion implantation is intended for fabricating a logic
gate.