

RESIST COMPOSITION AND METHOD OF FORMING RESIST PATTERN

BACKGROUND OF THE INVENTION

Field of the Invention

5 [0001]

The present invention relates to a resist composition and a method of forming a resist pattern.

Priority is claimed on Japanese Patent Application No. 2019-155681, filed on August 28, 2019, the content of which is incorporated herein by reference.

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Description of Related Art

[0002]

In lithography techniques, for example, a resist film formed of a resist material is formed on a substrate, and the resist film is subjected to selective exposure, followed by a developing treatment, thereby forming a resist pattern having a predetermined shape on the resist film. A resist material in which the light-exposed portion of the resist film becomes soluble in a developing solution is called positive-tone resist material, and a resist material in which the light-exposed portion of the resist film becomes insoluble in a developing solution is called negative-tone resist material.

20 In recent years, in the production of semiconductor elements and liquid crystal display elements, advances in lithography techniques have led to rapid progress in the field of pattern miniaturization. Typically, these miniaturization techniques involve shortening the wavelength (increasing the energy) of the light source for exposure. Specifically, ultraviolet radiation typified by g-line and i-line radiation has been used in
25 the related art, but nowadays KrF excimer lasers and ArF excimer lasers are used in mass

production of semiconductor elements. Furthermore, research is also being performed into lithography techniques that use an exposure light source having a wavelength shorter (energy higher) than these excimer lasers, such as electron beams (EB), extreme ultraviolet (EUV) rays and X rays.

5 [0003]

Resist materials for use with these types of light sources for exposure require lithography characteristics such as a high resolution capable of reproducing patterns of minute dimensions, and a high level of sensitivity to these types of light sources for exposure.

10 As a resist material that satisfies these requirements, in the related art, a chemically amplified resist composition which includes a base material component having solubility in a developing solution, which is changed by action of an acid, and an acid generator component that generates an acid upon exposure has been used.

For example, in a case where the developing solution is an alkali developing solution (alkali developing process), as a positive-tone chemically amplified resist composition, a composition which contains a resin component (base resin) having solubility in an alkali developing solution, which is increased by action of an acid, and an acid generator component has been typically used. In a case where a resist film formed using such a resist composition is selectively exposed at the time of forming a resist pattern, in the light-exposed portion, an acid is generated from the acid generator component, and the polarity of the base resin increases by action of the generated acid, thereby making the light-exposed portion of the resist film soluble in the alkali developing solution. Accordingly, a positive-tone pattern in which the light-unexposed portion of the resist film remains as a pattern is formed by performing alkali development.

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On the other hand, in a case where such a chemically amplified resist composition is applied to a solvent developing process using a developing solution containing an organic solvent (organic developing solution), since the solubility in an organic developing solution is relatively decreased at the time of an increase in the polarity of the base resin, the light-unexposed portion of the resist film is dissolved and removed by the organic developing solution, and a negative-tone resist pattern in which the light-exposed portion of the resist film remains is formed. Such a solvent developing process for forming a negative-tone resist pattern is also referred to as a "negative-tone developing process".

10 [0004]

Up till now, as a base resin of a chemically amplified resist composition, for example, for KrF excimer laser (248 nm), a resin having high transparency such as polyhydroxystyrene (PHS) and a resin (a PHS-based resin) in which a hydroxyl group of PHS is protected by an acid-dissociable and dissolution-inhibiting group has been used. In addition, for example, for ArF excimer laser (193 nm), a resin (a (meth)acrylic resin) in which a hydroxyl group of a carboxy group of (meth)acrylic acid is protected by an acid-dissociable and dissolution-inhibiting group has been used (for example, Japanese Unexamined Patent Application, First Publication No. 2003-241385).

As the acid-dissociable and dissolution-inhibiting group, a so-called acetal group such as a chain-like ether group represented by a 1-ethoxyethyl group or a cyclic ether group represented by a tetrahydropyranyl group, a tertiary alkyl group represented by a tert-butyl group, and a tertiary alkoxycarbonyl group represented by a tert-butoxycarbonyl group, and the like are mainly used.

[0005]

25 In addition, a wide variety of acid generators have been proposed as the acid

generator component used in the chemically amplified resist composition, and for example, onium salt-based acid generators such as iodonium salts and sulfonium salts, oxime sulfonate-based acid generators, diazomethane-based acid generators, nitrobenzylsulfonate-based acid generators, iminosulfonate-based acid generators,
5 disulfone-based acid generators, and the like are known.

Among these, onium salt-based acid generators are widely used, and those having an onium ion such as triphenylsulfonium in the cation moiety are mainly used. For an anion moiety of the onium salt-based acid generator, an alkyl sulfonate ion or a fluorinated alkyl sulfonate ion in which part or all of the hydrogen atoms of the alkyl
10 group are substituted with fluorine atoms is generally used.

[0006]

At present, with the increases in the integration of LSIs and the speed of communication, an increase in memory capacity is required, and further pattern miniaturization is rapidly progressing. Lithography using an electron beam or EUV
15 aims to form a fine pattern of several tens of nanometers. However, there are still many problems such as low productivity, and there is a limit in a technique using fine processing.

[0007]

On the other hand, in addition to miniaturization, the development of a three-
20 dimensional structure device for increasing the capacity of a memory by stacking cells in a stack is progressed.

SUMMARY OF THE INVENTION

[0008]

25 In the manufacture of the three-dimensional structure device, a process in which

a thick resist film having a film thickness greater than that of the related art, for example, a film thickness of 5 μm or more is formed on the surface of the processing target, a resist pattern is formed, and etching or the like is performed is included. In a case where a chemically amplified resist composition is used in this process, it is more difficult to maintain the sensitivity during exposure as the film thickness of the resist film increases. Accordingly, there is a problem in that the resolution for development is reduced and a desired resist pattern shape is not easily obtained. Further, there is also a problem in that cracking easily occurs in the resist pattern as the film thickness of the resist film increases.

10 [0009]

The present invention has been made in consideration of the above circumstances, and an object of the present invention is to provide a resist composition capable of forming a thick resist film, not easily causing cracking, and having good resolution, and a method of forming a resist pattern by using the resist composition.

15 [0010]

In order to achieve the above-described object, the present invention employs the following configurations.

That is, the first aspect of the present invention is a resist composition generating an acid upon exposure and having solubility in a developing solution, which is changed by action of an acid, which includes a base material component (A) having solubility in a developing solution, which is changed by action of an acid, and a polyether compound having a weight-average molecular weight of 400 or more, in which a content of the polyether compound is 0.8 to 32 parts by mass with respect to 100 parts by mass of the base material component (A) and a concentration of solid content of the resist composition is 25% by mass or more.

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[0011]

The second aspect of the present invention is a method of forming a resist pattern, including a step of forming a resist film on a supporting body using the resist composition according to the first aspect, a step of exposing the resist film, and a step of
5 developing the exposed resist film to form a resist pattern.

[0012]

According to the present invention, it is possible to provide a resist composition capable of forming a thick resist film, not easily causing cracking, and having good resolution, and a method of forming a resist pattern resist by using the resist composition.
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DETAILED DESCRIPTION OF THE INVENTION

[0013]

In the present specification and the scope of the present patent claims, the term “aliphatic” is a relative concept used with respect to the term “aromatic” and defines a
15 group or compound that has no aromaticity.

The term “alkyl group” includes a linear, branched or cyclic, monovalent saturated hydrocarbon group, unless otherwise specified. The same applies to the alkyl group in an alkoxy group.

The term “alkylene group” includes a linear, branched or cyclic, divalent
20 saturated hydrocarbon group, unless otherwise specified.

A “halogenated alkyl group” is a group in which part or all hydrogen atoms of an alkyl group are substituted with halogen atoms. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.

A “fluorinated alkyl group” or a “fluorinated alkylene group” is a group in
25 which part or all hydrogen atoms of an alkyl group or an alkylene group have been

substituted with fluorine atoms.

The term “constitutional unit” indicates a monomer unit that contributes to the formation of a high-molecular-weight compound (a resin, a polymer, or a copolymer).

The expression “may have a substituent” means a case where a hydrogen atom (-H) is substituted with a monovalent group or a case where a methylene (-CH₂-) group is substituted with a divalent group.

The term “exposure” is used as a general concept that includes irradiation with any form of radiation.

[0014]

The “base material component” is an organic compound having a film-forming ability, and an organic compound having a molecular weight of 500 or more is preferably used. In a case where the molecular weight of the organic compound is 500 or more, the film-forming ability is improved, and in addition, a nano-level resist pattern is easily formed. The organic compounds used as the base material component are roughly classified into a non-polymer and a polymer. As the non-polymer, those having a molecular weight of 500 or more and less than 4,000 are usually used. Hereinafter, a “low-molecular-weight compound” refers to a non-polymer having a molecular weight of 500 or more and less than 4,000. As the polymer, those having a molecular weight of 1,000 or more are usually used. Hereinafter, “resin”, “high-molecular-weight compound”, or “polymer” refers to a polymer having a molecular weight of 1,000 or more. As the molecular weight of the polymer, a polystyrene-equivalent weight-average molecular weight determined by gel permeation chromatography (GPC) is used.

[0015]

A “constitutional unit derived from acrylic acid ester” indicates a constitutional unit that is formed by the cleavage of the ethylenic double bond of acrylic acid ester.

The "acrylic acid ester" indicates a compound in which the terminal hydrogen atom of the carboxy group of acrylic acid ($\text{CH}_2=\text{CH}-\text{COOH}$) has been substituted with an organic group.

In the acrylic acid ester, the hydrogen atom bonded to the carbon atom at the α -position may be substituted with a substituent. The substituent ($\text{R}^{\alpha 0}$) for substituting the hydrogen atom bonded to the carbon atom at the α -position is an atom other than a hydrogen atom or a group, and examples thereof include an alkyl group having 1 to 5 carbon atoms and a halogenated alkyl group having 1 to 5 carbon atoms. Further, itaconic acid diester in which the substituent ($\text{R}^{\alpha 0}$) is substituted with a substituent having an ester bond or α -hydroxyacryl ester in which the substituent ($\text{R}^{\alpha 0}$) is substituted with a hydroxyalkyl group or a group obtained by modifying a hydroxyl group thereof can be mentioned as acrylic acid ester. A carbon atom at the α -position of acrylic acid ester indicates the carbon atom bonded to the carbonyl group of acrylic acid, unless otherwise specified.

Hereinafter, acrylic acid ester in which the hydrogen atom bonded to the carbon atom at the α -position is substituted with a substituent is also referred to as α -substituted acrylic acid ester". Further, acrylic acid ester and α -substituted acrylic acid ester are also collectively referred to as "(α -substituted) acrylic acid ester".

[0016]

A "constitutional unit derived from hydroxystyrene" indicates a constitutional unit that is formed by the cleavage of an ethylenic double bond of hydroxystyrene. A "constitutional unit derived from a hydroxystyrene derivative" indicates a constitutional unit formed by the cleavage of an ethylenic double bond of a hydroxystyrene derivative.

The term "hydroxystyrene derivative" includes compounds in which the hydrogen atom at the α -position of hydroxystyrene has been substituted with another

substituent such as an alkyl group or a halogenated alkyl group; and derivatives thereof. Examples of the derivatives thereof include hydroxystyrene in which the hydrogen atom of the hydroxyl group has been substituted with an organic group and may have the hydrogen atom at the α -position substituted with a substituent; and hydroxystyrene which
5 has a substituent other than a hydroxyl group bonded to the benzene ring and may have the hydrogen atom at the α -position substituted with a substituent. Further, the α -position (carbon atom at the α -position) indicates the carbon atom having the benzene ring bonded thereto, unless otherwise specified.

As the substituent for substituting the hydrogen atom at the α -position of
10 hydroxystyrene, the same substituent as that described above for the substituent at the α -position of the above-described α -substituted acrylic acid ester can be mentioned.

[0017]

A “constitutional unit derived from vinylbenzoic acid or a vinylbenzoic acid derivative” indicates a constitutional unit that is formed by the cleavage of the ethylenic
15 double bond of vinylbenzoic acid or a vinylbenzoic acid derivative.

The term “vinylbenzoic acid derivative” includes compounds in which the hydrogen atom at the α -position of vinylbenzoic acid has been substituted with another substituent such as an alkyl group or a halogenated alkyl group; and derivatives thereof. Examples of the derivatives thereof include vinylbenzoic acid in which the hydrogen
20 atom of the carboxy group has been substituted with an organic group and may have the hydrogen atom at the α -position substituted with a substituent; and vinylbenzoic acid which has a substituent other than a hydroxyl group and a carboxy group bonded to the benzene ring and may have the hydrogen atom at the α -position substituted with a substituent. Further, the α -position (carbon atom at the α -position) indicates the carbon
25 atom having the benzene ring bonded thereto, unless otherwise specified.

[0018]

As the alkyl group as a substituent at the α -position, a linear or branched alkyl group is preferable, and specific examples include alkyl groups of 1 to 5 carbon atoms, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, and a neopentyl group.

Specific examples of the halogenated alkyl group as the substituent at the α -position include groups in which part or all hydrogen atoms of the above-described “alkyl group as the substituent at the α -position” are substituted with halogen atoms.

Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom and, an iodine atom, and a fluorine atom is particularly preferable.

Specific examples of the hydroxyalkyl group as the substituent at the α -position include groups in which part or all hydrogen atoms of the above-described “alkyl group as the substituent at the α -position” are substituted with a hydroxyl group. The number of hydroxyl groups in the hydroxyalkyl group is preferably 1 to 5, and most preferably 1.

[0019]

In the present specification and the scope of the present patent claims, asymmetric carbons may be present or enantiomers or diastereomers may be present depending on the structures of the chemical formula. In that case, these isomers are represented by one chemical formula. These isomers may be used alone or in the form of a mixture.

[0020]

(Resist composition)

The resist composition according to the first aspect of the present invention is a resist composition generating an acid upon exposure and having solubility in a

developing solution, which is changed by action of an acid, which includes a base material component (A) (hereinafter also referred to as component (A)) having solubility in a developing solution, which is changed by action of an acid, and a polyether compound (hereinafter also referred to as component (Z)) having a weight-average molecular weight of 400 or more. In the resist composition of the present embodiment, the content of the component (Z) is 0.8 to 32 parts by mass with respect to 100 parts by mass of the component (A). In addition, a concentration of solid content of the resist composition of the present embodiment is 25% by mass or more.

In a case where a resist film is formed using such a resist composition, a thick resist film (for example, a film having a thickness of 5 μm or more) can be formed.

[0021]

In a case where a resist film is formed using such a resist composition and the formed resist film is subjected to selective exposure, an acid is generated at the light-exposed portion of the resist film, and the generated acid acts on the component (A) to change the solubility of the component (A) in a developing solution, whereas the solubility of the component (A) in a developing solution is not changed at the light-unexposed portion of the resist film, thereby generating the difference in solubility in the developing solution between the light-exposed portion and the light-unexposed portion of the resist film. Therefore, by subjecting the resist film to development, the light-exposed portion of the resist film is dissolved and removed to form a positive-tone resist pattern in a case where the resist composition is a positive-tone type, whereas the light-unexposed portion of the resist film is dissolved and removed to form a negative-tone resist pattern in a case where the resist composition is a negative-tone type.

[0022]

In the present specification, a resist composition which forms a positive-tone

resist pattern by dissolving and removing the light-exposed portion of the resist film is called a positive-tone resist composition, and a resist composition which forms a

negative-tone resist pattern by dissolving and removing the light-unexposed portion of the resist film is called a negative-tone resist composition. The resist composition of

5 the present embodiment may be a positive-tone resist composition or a negative-tone resist composition. Further, in the formation of a resist pattern, the resist composition of the present embodiment can be applied to an alkali developing process using an alkali developing solution in the developing treatment, or a solvent developing process using a developing solution containing an organic solvent (organic developing solution) in the
10 developing treatment.

[0023]

The resist composition of the present embodiment has a function of generating an acid upon exposure, the component (A) may generate an acid upon exposure, and an additive component that is separately blended from the component (A) may generate an
15 acid upon exposure.

Specifically, the resist composition of the present embodiment may (1) further contain an acid generator component (B) (hereinafter, referred to as “component (B)”) that generates an acid upon exposure; (2) have a component (A) that generates an acid upon exposure; and (3) have a component (A) that generates an acid upon exposure and
20 further contains component (B). That is, in the cases of (2) and (3) described above, the component (A) becomes a “base material component which generates an acid upon exposure and has solubility in a developing solution, which is changed by action of an acid”. In a case where the component (A) is a base material component which generates an acid upon exposure and has solubility in a developing solution, which is
25 changed by action of an acid, it is preferable that the component (A1) described below be

a high-molecular-weight compound which generates an acid upon exposure and has solubility in a developing solution, which is changed by action of an acid. As such a high-molecular-weight compound, a resin having a constitutional unit that generates an acid upon exposure can be used. As the constitutional unit that generates an acid upon exposure, a known constitutional unit can be used. Among them, the resist composition of the present embodiment is particularly preferably the case of the above (1).

[0024]

<Component (A)>

As the component (A) of the resist composition of the present embodiment, a resin component (A1) (hereinafter, also referred to as a “component (A1)”) having solubility in a developing solution, which is changed by action of an acid, can be included. In the alkali developing process and the solvent developing process, since the polarity of the base material component before and after the exposure is changed by using the component (A1), an excellent development contrast between an exposed portion and an unexposed portion can be obtained.

As the component (A), at least the component (A1) is used, and another high-molecular-weight compound and/or a low-molecular-weight compound may be used in combination with the component (A1).

[0025]

In a case of applying an alkali developing process, a base material component containing the component (A1) is substantially insoluble in an alkali developing solution prior to exposure, but in a case where an acid is generated from the component (B) upon exposure, the action of this acid causes an increase in the polarity of the base material component, thereby increasing the solubility of the base material component in an alkali developing solution. Therefore, in the formation of a resist pattern, by performing

selective exposure of a resist film formed by applying the resist composition onto a supporting body, the light-exposed portion of the resist film changes from an insoluble state to a soluble state in an alkali developing solution, whereas the light-unexposed portion of the resist film remains insoluble in an alkali developing solution, and thus, a positive-tone resist pattern is formed by alkali developing.

[0026]

Meanwhile, in a case of a solvent developing process, the base material component containing the component (A1) exhibits high solubility in an organic developing solution prior to exposure, and in a case where an acid is generated from the component (B) upon exposure, the polarity of the component (A1) is increased by the action of the generated acid, thereby decreasing the solubility of the component (A1) in an organic developing solution. Therefore, in the formation of a resist pattern, by performing selective exposure of a resist film formed by applying the resist composition onto a supporting body, the light-exposed portion of the resist film changes from a soluble state to an insoluble state in an organic developing solution, whereas the light-unexposed portion of the resist film remains soluble and does not change, thereby a contrast between the light-exposed portion and the light-unexposed portion can be obtained, and thus a negative-tone resist pattern is formed by developing in the organic developing solution.

[0027]

In the resist composition according to the present embodiment, the component (A) may be used alone or in combination of two or more kinds thereof.

[0028]

· In regard to component (A1)

The component (A1) is a resin component having solubility in a developing

solution, which is changed by action of an acid. The component (A1) preferably has a constitutional unit (a1) that includes an acid-decomposable group having a polarity which is increased by action of an acid.

The component (A1) may have other constitutional units as necessary in
5 addition to the constitutional unit (a1).

[0029]

<<Constitutional unit (a1)>>

The constitutional unit (a1) is a constitutional unit that contains an acid-decomposable group having a polarity which is increased by action of an acid.

10 The term "acid-decomposable group" indicates a group in which at least a part of a bond in the structure of the acid-decomposable group can be cleaved by action of an acid.

Examples of the acid-decomposable group having a polarity which is increased by action of an acid include groups which are decomposed by action of an acid to
15 generate a polar group.

Examples of the polar group include a carboxy group, a hydroxyl group, an amino group, and a sulfo group ($-\text{SO}_3\text{H}$). Among these, a polar group containing $-\text{OH}$ in the structure thereof (hereinafter, also referred to as an "OH-containing polar group") is preferable, a carboxy group or a hydroxyl group is more preferable, and a carboxy
20 group is particularly preferable.

More specific examples of the acid-decomposable group include a group in which the above-described polar group has been protected with an acid-dissociable group (such as a group in which a hydrogen atom of the OH-containing polar group has been protected with an acid-dissociable group).

25 [0030]

Here, the "acid-dissociable group" indicates both (i) a group in which a bond between the acid-dissociable group and an atom adjacent to the acid-dissociable group can be cleaved by action of an acid; and (ii) a group in which some bonds are cleaved by action of an acid, and then a decarboxylation reaction occurs, thereby cleaving the bond
5 between the acid-dissociable group and the atom adjacent to the acid-dissociable group."

It is necessary that the acid-dissociable group that constitutes the acid-decomposable group be a group which exhibits a lower polarity than the polar group generated by the dissociation of the acid-dissociable group. Thus, in a case where the acid-dissociable group is dissociated by action of an acid, a polar group exhibiting a
10 higher polarity than that of the acid-dissociable group is generated, thereby increasing the polarity. As a result, the polarity of the entire component (A1) is increased. By the increase in the polarity, the solubility in a developing solution relatively changes. The solubility in an alkali developing solution is increased in a case where the developing solution is an alkali developing solution, whereas the solubility in an organic developing
15 solution is decreased in a case where the developing solution is an alkali developing solution.

[0031]

Examples of the acid-dissociable group are the same as those which have been proposed as acid-dissociable groups for the base resin for a chemically amplified resist
20 composition.

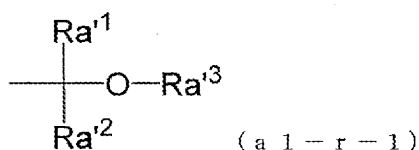
Specific examples of acid-dissociable groups of the base resin for a conventional chemically amplified resist composition include an "acetal-type acid-dissociable group", a "tertiary alkyl ester-type acid-dissociable group", and a "tertiary alkyloxycarbonyl acid-dissociable group" described below.

25 [0032]

Acetal-type acid-dissociable group:

Examples of the acid-dissociable group for protecting a carboxy group or a hydroxyl group as a polar group include the acid-dissociable group represented by General Formula (a1-r-1) shown below (hereinafter, also referred to as an "acetal-type acid-dissociable group").

[0033]



[In the formula, Ra'¹ to Ra'² represent hydrogen atoms or alkyl groups. Ra'³ represents a hydrocarbon group, and Ra'³ may be bonded to Ra'¹ or Ra'² to form a ring.]

[0034]

In Formula (a1-r-1), it is preferable that at least one of Ra'¹ and Ra'² represent a hydrogen atom and more preferable that both of Ra'¹ and Ra'² represent hydrogen atoms.

In a case where Ra'¹ or Ra'² represents an alkyl group, examples of the alkyl group include the same alkyl groups mentioned as the substituent which may be bonded to the carbon atom at the α -position in the description on the α -substituted acrylic acid ester. Among these, an alkyl group having 1 to 5 carbon atoms is preferable. Specific examples thereof include linear or branched alkyl groups. Specific examples of the alkyl group include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, and a neopentyl group. Among these, a methyl group or an ethyl group is preferable, and a methyl group is particularly preferable.

[0035]

In Formula (a1-r-1), examples of the hydrocarbon group as Ra'^3 include a linear or branched alkyl group and a cyclic hydrocarbon group.

The linear alkyl group preferably has 1 to 5 carbon atoms, more preferably 1 to 4 carbon atoms, and still more preferably 1 or 2 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, an n-propyl group, an n-butyl group, and an n-pentyl group. Among these, a methyl group, an ethyl group, or an n-butyl group is preferable, and a methyl group or an ethyl group is more preferable.

[0036]

The branched alkyl group preferably has 3 to 10 carbon atoms and more preferably 3 to 5 carbon atoms. Specific examples thereof include an isopropyl group, an isobutyl group, a tert-butyl group, an isopentyl group, a neopentyl group, a 1,1-diethylpropyl group, and a 2,2-dimethylbutyl group. Among these, an isopropyl group is preferable.

[0037]

In a case where Ra'^3 represents a cyclic hydrocarbon group, the cyclic hydrocarbon group may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group and may be a polycyclic group or a monocyclic group.

As the aliphatic hydrocarbon group which is a monocyclic group, a group in which one hydrogen atom has been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

As the aliphatic hydrocarbon group which is a polycyclic group, a group in which one hydrogen atom has been removed from a polycycloalkane is preferable. As the polycycloalkane, a group having 7 to 12 carbon atoms is preferable, and specific examples of the polycycloalkane include adamantane, norbornane, isobornane,

tricyclodecane, and tetracyclododecane.

[0038]

In a case where the cyclic hydrocarbon group as Ra'^3 is an aromatic hydrocarbon group, the aromatic hydrocarbon group is a hydrocarbon group having at least one aromatic ring.

The aromatic ring is not particularly limited as long as it is a cyclic conjugated system having $(4n + 2) \pi$ electrons, and may be monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, still more preferably 6 to 15 carbon atoms, and particularly preferably 6 to 12 carbon atoms. Specific examples of the aromatic ring include aromatic hydrocarbon rings such as benzene, naphthalene, anthracene, and phenanthrene; and aromatic hetero rings in which some carbon atoms constituting the above-described aromatic hydrocarbon rings have been substituted with hetero atoms. Examples of the hetero atom in the aromatic hetero rings include an oxygen atom, a sulfur atom, and a nitrogen atom. Specific examples of the aromatic hetero ring include a pyridine ring and a thiophene ring.

Specific examples of the aromatic hydrocarbon group as Ra'^3 include a group in which one hydrogen atom has been removed from the above-described aromatic hydrocarbon ring or aromatic hetero ring (an aryl group or a heteroaryl group); a group in which one hydrogen atom has been removed from an aromatic compound having two or more aromatic rings (biphenyl, fluorene or the like); and a group in which one hydrogen atom of the above-described aromatic hydrocarbon ring or aromatic hetero ring has been substituted with an alkylene group (an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group). The number of carbon atoms in the alkylene group bonded to the aromatic hydrocarbon ring or aromatic hetero ring is preferably in a range

of 1 to 4, more preferably 1 or 2, and particularly preferably 1.

[0039]

The cyclic hydrocarbon group in Ra'^3 may have a substituent. Examples of the substituent include, $-R^{P1}$, $-R^{P2}-O-R^{P1}$, $-R^{P2}-CO-R^{P1}$, $-R^{P2}-CO-OR^{P1}$, $-R^{P2}-O-CO-R^{P1}$, $-R^{P2}-OH$, $-R^{P2}-CN$, and $-R^{P2}-COOH$ (hereinafter, these substituents are also collectively referred to as " Ra^{05} ").

Here, R^{P1} represents a monovalent chain-like saturated hydrocarbon group having 1 to 10 carbon atoms, a monovalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms, or a monovalent aromatic hydrocarbon group having 6 to 30 carbon atoms. In addition, R^{P2} represents a single bond, a divalent chain-like saturated hydrocarbon group having 1 to 10 carbon atoms, a divalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms, or a divalent aromatic hydrocarbon group having 6 to 30 carbon atoms. However, part or all of the hydrogen atoms included in the chain-like saturated hydrocarbon group, the aliphatic cyclic saturated hydrocarbon group, and the aromatic hydrocarbon group of R^{P1} and R^{P2} may be substituted with fluorine atoms. In the aliphatic cyclic hydrocarbon group, one or more of the above-described substituents may be included as a single kind, or one or more of the above-described substituents may be included as a plurality of kinds.

Examples of the monovalent chain-like saturated hydrocarbon group having 1 to 10 carbon atoms include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, and a decyl group.

Examples of the monovalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms include: monocyclic aliphatic saturated hydrocarbon groups such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclodecyl group, and cyclododecyl

group; and polycyclic aliphatic saturated hydrocarbon groups such as a bicyclo[2.2.2]octanyl group, a tricyclo[5.2.1.0^{2,6}]decanyl group, a tricyclo[3.3.1.1^{3,7}]decanyl group, a tetracyclo[6.2.1.1^{3,6}.0^{2,7}] dodecanyl group, and an adamantyl group.

- 5 Examples of the monovalent aromatic hydrocarbon group having 6 to 30 carbon atoms include groups obtained by removing one hydrogen atom from an aromatic hydrocarbon ring such as benzene, biphenyl, fluorene, naphthalene, anthracene, and phenanthrene.

[0040]

- 10 In a case where Ra'³ is bonded to Ra'¹ or Ra'² to form a ring, the cyclic group is preferably a 4- to 7-membered ring, and more preferably a 4- to 6-membered ring. Specific examples of the cyclic group include a tetrahydropyranyl group and a tetrahydrofuran group.

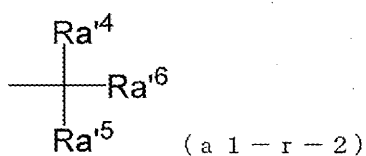
[0041]

- 15 Tertiary alkyl ester-type acid-dissociable group:

Examples of the acid-dissociable group for protecting the carboxy group as a polar group include the acid-dissociable group represented by General Formula (a1-r-2) shown below.

- 20 Among the acid-dissociable groups represented by Formula (a1-r-2), for convenience, a group which is constituted of alkyl groups is referred to as a "tertiary alkyl ester-type acid-dissociable group".

[0042]



[In the formula, Ra'⁴ to Ra'⁶ each represents a hydrocarbon group, and Ra'⁵ and Ra'⁶ may be bonded with each other to form a ring.]

[0043]

5 Examples of the hydrocarbon group as Ra'⁴ include a linear or branched alkyl group and a cyclic hydrocarbon group, a linear or cyclic alkenyl group, and a cyclic hydrocarbon group.

The linear or branched alkyl group and the cyclic hydrocarbon group (an aliphatic hydrocarbon group which is a monocyclic group, an aliphatic hydrocarbon
10 group which is a polycyclic group, or an aromatic hydrocarbon group) as Ra'⁴ are the same as those mentioned as Ra'³ described above.

The chain-like or cyclic alkenyl group as Ra'⁴ is preferably an alkenyl group having 2 to 10 carbon atoms.

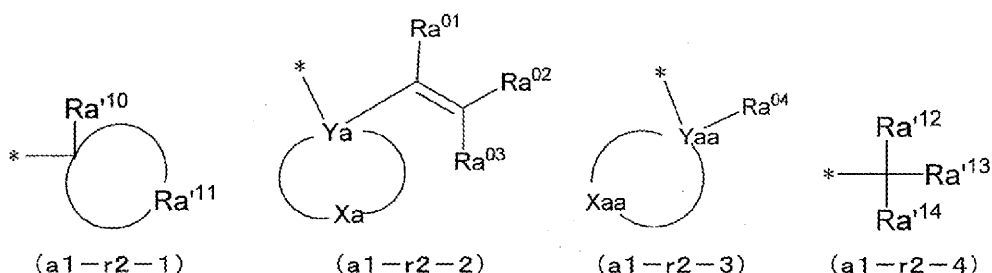
Examples of the hydrocarbon group as Ra'⁵ or Ra'⁶ are the same as those
15 mentioned above as Ra'³.

[0044]

In a case where Ra'⁵ to Ra'⁶ are bonded to each other to form a ring, groups represented by General Formula (a1-r2-1), General Formula (a1-r2-2), and General Formula (a1-r2-3) can be suitably mentioned.

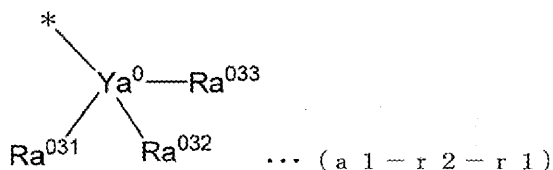
20 Meanwhile, in a case where Ra'⁴ to Ra'⁶ are not bonded with each other and represent an independent hydrocarbon group, a group represented by General Formula (a1-r2-4) can be suitably mentioned.

[0045]



[In Formula (a1-r2-1), Ra'^{10} represents an alkyl group having 1 to 10 carbon atoms or a group represented by General Formula (a1-r2-r1). Ra'^{11} represents a group that forms an aliphatic cyclic group together with a carbon atom to which Ra'^{10} is bonded. In Formula (a1-r2-2), Ya represents a carbon atom. Xa is a group that forms a cyclic hydrocarbon group together with Ya . Part or all of the hydrogen atoms which the cyclic hydrocarbon group has may be substituted. Ra'^{01} to Ra'^{03} each independently represents a hydrogen atom, a chain-like saturated hydrocarbon group having 1 to 10 carbon atoms, or a monovalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms. Part or all of the hydrogen atoms which the chain-like saturated hydrocarbon group and the aliphatic cyclic saturated hydrocarbon group have may be substituted. Two or more of Ra'^{01} to Ra'^{03} may be bonded with each other to form a cyclic structure. In Formula (a1-r2-3), Yaa represents a carbon atom. Xaa is a group that forms an aliphatic cyclic group together with Yaa . Ra'^{04} represents an aromatic hydrocarbon group which may have a substituent. In Formula (a1-r2-4), Ra'^{12} and Ra'^{13} each independently represents a chain-like saturated hydrocarbon group having 1 to 10 carbon atoms or a hydrogen atom. Part or all of the hydrogen atoms which the chain-like saturated hydrocarbon group has may be substituted. Ra'^{14} represents a hydrocarbon group which may have a substituent. * represents a bond.]

[0046]



[In the formula, Ya^0 represents a quaternary carbon atom. Ra^{031} , Ra^{032} , and Ra^{033} each independently represents a hydrocarbon group which may have a substituent.

- 5 Here, one or more of Ra^{031} , Ra^{032} , and Ra^{033} are hydrocarbon groups having at least one polar group.]

[0047]

In Formula (a1-r2-1) described above, as the alkyl group having 1 to 10 carbon atoms as Ra'^{10} , the groups mentioned as the linear or branched alkyl group as Ra'^3 in

- 10 Formula (a1-r-1) are preferable. It is preferable that Ra'^{10} represent an alkyl group having 1 to 5 carbon atoms.

[0048]

In Formula (a1-r2-r1), Ya^0 represents a quaternary carbon atom. That is, there are four adjacent carbon atoms bonded to Ya^0 (carbon atom).

- 15 [0049]

In Formula (a1-r2-r1), Ra^{031} , Ra^{032} , and Ra^{033} each independently represents a hydrocarbon group which may have a substituent. The hydrocarbon groups as Ra^{031} , Ra^{032} , and Ra^{033} each independently include a linear or branched alkyl group and a cyclic hydrocarbon group, a chain-like or cyclic alkenyl group, and a cyclic hydrocarbon group.

- 20 [0050]

The linear alkyl groups as Ra^{031} , Ra^{032} , and Ra^{033} preferably have 1 to 5 carbon atoms, more preferably 1 to 4 carbon atoms, and still more preferably 1 or 2 carbon

atoms. Specific examples thereof include a methyl group, an ethyl group, an n-propyl group, an n-butyl group, and an n-pentyl group. Among these, a methyl group, an ethyl group, or an n-butyl group is preferable, and a methyl group or an ethyl group is more preferable.

5 The branched alkyl groups as Ra^{031} , Ra^{032} , and Ra^{033} preferably have 3 to 10 carbon atoms and more preferably 3 to 5 carbon atoms. Specific examples thereof include an isopropyl group, an isobutyl group, a tert-butyl group, an isopentyl group, a neopentyl group, a 1,1-diethylpropyl group, and a 2,2-dimethylbutyl group. Among these, an isopropyl group is preferable.

10 The chain-like or cyclic alkenyl groups as Ra^{031} , Ra^{032} , and Ra^{033} are preferably an alkenyl group having 2 to 10 carbon atoms.

[0051]

 The cyclic hydrocarbon group as Ra^{031} , Ra^{032} , and Ra^{033} may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group and may be a polycyclic group or a
15 monocyclic group.

 As the aliphatic hydrocarbon group which is a monocyclic group, a group in which one hydrogen atom has been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

20 As the aliphatic hydrocarbon group which is a polycyclic group, a group in which one hydrogen atom has been removed from a polycycloalkane is preferable. As the polycycloalkane, a group having 7 to 12 carbon atoms is preferable, and specific examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane.

25 [0052]

The aromatic hydrocarbon groups as Ra^{031} , Ra^{032} , and Ra^{033} are a hydrocarbon group having at least one aromatic ring. The aromatic ring is not particularly limited as long as it is a cyclic conjugated system having $(4n + 2) \pi$ electrons, and may be monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, still more preferably 6 to 15 carbon atoms, and particularly preferably 6 to 12 carbon atoms. Specific examples of the aromatic ring include aromatic hydrocarbon rings such as benzene, naphthalene, anthracene, and phenanthrene; and aromatic hetero rings in which some carbon atoms constituting the above-described aromatic hydrocarbon rings have been substituted with hetero atoms.

Examples of the hetero atom in the aromatic hetero rings include an oxygen atom, a sulfur atom, and a nitrogen atom. Specific examples of the aromatic hetero ring include a pyridine ring and a thiophene ring. Specific examples of the aromatic hydrocarbon group include a group in which one hydrogen atom has been removed from the above-described aromatic hydrocarbon ring or aromatic hetero ring (an aryl group or a heteroaryl group); a group in which one hydrogen atom has been removed from an aromatic compound having two or more aromatic rings (biphenyl, fluorene or the like); and a group in which one hydrogen atom of the above-described aromatic hydrocarbon ring or aromatic hetero ring has been substituted with an alkylene group (an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group). The number of carbon atoms in the alkylene group bonded to the aromatic hydrocarbon ring or aromatic hetero ring is preferably in a range of 1 to 4, more preferably 1 or 2, and particularly preferably 1.

[0053]

In a case where the hydrocarbon groups represented by Ra^{031} , Ra^{032} , and Ra^{033}

are substituted, examples of the substituent include a hydroxyl group, a carboxy group, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, and the like), an alkoxy group (a methoxy group, an ethoxy group, a propoxy group, a butoxy group, and the like), an alkyloxycarbonyl group.

5 [0054]

Among the above examples, as Ra^{031} , Ra^{032} , and Ra^{033} , the hydrocarbon group which may have a substituent is preferably a linear or branched alkyl group which may have a substituent and more preferably a linear alkyl group.

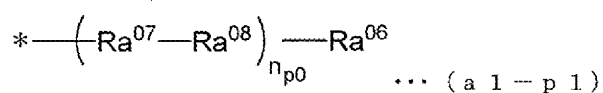
[0055]

10 Here, one or more of Ra^{031} , Ra^{032} , and Ra^{033} are hydrocarbon groups having at least a polar group.]

The “hydrocarbon group having a polar group” includes any one of a hydrocarbon group in which a methylene group ($-CH_2-$) constituting the hydrocarbon group is substituted with a polar group and a hydrocarbon group in which at least one
15 hydrogen atom constituting the hydrocarbon group is substituted with a polar group.

As such a “hydrocarbon group having a polar group”, a functional group represented by General Formula (a1-p1) is preferable.

[0056]



20 [In the formula, Ra^{07} represents a divalent hydrocarbon group having 2 to 12 carbon atoms. Ra^{08} represents a divalent linking group including a hetero atom. Ra^{06} represents a monovalent hydrocarbon group having 1 to 12 carbon atoms. n_{p0} represents an integer of 1 to 6.]

[0057]

In Formula (a1-p1), Ra^{07} represents a divalent hydrocarbon group having 2 to 12 carbon atoms. Ra^{07} has 2 to 12 carbon atoms, preferably has 2 to 8 carbon atoms, more preferably 2 to 6 carbon atoms, still more preferably 2 to 4 carbon atoms, and particularly
5 preferably 2 carbon atoms.

The hydrocarbon group as Ra^{07} is preferably a chain-like or cyclic aliphatic hydrocarbon group and more preferably a chain-like hydrocarbon group.

Examples of Ra^{07} include: linear alkanediyl groups such as an ethylene group, a propane-1,3-diyl group, a butane-1,4-diyl group, a pentane-1,5-diyl group, a hexane-1,6-
10 diyl group, a heptane-1,7-diyl group, an octane-1,8-diyl group, a nonane-1,9-diyl group, a decane-1,10-diyl group, an undecane-1,11-diyl group, and a dodecane-1,12-diyl group; branched alkanediyl groups such as a propane-1,2-diyl group, a 1-methylbutane-1,3-diyl group, a 2-methylpropane-1,3-diyl group, a pentane-1,4-diyl group, and a 2-methylbutane-1,4-diyl group; cycloalkanediyl groups such as a cyclobutane-1,3-diyl
15 group, a cyclopentane-1,3-diyl group, a cyclohexane-1,4-diyl group, a cyclooctane-1,5-diyl group; and polycyclic divalent alicyclic hydrocarbon groups such as a norbornane-1,4-diyl group, a norbornane-2,5-diyl group, an adamantane-1,5-diyl group, and an adamantane-2,6-diyl group.

Among them, an alkanediyl group is preferable, and a linear alkanediyl group is
20 more preferable.

[0058]

In Formula (a1-p1), Ra^{08} represents a divalent linking group including a hetero atom.

Examples of Ra^{08} include -O-, -C(=O)-O-, -C(=O)-, -O-C(=O)-O-, -C(=O)-NH-,
25 -NH-, -NH-C(=NH)- (H may be substituted with a substituent such as an alkyl group and

an acyl group), -S-, -S(=O)₂-, and -S(=O)₂-O-.

Among these, Ra⁰⁸ is preferably -O-, -C(=O)-O-, -C(=O)-, and -O-C(=O)-O-, and more preferably -O- and -C(=O)- from the viewpoint of the solubility in a developing solution.

5 [0059]

In Formula (a1-p1), Ra⁰⁶ represents a monovalent hydrocarbon group having 1 to 12 carbon atoms. Ra⁰⁶ has 1 to 12 carbon atoms and preferably has 1 to 8 carbon atoms, more preferably 1 to 5 carbon atoms, still more preferably 1 to 3 carbon atoms, particularly preferably 1 or 2 carbon atoms, and most preferably 1 carbon atoms, from
10 the viewpoint of the solubility in a developing solution.

[0060]

The hydrocarbon group as Ra⁰⁶ include a chain-like hydrocarbon group or a cyclic hydrocarbon group, or a hydrocarbon group obtained by combining a chain-like hydrocarbon group or a cyclic hydrocarbon group.

15 Examples of the chain-like hydrocarbon group include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, a sec-butyl group, a tert-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, a 2-ethylhexyl group, an n-octyl group, an n-nonyl group, an n-decyl group, an n-undecyl group, and an n-dodecyl group.

20 [0061]

The cyclic hydrocarbon group may be an alicyclic hydrocarbon group or an aromatic hydrocarbon group.

Examples of the alicyclic hydrocarbon group may be either monocyclic or polycyclic, and examples of the monocyclic alicyclic hydrocarbon group include
25 cycloalkyl groups such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group,

a cyclohexyl group, a methylcyclohexyl group, a dimethylcyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclononyl group, and a cyclodecyl group.

Examples of the polycyclic alicyclic hydrocarbon group include a decahydronaphthyl group, an adamantyl group, a 2-alkyladamantan-2-yl group, a 1-(adamantan-1-yl)alkane-

5 1-yl group, a norbornyl group, a methylnorbornyl group, and an isobornyl group.

Examples of the aromatic hydrocarbon group include a phenyl group, a naphthyl group, an anthryl group, a p-methylphenyl group, a p-tert-butylphenyl group, a p-adamantylphenyl group, a tolyl group, a xylyl group, a cumenyl group, a mesityl group, a biphenyl group, a phenanthryl group, a 2,6-diethylphenyl group, and a 2-methyl-6-

10 ethylphenyl group.

[0062]

From the viewpoint of solubility in a developing solution, Ra^{06} is preferably a chain-like hydrocarbon group, more preferably an alkyl group, and still more preferably a linear alkyl group.

15 [0063]

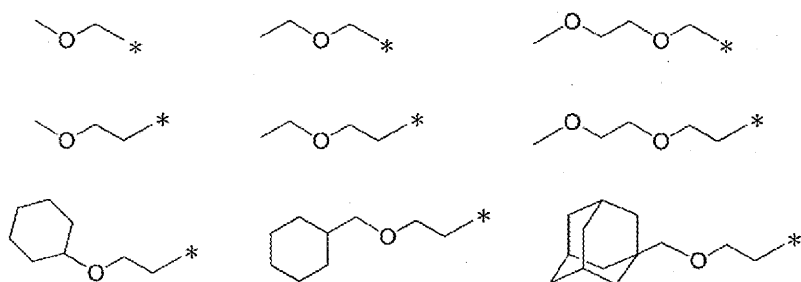
In Formula (a1-p1) n_{p0} represents an integer of 1 to 6, is preferably an integer of 1 to 3, more preferably an integer of 1 or 2, and still more preferably 1.

[0064]

Specific examples of the hydrocarbon group having at least a polar group are
20 described below.

In the following formulae, * is a bond that bonds to the quaternary carbon atom (Y_a^0).

[0065]



[0066]

In Formula (a1-r2-r1), the number of hydrocarbon groups having at least a polar group among Ra^{031} , Ra^{032} , and Ra^{033} is one or more. The number of hydrocarbon

- 5 groups may be appropriately determined in consideration of the solubility in a developing solution at the time of forming a resist pattern, for example, one or two are preferable, and one is particularly preferable among Ra^{031} , Ra^{032} , and Ra^{033} .

[0067]

- The hydrocarbon group having at least a polar group may have a substituent
10 other than the polar group. Examples of the substituent include a halogen atom (a fluorine atom, a chlorine atom, a bromine atom and the like) and a halogenated alkyl group having 1 to 5 carbon atoms.

[0068]

- In Formula (a1-r2-1), Ra'^{11} (an aliphatic cyclic group that is formed together
15 with the carbon atom to which Ra'^{10} is bonded) is preferably the group mentioned as the aliphatic hydrocarbon group which is a monocyclic group or a polycyclic group as Ra'^3 in Formula (a1-r-1).

[0069]

- In formula (a1-r2-2), examples of the cyclic hydrocarbon groups formed by Xa
20 together with Ya include, for example, a group in which one or more hydrogen atoms are

further removed from a cyclic monovalent hydrocarbon group (an aliphatic hydrocarbon group) as Ra'^3 in Formula (a1-r-1).

The cyclic hydrocarbon group which is formed by Xa together with Ya may have a substituent. Examples of these substituents include the same groups as the substituents which the cyclic hydrocarbon group as Ra'^3 may have.

In Formula (a1-r2-2), as Ra^{01} to Ra^{03} , examples of the monovalent chain-like saturated hydrocarbon group having 1 to 10 carbon atoms include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, and a decyl group.

Examples of the monovalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms, as Ra^{01} to Ra^{03} , include: monocyclic aliphatic saturated hydrocarbon groups such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclodecyl group, and cyclododecyl group; and polycyclic aliphatic saturated hydrocarbon groups such as a bicyclo[2.2.2]octanyl group, a tricyclo[5.2.1.0^{2,6}]decanyl group, a tricyclo[3.3.1.1^{3,7}]decanyl group, a tetracyclo[6.2.1.1^{3,6}.0^{2,7}] dodecanyl group, and an adamantyl group.

Among them, Ra^{01} to Ra^{03} are preferably a hydrogen atom or a monovalent chain-like saturated hydrocarbon group having 1 to 10 carbon atoms, and from the viewpoint of easy synthesis of a monomer compound from which the constitutional unit (a1) is derived, among them, a hydrogen atom, a methyl group, and an ethyl group are more preferable, and a hydrogen atom is particularly preferable.

[0070]

Examples of the substituent which the chain-like saturated hydrocarbon group represented by Ra^{01} to Ra^{03} or the aliphatic cyclic saturated hydrocarbon group has

include the same groups as Ra⁰⁵ described above.

[0071]

Examples of the group including a carbon-carbon double bond generated by forming a cyclic structure, in which two or more of Ra⁰¹ to Ra⁰³ are bonded with each other, include, a cyclopentenyl group, a cyclohexenyl group, a methylcyclopentenyl group, a methylcyclohexenyl group, a cyclopentylideneethenyl group, and a cyclohexylideneethenyl group. Among these, a cyclopentenyl group, a cyclohexenyl group, and a cyclopentylideneethenyl group are preferable from the viewpoint of easy synthesis of a monomer compound from which the constitutional unit (a1) is derived.

[0072]

In Formula (a1-r2-3), an aliphatic cyclic group that is formed by Xaa together with Yaa is preferably the group mentioned as the aliphatic hydrocarbon group which is a monocyclic group or a polycyclic group as Ra'³ in Formula (a1-r-1).

In Formula (a1-r2-3), Examples of the aromatic hydrocarbon group as Ra⁰⁴ include a group obtained by removing one or more hydrogen atoms from an aromatic hydrocarbon ring having 5 to 30 carbon atoms. Among them, Ra⁰⁴ is preferably a group obtained by removing one or more hydrogen atoms from an aromatic hydrocarbon ring having 6 to 15 carbon atoms, more preferably a group obtained by removing one or more hydrogen atoms from benzene, naphthalene, anthracene, or phenanthrene, still more preferably a group obtained by removing one or more hydrogen atoms from benzene, naphthalene, or anthracene, particularly preferably a group obtained by removing one or more hydrogen atoms from benzene or naphthalene, and most preferably a group obtained by removing one or more hydrogen atoms from benzene.

[0073]

Examples of the substituent which Ra⁰⁴ in Formula (a1-r2-3) may have include a

methyl group, an ethyl group, propyl group, a hydroxyl group, a carboxyl group, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, and the like), an alkoxy group (a methoxy group, an ethoxy group, a propoxy group, a butoxy group, and the like), and an alkyloxycarbonyl group.

5 [0074]

In Formula (a1-r2-4), Ra'^{12} and Ra'^{13} each independently represents a chain-like saturated hydrocarbon group having 1 to 10 carbon atoms or a hydrogen atom.

Examples of the monovalent chain-like saturated hydrocarbon group having 1 to 10 carbon atoms as Ra'^{12} and Ra'^{13} include the same monovalent chain-like saturated hydrocarbon groups as those having 1 to 10 carbon atoms as Ra^{01} to Ra^{03} as described above. Part or all of the hydrogen atoms which the chain-like saturated hydrocarbon group has may be substituted.

Among them, Ra'^{12} and Ra'^{13} are preferably a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, more preferably an alkyl group having 1 to 5 carbon atoms, still more preferably a methyl group or an ethyl group, and particularly preferably a methyl group.

In a case where the chain-like saturated hydrocarbon groups represented by Ra'^{12} and Ra'^{13} are substituted, examples of the substituent include the same group as Ra^{05} described above.

20 [0075]

In Formula (a1-r2-4), Ra'^{14} represents a hydrocarbon group which may have a substituent. Examples of the hydrocarbon group as Ra'^{14} include a linear or branched alkyl group and a cyclic hydrocarbon group.

[0076]

25 The linear alkyl group as Ra'^{14} preferably has 1 to 5 carbon atoms, more

preferably 1 to 4 carbon atoms, and still more preferably 1 or 2 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, an n-propyl group, an n-butyl group, and an n-pentyl group. Among these, a methyl group, an ethyl group, or an n-butyl group is preferable, and a methyl group or an ethyl group is more preferable.

5 [0077]

The branched alkyl group as Ra'^{14} preferably has 3 to 10 carbon atoms and more preferably 3 to 5 carbon atoms. Specific examples thereof include an isopropyl group, an isobutyl group, a tert-butyl group, an isopentyl group, a neopentyl group, a 1,1-diethylpropyl group, and a 2,2-dimethylbutyl group. Among these, an isopropyl group is preferable.

10

[0078]

In a case where Ra'^{14} represents a cyclic hydrocarbon group, the cyclic hydrocarbon group may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group and may be a polycyclic group or a monocyclic group.

15

As the aliphatic hydrocarbon group which is a monocyclic group, a group in which one hydrogen atom has been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

20

As the aliphatic hydrocarbon group which is a polycyclic group, a group in which one hydrogen atom has been removed from a polycycloalkane is preferable. As the polycycloalkane, a group having 7 to 12 carbon atoms is preferable, and specific examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane.

[0079]

25

As the aromatic hydrocarbon group as Ra''^{14} , the same group as the aromatic

hydrocarbon group as R^{04} can be mentioned. Among them, Ra'^{14} is preferably a group obtained by removing one or more hydrogen atoms from an aromatic hydrocarbon ring having 6 to 15 carbon atoms, more preferably a group obtained by removing one or more hydrogen atoms from benzene, naphthalene, anthracene, or phenanthrene, still more preferably a group obtained by removing one or more hydrogen atoms from benzene, naphthalene, or anthracene, particularly preferably a group obtained by removing one or more hydrogen atoms from naphthalene or anthracene, and most preferably a group obtained by removing one or more hydrogen atoms from naphthalene.

As the substituent which may be included in Ra'^{14} , the same group as the substituent which may be included in Ra^{04} can be mentioned.

[0080]

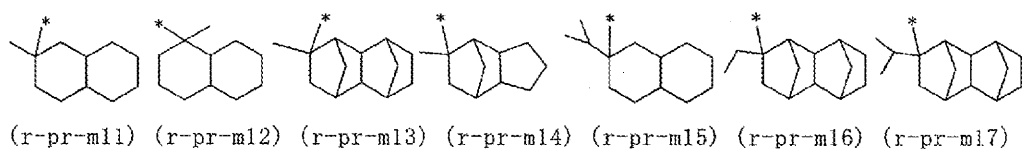
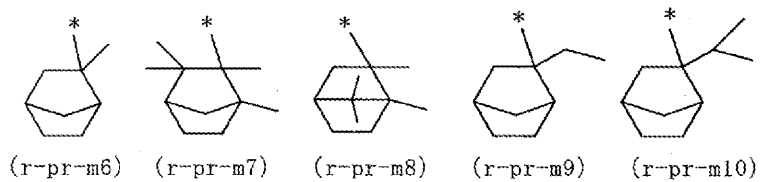
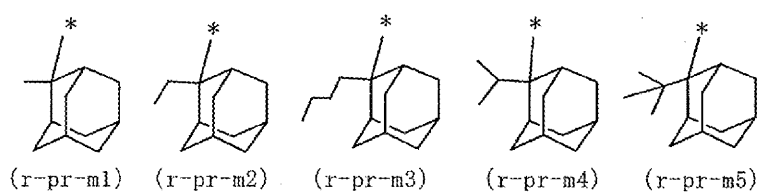
In a case where Ra'^{14} in Formula (a1-r2-4) is a naphthyl group, the position at which the tertiary carbon atom in Formula (a1-r2-4) is bonded is any of the 1-position and the 2-position of the naphthyl group.

In a case where Ra'^{14} in Formula (a1-r2-4) is an anthryl group, the position at which the tertiary carbon atom in Formula (a1-r2-4) is bonded is any of the 1-position, the 2-position, and 9-position of the anthryl group.

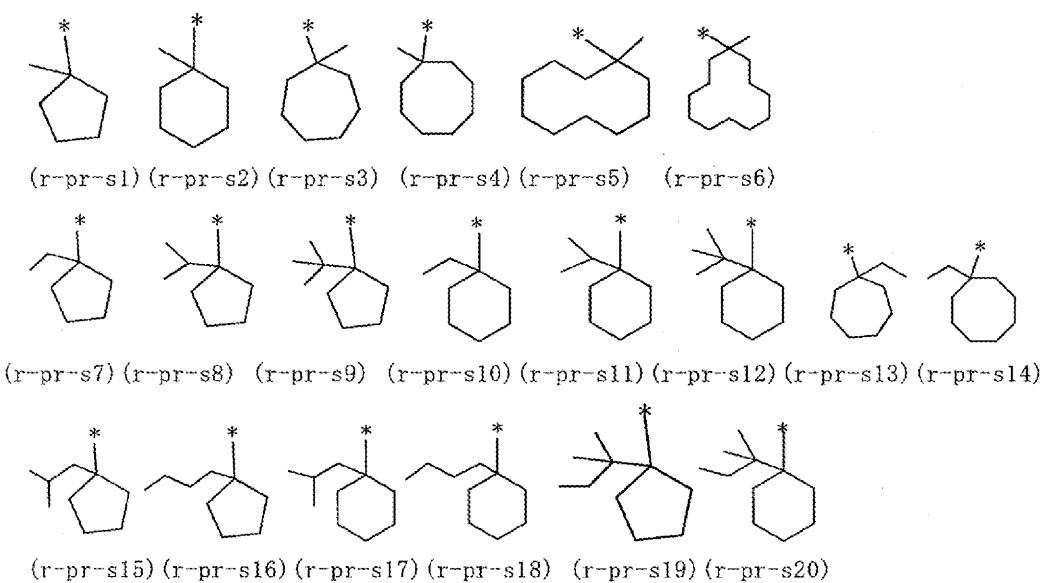
[0081]

Specific examples of the group represented by Formula (a1-r2-1) are shown below.

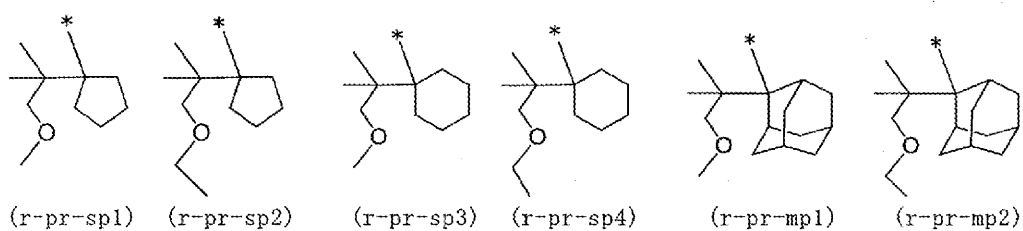
[0082]



[0083]



[0084]

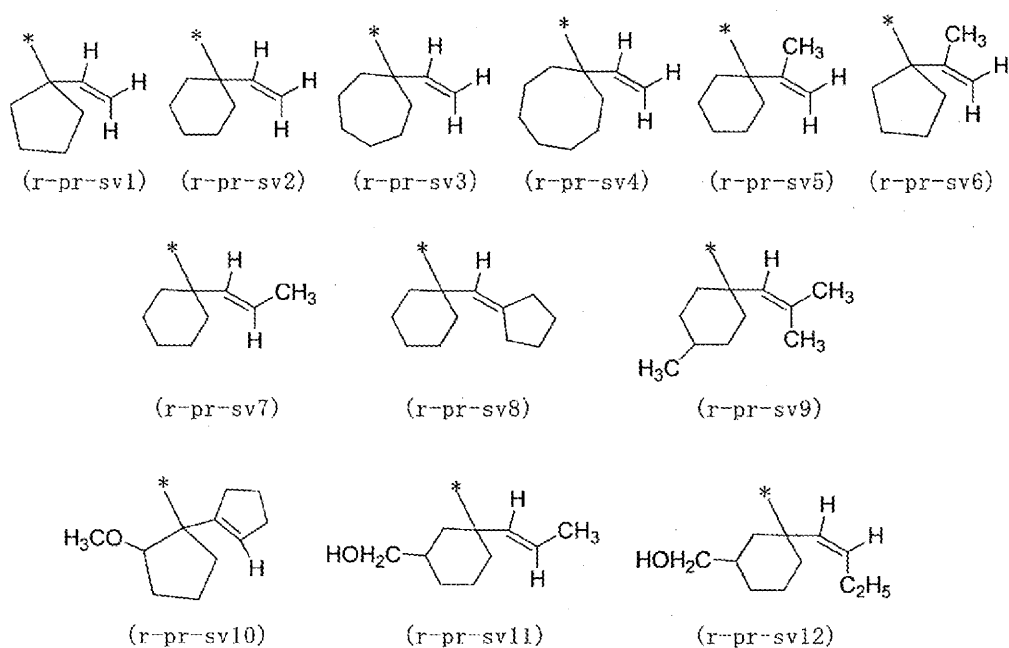


[0085]

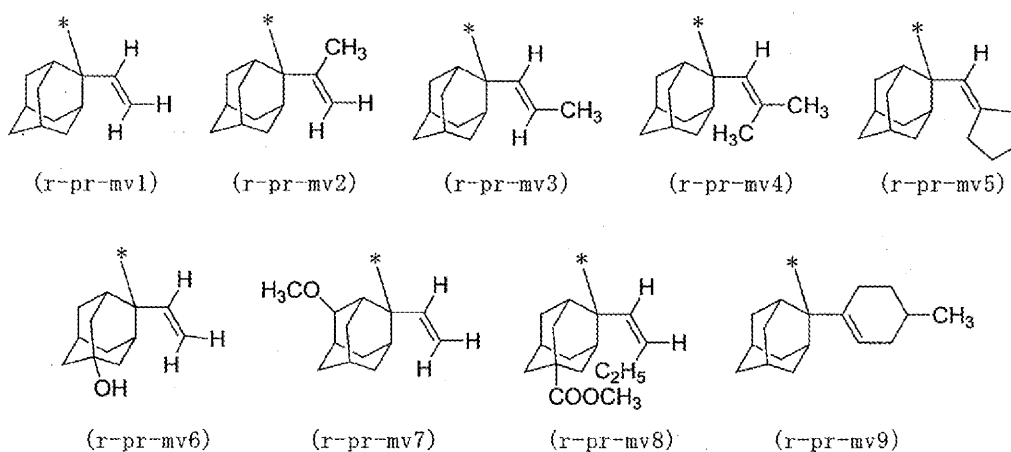
Specific examples of the group represented by Formula (a1-r2-2) are shown below.

5

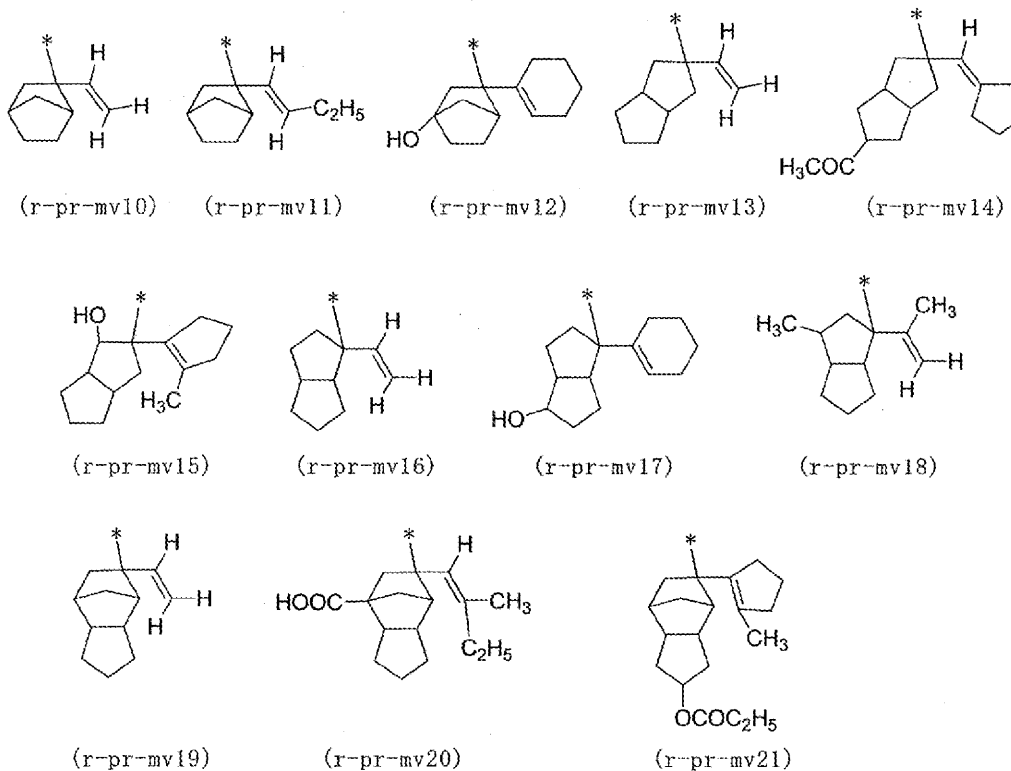
[0086]



[0087]



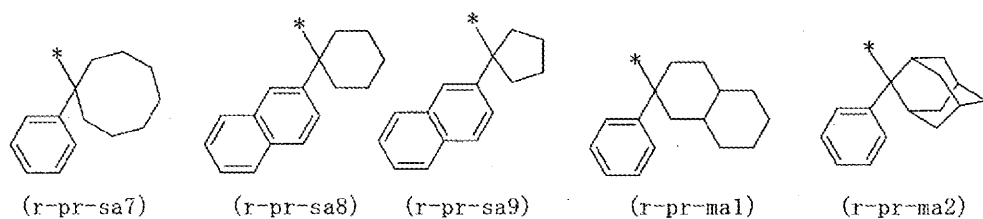
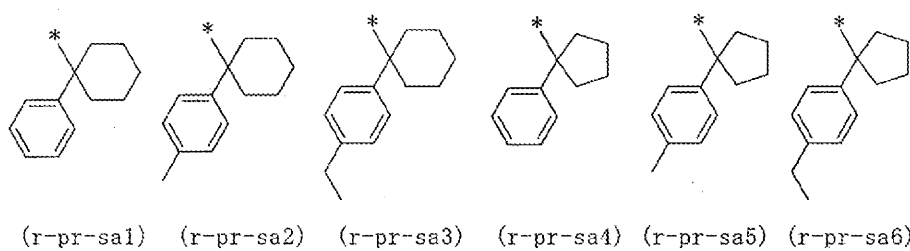
[0088]



[0089]

5 Specific examples of the group represented by Formula (a1-r2-3) are shown below.

[0090]



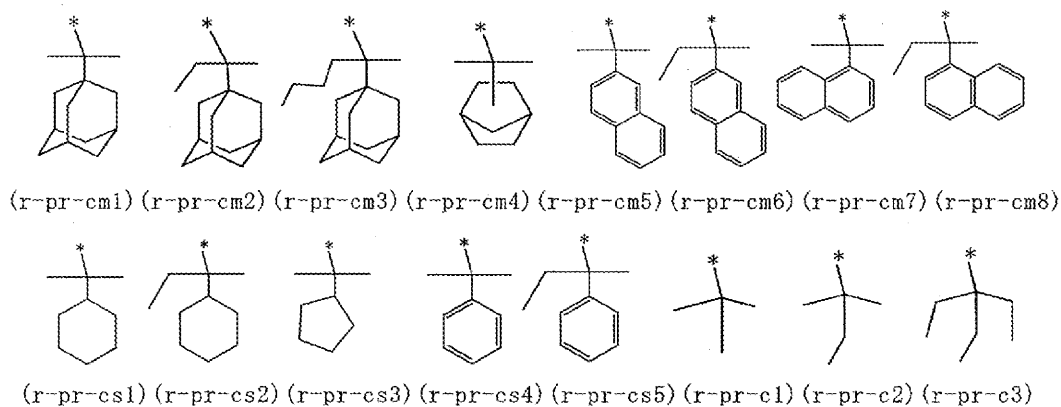
[0091]

Specific examples of the group represented by Formula (a1-r2-4) are shown

below.

5

[0092]



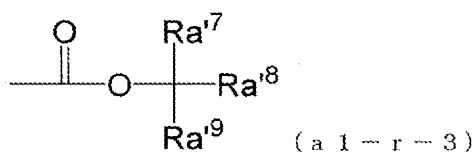
[0093]

Tertiary alkyloxycarbonyl acid-dissociable group:

Examples of the acid-dissociable group for protecting a hydroxyl group as a

10 polar group include an acid-dissociable group (hereinafter, for convenience, also referred to as a "tertiary alkyloxycarbonyl type acid-dissociable group") represented by General Formula (a1-r-3) shown below.

[0094]



[In the formula, Ra'⁷ to Ra'⁹ each represents an alkyl group.]

[0095]

- 5 In Formula (a1-r-3), Ra'⁷ to Ra'⁹ each independently preferably represents an alkyl group having 1 to 5 carbon atoms and more preferably an alkyl group having 1 to 3 carbon atoms.

Further, the total number of carbon atoms in each alkyl group is preferably in a range of 3 to 7, more preferably in a range of 3 to 5, and most preferably 3 or 4.

10 [0096]

The constitutional unit (a1) is preferably a unit including an acid-dissociable group represented by General Formula (a1-r-2) and more preferably a unit including an acid-dissociable group represented by General Formula (a1-r2-4), from the viewpoint of suppressing the decrease in light transmittance of a thick resist film. In General

- 15 Formula (a1-r2-4), Ra'¹² and Ra'¹³ are each independently preferably a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, more preferably an alkyl group having 1 to 3 carbon atoms, still more preferably a methyl group or an ethyl group, and particularly preferably a methyl group. In General Formula (a1-r2-4), Ra'¹⁴ is preferably a
- 20 hydrogen atom or an alkyl group having 1 to 5 carbon atoms, more preferably an alkyl group having 1 to 3 carbon atoms, still more preferably a methyl group or an ethyl group, and particularly preferably a methyl group.

[0097]

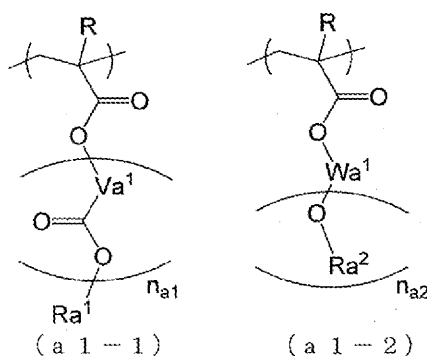
Examples of the constitutional unit (a1) include a constitutional unit derived from acrylic acid ester in which the hydrogen atom bonded to the carbon atom at the α -position may be substituted with a substituent; a constitutional unit derived from acrylamide; a constitutional unit in which at least some hydrogen atoms in a hydroxyl group of a constitutional unit derived from hydroxystyrene or a hydroxystyrene derivative are protected by the substituent including an acid-decomposable group; and a constitutional unit in which some hydrogen atoms in $-C(=O)-OH$ of a constitutional unit derived from vinylbenzoic acid or a vinylbenzoic acid derivative are protected by the substituent including an acid-decomposable group.

10 [0098]

Among the examples, as the constitutional unit (a1), a constitutional unit derived from acrylic acid ester in which the hydrogen atom bonded to the carbon atom at the α -position may be substituted with a substituent is preferable. Preferred specific examples of such a constitutional unit (a1) include constitutional units represented by General

15 Formula (a1-1) or (a1-2).

[0099]



[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Va¹ represents a divalent hydrocarbon group which may have an ether bond. n_{a1} represents an integer

20

of 0 to 2. Ra^1 is an acid-dissociable group represented by General Formula (a1-r-1) or (a1-r-2). Wa^1 represents a $(n_{a2} + 1)$ -valent hydrocarbon group, n_{a2} represents an integer of 1 to 3, and Ra^2 represents an acid-dissociable group represented by General Formula (a1-r-1) or (a1-r-3).]

5 [0100]

In Formula (a1-1), as the alkyl group having 1 to 5 carbon atoms as R, a linear or branched alkyl group having 1 to 5 carbon atoms is preferable, and specific examples thereof include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, and
10 a neopentyl group. The halogenated alkyl group having 1 to 5 carbon atoms is a group in which part or all hydrogen atoms in the alkyl group having 1 to 5 carbon atoms have been substituted with halogen atoms. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom and, an iodine atom, and a fluorine atom is particularly preferable.

15 As R, a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a fluorinated alkyl group having 1 to 5 carbon atoms is preferable, and a hydrogen atom or a methyl group is most preferable in terms of industrial availability.

[0101]

In Formula (a1-1), the divalent hydrocarbon group as Va^1 may be an aliphatic
20 hydrocarbon group or an aromatic hydrocarbon group.

[0102]

The aliphatic hydrocarbon group as the divalent hydrocarbon group represented by Va^1 may be saturated or unsaturated.

In general, it is preferable that the aliphatic hydrocarbon group be saturated.

25 Specific examples of the aliphatic hydrocarbon group include a linear or branched

aliphatic hydrocarbon group, and an aliphatic hydrocarbon group containing a ring in the structure thereof.

[0103]

The linear aliphatic hydrocarbon group described above preferably has 1 to 10
 5 carbon atoms, more preferably 1 to 6 carbon atoms, still more preferably 1 to 4 carbon atoms, and most preferably 1 to 3 carbon atoms. The linear aliphatic hydrocarbon group is preferably a linear alkylene group, and specific examples thereof include a methylene group $[-CH_2-]$, an ethylene group $[-(CH_2)_2-]$, a trimethylene group $[-(CH_2)_3-]$, a tetramethylene group $[-(CH_2)_4-]$, and a pentamethylene group $[-(CH_2)_5-]$.

10 The branched aliphatic hydrocarbon group described above preferably has 2 to 10 carbon atoms, more preferably 3 to 6 carbon atoms, still more preferably 3 or 4 carbon atoms, and most preferably 3 carbon atoms. As the branched aliphatic hydrocarbon group, a branched alkylene group is preferred, and specific examples thereof include alkylalkylene groups, for example, alkylmethylene groups such as $-CH(CH_3)-$, $-CH(CH_2CH_3)-$, $-C(CH_3)_2-$, $-C(CH_3)(CH_2CH_3)-$, $-C(CH_3)(CH_2CH_2CH_3)-$, and $-C(CH_2CH_3)_2-$; alkylethylene groups such as $-CH(CH_3)CH_2-$, $-CH(CH_3)CH(CH_3)-$, $-C(CH_3)_2CH_2-$, $-CH(CH_2CH_3)CH_2-$, and $-C(CH_2CH_3)_2-CH_2-$; alkyltrimethylene groups such as $-CH(CH_3)CH_2CH_2-$, and $-CH_2CH(CH_3)CH_2-$; and alkyltetramethylene groups such as $-CH(CH_3)CH_2CH_2CH_2-$, and $-CH_2CH(CH_3)CH_2CH_2-$. As the alkyl group in the
 15 alkylalkylene group, a linear alkyl group having 1 to 5 carbon atoms is preferable.
 20

[0104]

Examples of the aliphatic hydrocarbon group containing a ring in the structure thereof include an alicyclic hydrocarbon group (a group in which two hydrogen atoms have been removed from an aliphatic hydrocarbon ring), a group in which the alicyclic
 25 hydrocarbon group is bonded to the terminal of the above-described branched aliphatic

hydrocarbon group, and a group in which the alicyclic hydrocarbon group is interposed in the above-described linear or branched aliphatic hydrocarbon group. The linear or branched aliphatic hydrocarbon group is the same as that defined for the above-described linear aliphatic hydrocarbon group or the above-described branched aliphatic

5 hydrocarbon group.

The alicyclic hydrocarbon group preferably has 3 to 20 carbon atoms and more preferably 3 to 12 carbon atoms.

The alicyclic hydrocarbon group may be monocyclic or polycyclic. As the monocyclic alicyclic hydrocarbon group, a group in which two hydrogen atoms have
10 been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane. As the polycyclic alicyclic hydrocarbon group, a group in which two hydrogen atoms have been removed from a polycycloalkane is preferable. As the polycycloalkane, a group having 7 to 12 carbon atoms is preferable. Specific examples
15 of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane.

[0105]

The aromatic hydrocarbon group as the divalent hydrocarbon group represented by Va¹ is a hydrocarbon group having an aromatic ring.

20 The aromatic hydrocarbon group preferably has 3 to 30 carbon atoms, more preferably 5 to 30 carbon atoms, still more preferably 5 to 20 carbon atoms, particularly preferably 6 to 15 carbon atoms, and most preferably 6 to 12 carbon atoms. Here, the number of carbon atoms in a substituent is not included in the number of carbon atoms. Specific examples of the aromatic ring which the aromatic hydrocarbon group has
25 include aromatic hydrocarbon rings such as benzene, biphenyl, fluorene, naphthalene,

anthracene, and phenanthrene; and aromatic hetero rings in which some carbon atoms constituting the above-described aromatic hydrocarbon rings have been substituted with hetero atoms. Examples of the hetero atom in the aromatic hetero rings include an oxygen atom, a sulfur atom, and a nitrogen atom.

5 Specific examples of the aromatic hydrocarbon group include a group in which two hydrogen atoms have been removed from the above-described aromatic hydrocarbon ring (an arylene group); and a group in which one hydrogen atom of a group (an aryl group) formed by removing one hydrogen atom from the aromatic hydrocarbon ring has been substituted with an alkylene group (a group formed by removing one more
10 hydrogen atom from an aryl group in an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group). The alkylene group (an alkyl chain in the arylalkyl group) preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and particularly preferably 1 carbon atom.

15 [0106]

In Formula (a1-1), Ra^1 is an acid-dissociable group represented by Formula (a1-r-1) or (a1-r-2).

[0107]

In Formula (a1-1), n_{a1} is an integer of 0 to 2. n_{a1} is preferably 0 or 1 and more
20 preferably 0.

[0108]

In Formula (a1-2), the $(n_{a2}+1)$ -valent hydrocarbon group as Wa^1 may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group. The aliphatic hydrocarbon group indicates a hydrocarbon group that has no aromaticity, and may be
25 saturated or unsaturated. In general, it is preferable that the aliphatic hydrocarbon group

be saturated. Examples of the aliphatic hydrocarbon group include a linear or branched aliphatic hydrocarbon group, an aliphatic hydrocarbon group containing a ring in the structure thereof, and a combination of the linear or branched aliphatic hydrocarbon group and the aliphatic hydrocarbon group containing a ring in the structure thereof.

- 5 The valency of $n_{a2}+1$ is preferably divalent, trivalent or tetravalent, and divalent or trivalent is more preferable.

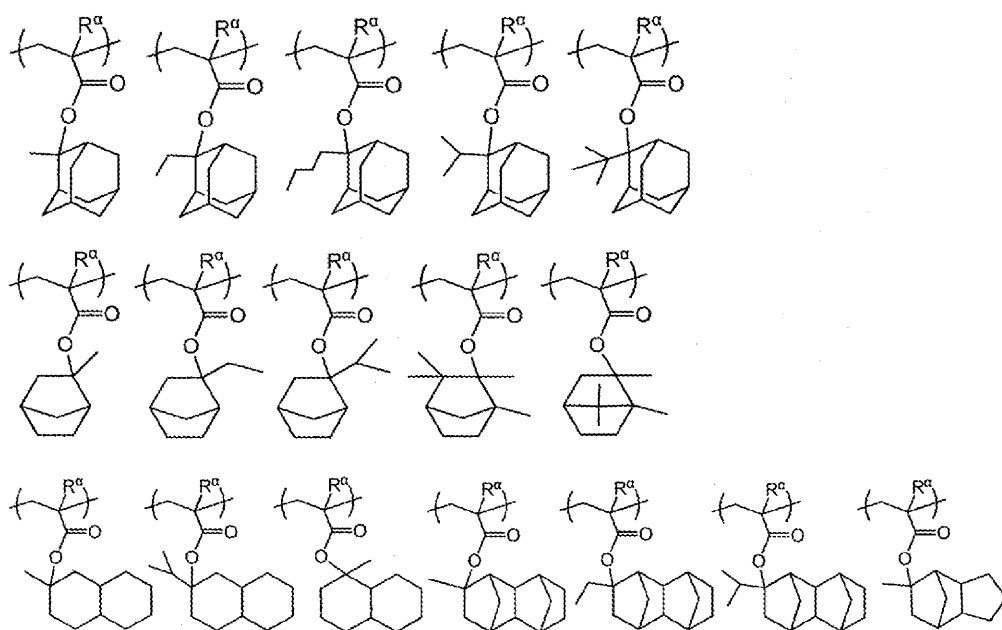
[0109]

In General Formula (a1-2), Ra^2 is an acid-dissociable group represented by Formula (a1-r-1) or (a1-r-3).

10 [0110]

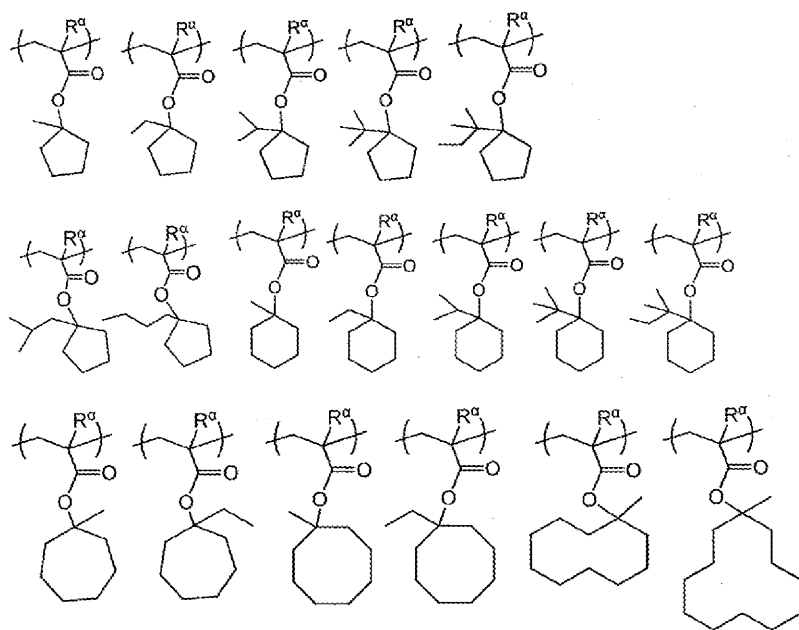
Specific examples of the constitutional unit represented by Formula (a1-1) are shown below. In the formulae shown below, R^a represents a hydrogen atom, a methyl group, or a trifluoromethyl group.

[0111]

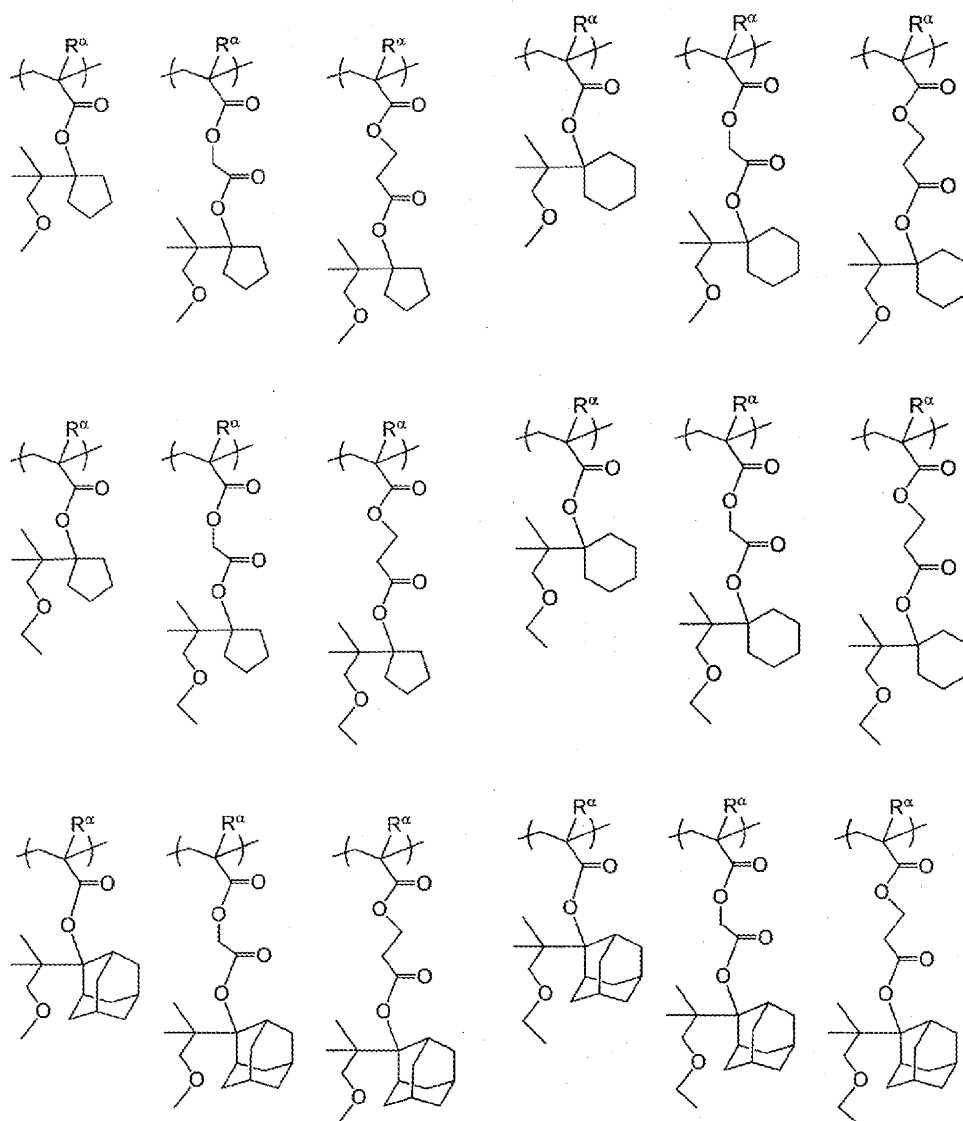


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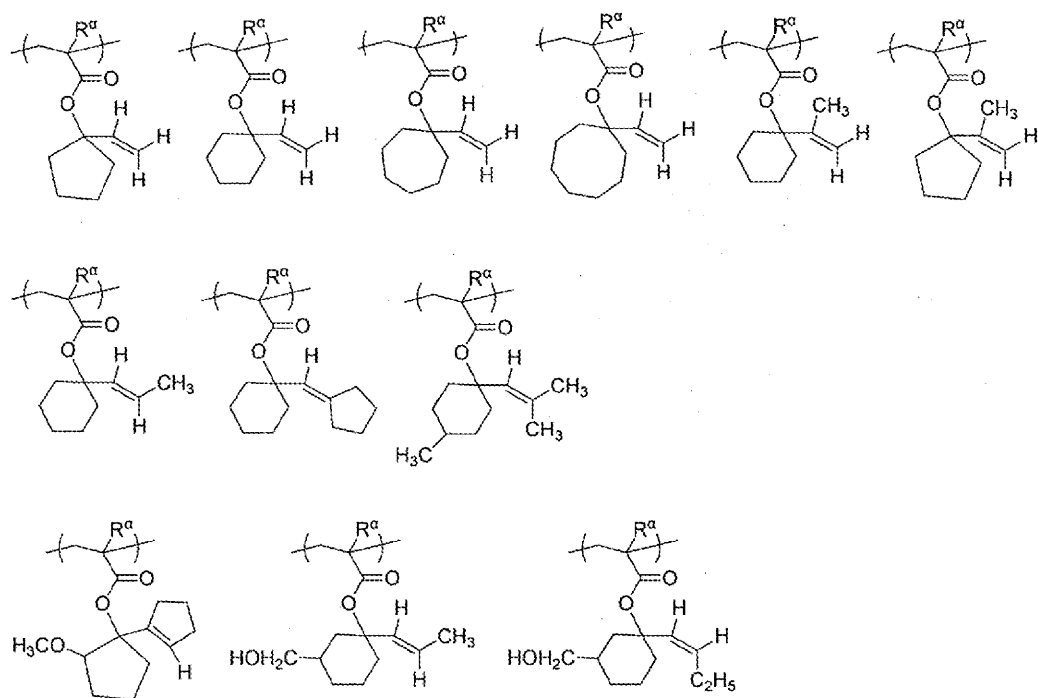
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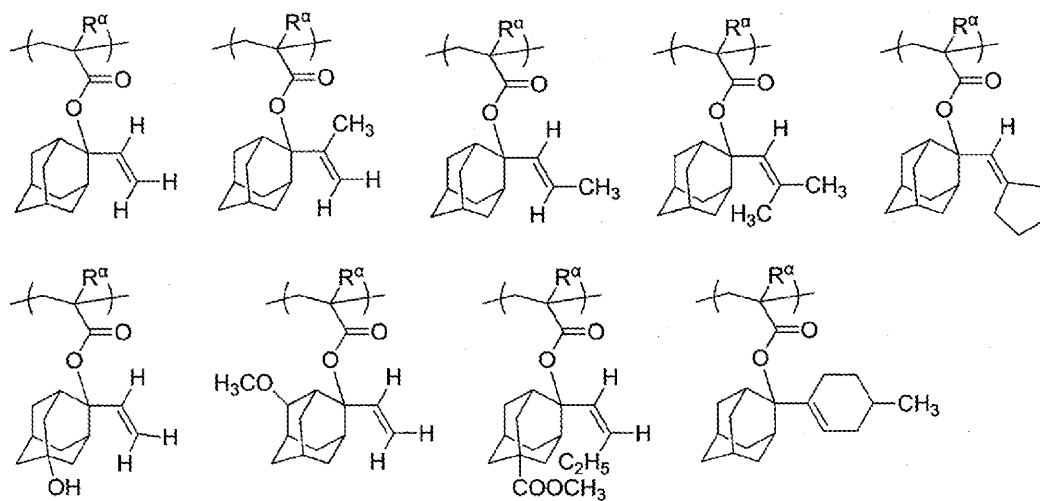
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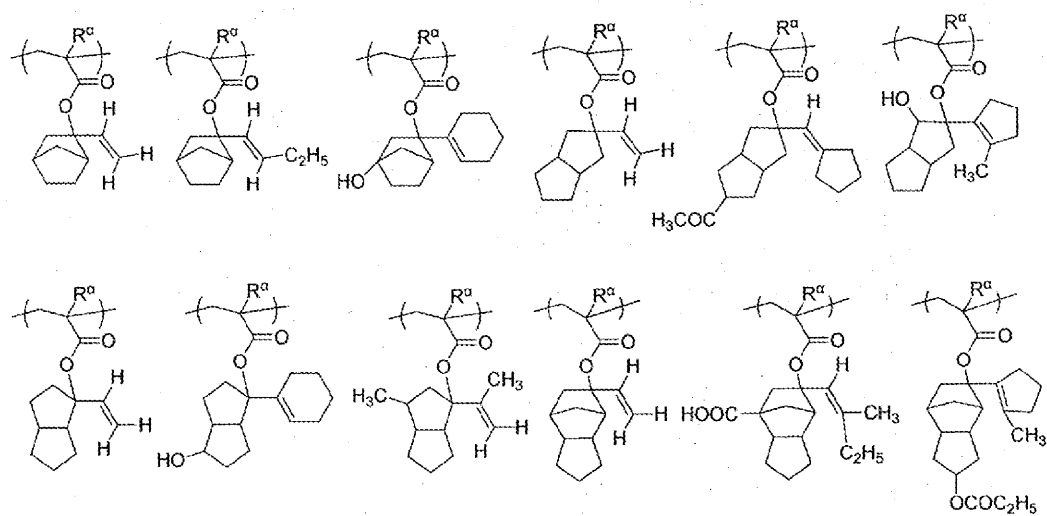
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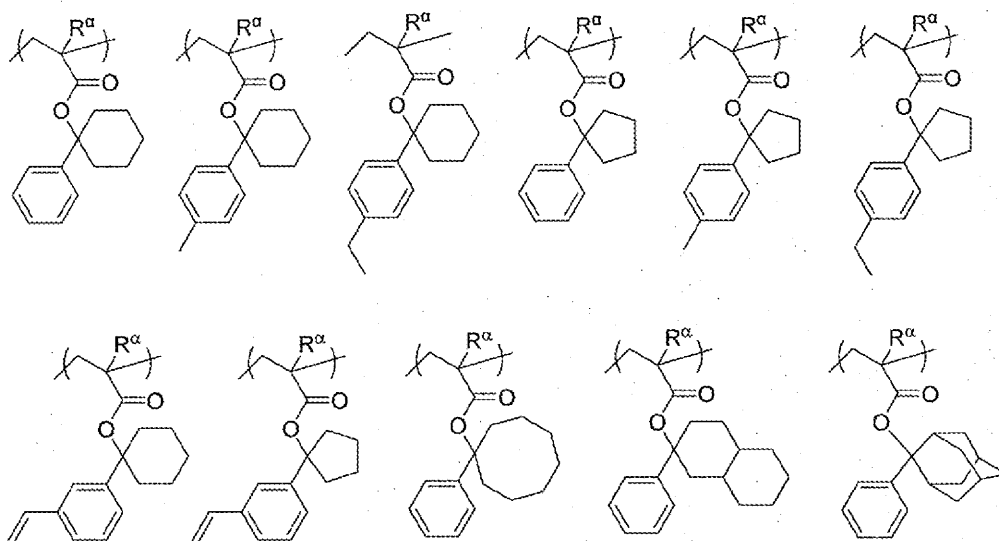
[0115]



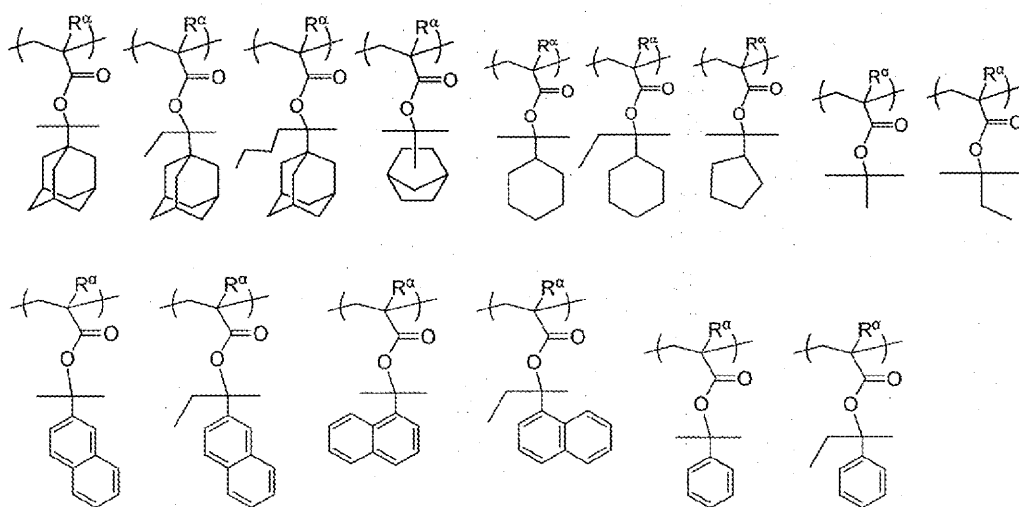
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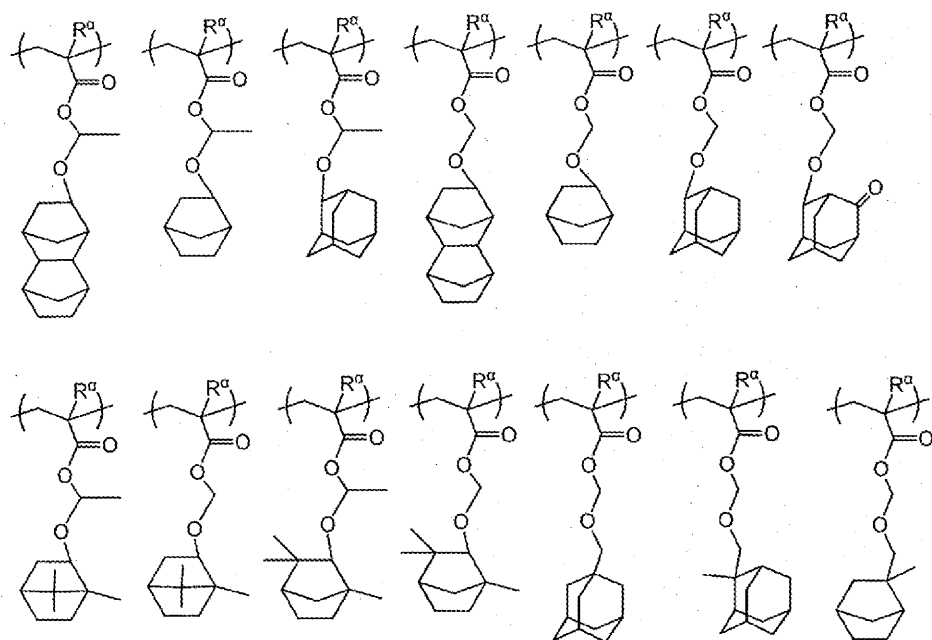
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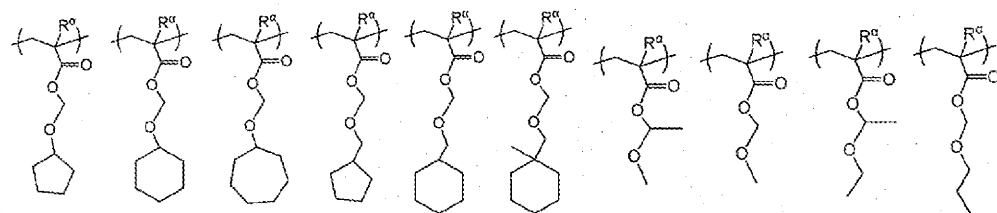
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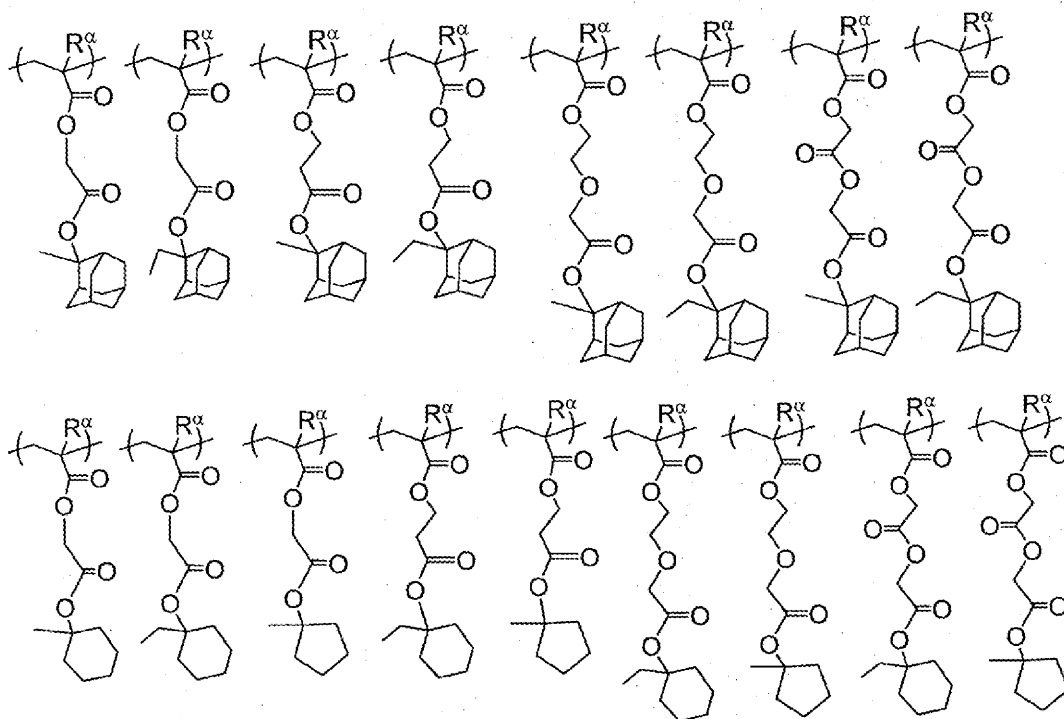
[0119]



[0120]



[0121]

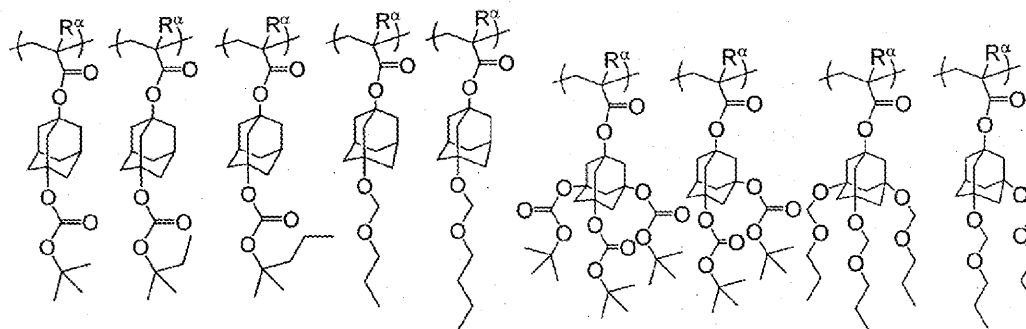


[0122]

Specific examples of the constitutional unit represented by Formula (a1-2) are

5 shown below.

[0123]



[0124]

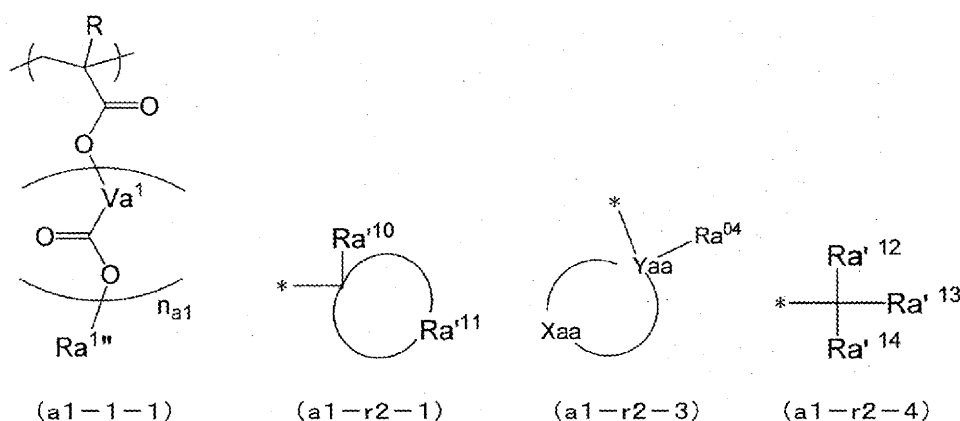
The constitutional unit (a1) which the component (A1) has may be one kind or

10 may be two or more kinds.

The constitutional unit (a1) is more preferably a constitutional unit represented by Formula (a1-1) since lithography characteristics (sensitivity, shape, and the like) in lithography depending on an electron beam or EUV can be more easily increased.

Among them, the constitutional unit (a1) particularly preferably includes a constitutional unit represented by General Formula (a1-1-1) shown below.

[0125]



[In the formula, $Ra^{1''}$ is an acid-dissociable group represented by General Formula (a1-r2-1), (a1-r2-3), or (a1-r2-4).]

[0126]

[In Formula (a1-1-1), R , Va^1 , and n_{a1} are respectively the same as R , Va^1 , and n_{a1} in Formula (a1-1).

The description for the acid-dissociable group represented by General Formula (a1-r2-1), (a1-r2-3), or (a1-r2-4) is as described above. $Ra^{1''}$ is preferably an acid-dissociable group represented by General Formula (a1-r2-4) from the viewpoint of maintaining transparency in a thick resist film. Preferred examples of Ra^{12} , Ra^{13} , and Ra^{14} in General Formula (a1-r2-4) are as described above.

[0127]

The proportion of the constitutional unit (a1) in the component (A1) is

preferably in a range of 5% to 80% by mole, more preferably in a range of 10% to 75% by mole, still more preferably in a range of 30% to 70% by mole, and particularly preferably in a range of 30% to 60% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

5 In a case where the proportion of the constitutional unit (a1) is equal to or more than the lower limit of the preferred range described above, lithography characteristics such as sensitivity, resolution, and roughness are improved. On the other hand, in a case where the proportion is equal to or less than the upper limit of the preferred range, balance with other constitutional units can be obtained, and various lithography
10 characteristics are improved.

[0128]

<<Other constitutional units>>

The component (A1) may have other constitutional units as necessary in addition to the constitutional unit (a1) described above.

15 Examples of other constitutional units include: a constitutional unit (a2) containing a lactone-containing cyclic group, a -SO₂-containing cyclic group, or a carbonate-containing cyclic group; and a constitutional unit (a3) containing a polar group-containing aliphatic hydrocarbon group; a constitutional unit (a4) containing an acid non-dissociable aliphatic cyclic group; a constitutional unit (a10) represented by
20 General Formula (a10-1) described later; and a constitutional unit (st) derived from styrene or a derivative thereof.

[0129]

In regard to constitutional unit (a2):

The component (A1) may further have, as necessary, a constitutional unit (a2)
25 (provided that a group having the constitutional unit (a1) is excluded) containing a

lactone-containing cyclic group, a -SO₂--containing cyclic group, or a carbonate-containing cyclic group, in addition to the constitutional unit (a1).

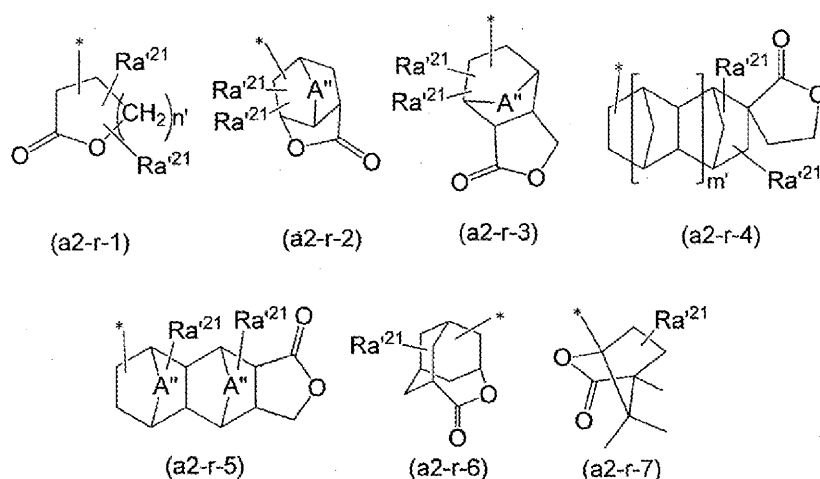
In a case where the component (A1) is used for forming a resist film, the lactone-containing cyclic group, the -SO₂--containing cyclic group, or the carbonate-containing cyclic group in the constitutional unit (a2) is effective for improving the adhesiveness of the resist film to the substrate. Further, due to having the constitutional unit (a2), lithography characteristics can be improved, for example, by the effects obtained by appropriately adjusting the acid diffusion length, increasing the adhesiveness of the resist film to the substrate, and appropriately adjusting the solubility during development.

[0130]

The term “lactone-containing cyclic group” indicates a cyclic group that contains a ring (lactone ring) containing a -O-C(=O)- in the ring skeleton. In a case where the lactone ring is counted as the first ring and the group contains only the lactone ring, the group is referred to as a monocyclic group. Further, in a case where the group has other ring structures, the group is referred to as a polycyclic group regardless of the structures. The lactone-containing cyclic group may be a monocyclic group or a polycyclic group.

The lactone-containing cyclic group for the constitutional unit (a2) is not particularly limited, and an optional constitutional unit may be used. Specific examples thereof include groups each represented by General Formulae (a2-r-1) to (a2-r-7) shown below.

[0131]



[In the formulae, each Ra'^{21} independently represents a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, -COOR'', -OC(=O)R'', a hydroxyalkyl group, or a cyano group; R'' represents a hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group, or a -SO₂--containing cyclic group; A'' represents an oxygen atom, a sulfur atom, or an alkylene group having 1 to 5 carbon atoms, which may contain an oxygen (-O-) atom or a sulfur atom (-S-); and n' represents an integer of 0 to 2, and m' is 0 or 1.]

[0132]

In General Formulae (a2-r-1) to (a2-r-7), the alkyl group as Ra'^{21} is preferably an alkyl group having 1 to 6 carbon atoms. The alkyl group is preferably a linear alkyl group or a branched alkyl group. Specific examples thereof include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, a neopentyl group, and a hexyl group. Among these, a methyl group or ethyl group is preferable, and a methyl group is particularly preferable.

The alkoxy group as Ra'^{21} is preferably an alkoxy group having 1 to 6 carbon atoms. Further, the alkoxy group is preferably a linear or branched alkoxy group.

Specific examples of the alkoxy groups include a group formed by linking the above-described alkyl group mentioned as the alkyl group represented by Ra'^{21} to an oxygen atom (-O-).

Examples of the halogen atom as Ra'^{21} include a fluorine atom, a chlorine atom,
5 a bromine atom, and an iodine atom. Among these, a fluorine atom is preferable.

Examples of the halogenated alkyl group as Ra'^{21} include groups in which part or all hydrogen atoms in the above-described alkyl group as Ra'^{21} have been substituted with the above-described halogen atoms. As the halogenated alkyl group, a fluorinated alkyl group is preferable, and a perfluoroalkyl group is particularly preferable.

10 [0133]

In -COOR'' and -OC(=O)R'' as Ra'^{21} , R'' represents a hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group, or a -SO₂-containing cyclic group.

The alkyl group as R'' may be linear, branched, or cyclic, and preferably has 1 to
15 15 carbon atoms.

In a case where R'' represents a linear or branched alkyl group, it is preferably an alkyl group having 1 to 10 carbon atoms, more preferably an alkyl group having 1 to 5 carbon atoms, and particularly preferably a methyl group or an ethyl group.

In a case where R'' represents a cyclic alkyl group, the number of carbon atoms
20 thereof is preferably in a range of 3 to 15, more preferably in a range of 4 to 12, and particularly preferably in a range of 5 to 10. Specific examples thereof include groups in which one or more hydrogen atoms have been removed from a monocycloalkane, which may or may not be substituted with a fluorine atom or a fluorinated alkyl group; and groups in which one or more hydrogen atoms have been removed from a
25 polycycloalkane such as bicycloalkane, tricycloalkane, or tetracycloalkane. More

specific examples thereof include groups in which one or more hydrogen atoms have been removed from a monocycloalkane such as cyclopentane or cyclohexane; and groups in which one or more hydrogen atoms have been removed from a polycycloalkane such as adamantane, norbornane, isobornane, tricyclodecane, or tetracyclododecane.

5 Examples of the lactone-containing cyclic group as R'' include the same groups as those each represented by General Formulae (a2-r-1) to (a2-r-7).

 The carbonate-containing cyclic group as R'' has the same definition as that for the carbonate-containing cyclic group described below. Specific examples of the carbonate-containing cyclic group include groups each represented by General Formulae
10 (ax3-r-1) to (ax3-r-3).

 The -SO₂--containing cyclic group as R'' has the same definition as that for the -SO₂--containing cyclic group described below. Specific examples of the -SO₂--containing cyclic group include groups each represented by General Formulae (a5-r-1) to (a5-r-4).

15 The hydroxyalkyl group as Ra'²¹ preferably has 1 to 6 carbon atoms, and specific examples thereof include a group in which at least one hydrogen atom in the alkyl group as Ra'²¹ has been substituted with a hydroxyl group.

[0134]

 In General Formulae (a2-r-2), (a2-r-3) and (a2-r-5), as the alkylene group having
20 1 to 5 carbon atoms as A'', a linear or branched alkylene group is preferable, and examples thereof include a methylene group, an ethylene group, an n-propylene group, and an isopropylene group. Specific examples of the alkylene groups that contain an oxygen atom or a sulfur atom include groups in which -O- or -S- is interposed in the terminal of the alkylene group or between the carbon atoms of the alkylene group, and
25 examples thereof include -O-CH₂-, -CH₂-O-CH₂-, -S-CH₂-, and -CH₂-S-CH₂-. As A'',

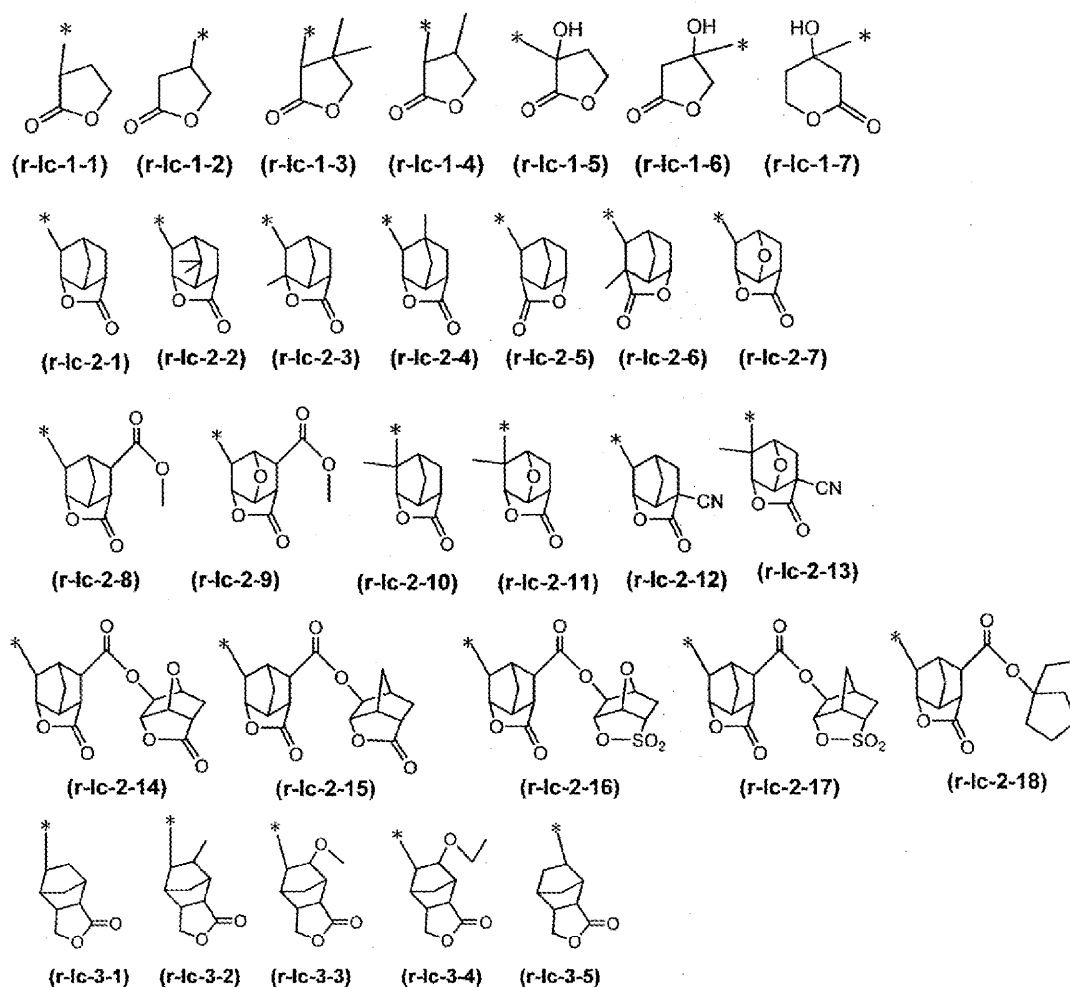
an alkylene group having 1 to 5 carbon atoms or -O- is preferable, an alkylene group having 1 to 5 carbon atoms is more preferable, and a methylene group is most preferable.

[0135]

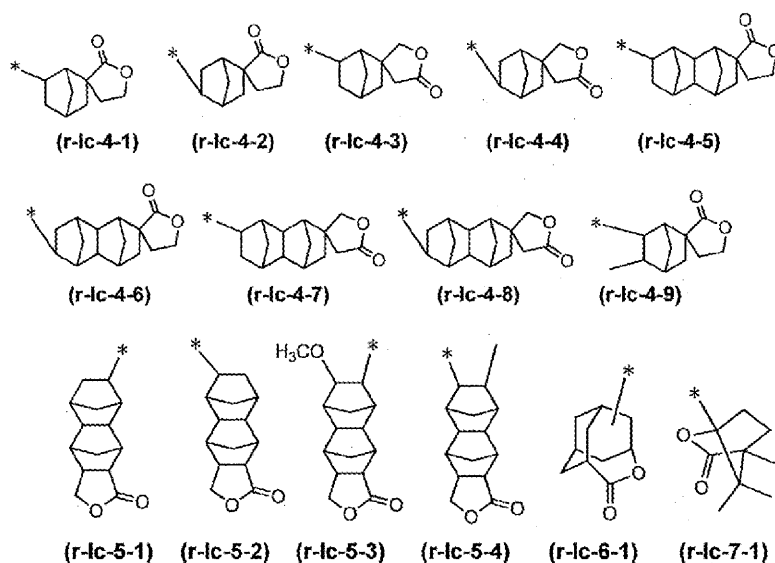
Specific examples of the groups each represented by General Formulae (a2-r-1)

5 to (a2-r-7) are shown below.

[0136]



[0137]



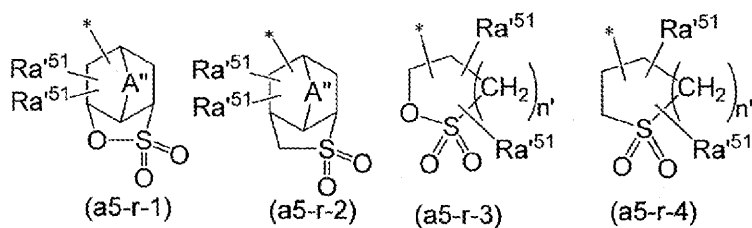
[0138]

The "-SO₂--containing cyclic group" indicates a cyclic group having a ring containing -SO₂- in the ring skeleton thereof. Specifically, the -SO₂--containing cyclic group is a cyclic group in which the sulfur atom (S) in -SO₂- forms a part of the ring skeleton of the cyclic group. In a case where the ring containing -SO₂- in the ring skeleton thereof is counted as the first ring and the group contains only the ring, the group is referred to as a monocyclic group. Further, in a case where the group has other ring structures, the group is referred to as a polycyclic group regardless of the structures.

- 10 The -SO₂--containing cyclic group may be a monocyclic group or a polycyclic group. As the -SO₂--containing cyclic group, a cyclic group containing -O-SO₂- in the ring skeleton thereof, in other words, a cyclic group containing a sultone ring in which -O-S- in the -O-SO₂- group forms a part of the ring skeleton thereof is particularly preferable.

- 15 More specific examples of the -SO₂--containing cyclic group include groups each represented by General Formulae (a5-r-1) to (a5-r-4) shown below.

[0139]



[In the formulae, each Ra'^{51} independently represents a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, -COOR'', -OC(=O)R'', a hydroxyalkyl group, or a cyano group; R'' represents a hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group, or a -SO₂--containing cyclic group; A'' represents an oxygen atom, a sulfur atom, or an alkylene group having 1 to 5 carbon atoms, which may contain an oxygen atom or a sulfur atom; and n' represents an integer of 0 to 2.]

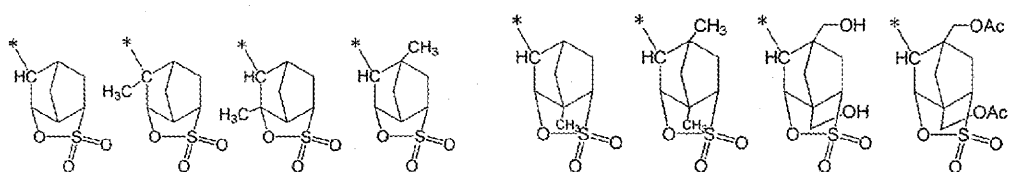
[0140]

10 In General Formulae (a5-r-1) and (a5-r-2), A'' has the same definition as that for A'' in General Formulae (a2-r-2), (a2-r-3) and (a2-r-5).

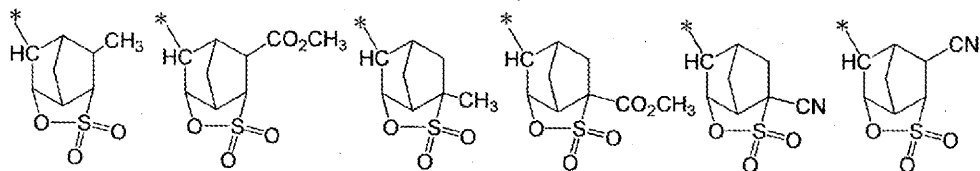
Examples of the alkyl group, the alkoxy group, the halogen atom, the halogenated alkyl group, -COOR'', -OC(=O)R'', and the hydroxyalkyl group as Ra'^{51} include the same groups as those described above in the explanation of Ra'^{21} in General Formulae (a2-r-1) to (a2-r-7).

Specific examples of the groups each represented by General Formulae (a5-r-1) to (a5-r-4) are shown below. In the formulae shown below, "Ac" represents an acetyl group.

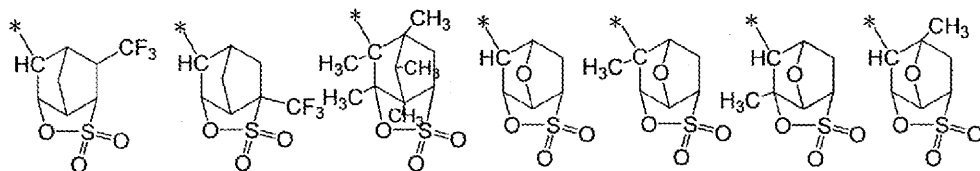
[0141]



(r-sl-1-1) (r-sl-1-2) (r-sl-1-3) (r-sl-1-4) (r-sl-1-5) (r-sl-1-6) (r-sl-1-7) (r-sl-1-8)

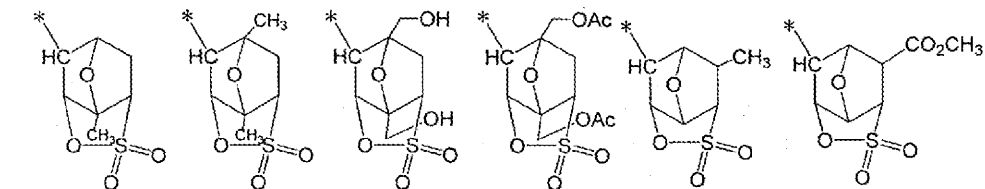


(r-sl-1-9) (r-sl-1-10) (r-sl-1-11) (r-sl-1-12) (r-sl-1-13) (r-sl-1-14)

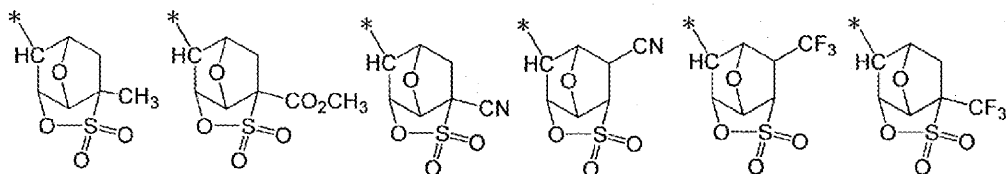


(r-sl-1-15) (r-sl-1-16) (r-sl-1-17) (r-sl-1-18) (r-sl-1-19) (r-sl-1-20) (r-sl-1-21)

[0142]

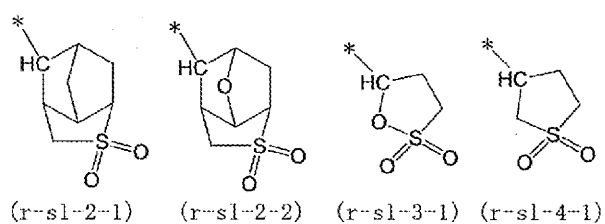


(r-sl-1-22) (r-sl-1-23) (r-sl-1-24) (r-sl-1-25) (r-sl-1-26) (r-sl-1-27)



(r-sl-1-28) (r-sl-1-29) (r-sl-1-30) (r-sl-1-31) (r-sl-1-32) (r-sl-1-33)

[0143]

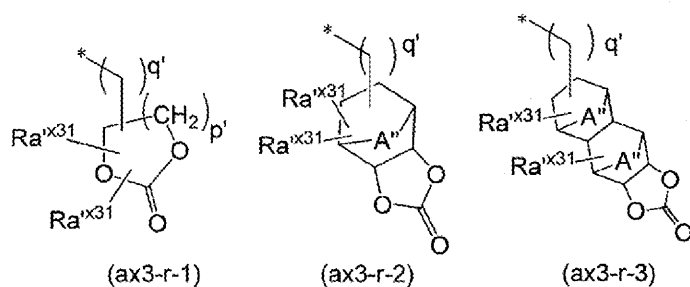


[0144]

The "carbonate-containing cyclic group" indicates a cyclic group having a ring (a carbonate ring) containing -O-C(=O)-O- in the ring skeleton thereof. In a case where the carbonate ring is counted as the first ring and the group contains only the carbonate ring, the group is referred to as a monocyclic group. Further, in a case where the group has other ring structures, the group is referred to as a polycyclic group regardless of the structures. The carbonate-containing cyclic group may be a monocyclic group or a polycyclic group.

The carbonate ring-containing cyclic group is not particularly limited, and an optional group may be used. Specific examples thereof include groups each represented by General Formulae (ax3-r-1) to (ax3-r-3) shown below.

[0145]



[In the formulae, each $\text{Ra}'^{\text{x}31}$ independently represents a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, -COOR'' , -OC(=O)R'' , a hydroxyalkyl group, or a cyano group; R'' represents a hydrogen

atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group, or a $\text{-SO}_2\text{-}$ -containing cyclic group; A'' represents an oxygen atom, a sulfur atom, or an alkylene group having 1 to 5 carbon atoms, which may contain an oxygen atom or a sulfur atom; and p' represents an integer of 0 to 3, and q' is 0 or 1.]

5 [0146]

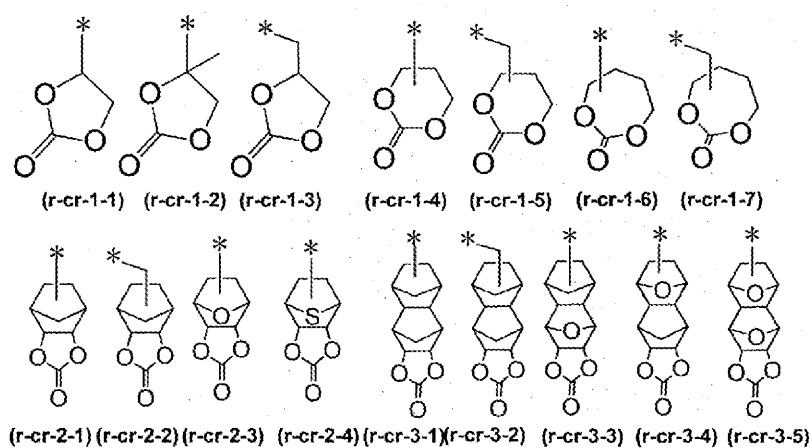
In General Formulae (ax3-r-2) and (ax3-r-3), A'' has the same definition as that for A'' in General Formulae (a2-r-2), (a2-r-3) and (a2-r-5).

Examples of the alkyl group, the alkoxy group, the halogen atom, the halogenated alkyl group, -COOR'' , -OC(=O)R'' , and the hydroxyalkyl group as Ra^{31}

10 include the same groups as those described above in the explanation of Ra^{21} in General Formulae (a2-r-1) to (a2-r-7).

Specific examples of the groups each represented by General Formulae (ax3-r-1) to (ax3-r-3) are shown below.

[0147]



15

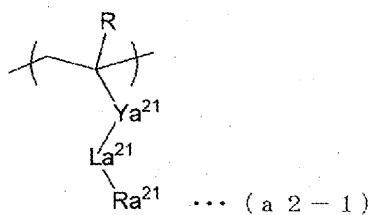
[0148]

As the constitutional unit (a2), a constitutional unit derived from acrylic acid ester in which the hydrogen atom bonded to the carbon atom at the α -position may be

substituted with a substituent is preferable.

The constitutional unit (a2) is preferably a constitutional unit represented by General Formula (a2-1).

[0149]



5

[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Ya^{21} represents a single bond or a divalent linking group. La^{21} represents -O-, -COO-, -CON(R')-, -OCO-, -CONHCO- or -CONHCS-, and R' represents a hydrogen atom or a methyl group. However, in a case where La^{21} represents -O-, Ya^{21} does not represent -CO-. Ra^{21} represents a lactone-containing cyclic group, a carbonate-containing cyclic group, or a -SO₂--containing cyclic group.]

10

[0150]

In Formula (a2-1), R has the same definition as described above. As R, a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a fluorinated alkyl group having 1 to 5 carbon atoms is preferable, and a hydrogen atom or a methyl group is particularly preferable in terms of industrial availability.

15

[0151]

In Formula (a2-1), the divalent linking group as Ya^{21} is not particularly limited, and suitable examples thereof include a divalent hydrocarbon group which may have a substituent and a divalent linking group having hetero atoms.

20

[0152]

· Divalent hydrocarbon group which may have substituent:

In a case where Y^{a21} represents a divalent hydrocarbon group which may have a substituent, the hydrocarbon group may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

5 [0153]

· Aliphatic hydrocarbon group as Y^{a21}

The aliphatic hydrocarbon group indicates a hydrocarbon group that has no aromaticity. The aliphatic hydrocarbon group may be saturated or unsaturated. In general, it is preferable that the aliphatic hydrocarbon group be saturated. Examples of
10 the aliphatic hydrocarbon group include a linear or branched aliphatic hydrocarbon group, and an aliphatic hydrocarbon group containing a ring in the structure thereof.

[0154]

·· Linear or branched aliphatic hydrocarbon group

The linear aliphatic hydrocarbon group preferably has 1 to 10 carbon atoms,
15 more preferably 1 to 6 carbon atoms, still more preferably 1 to 4 carbon atoms, and most preferably 1 to 3 carbon atoms.

The linear aliphatic hydrocarbon group is preferably a linear alkylene group, and specific examples thereof include a methylene group $[-CH_2-]$, an ethylene group $[-(CH_2)_2-]$, a trimethylene group $[-(CH_2)_3-]$, a tetramethylene group $[-(CH_2)_4-]$, and a
20 pentamethylene group $[-(CH_2)_5-]$.

The branched aliphatic hydrocarbon group preferably has 2 to 10 carbon atoms, more preferably 3 to 6 carbon atoms, still more preferably 3 or 4 carbon atoms, and most preferably 3 carbon atoms.

As the branched aliphatic hydrocarbon group, a branched alkylene group is
25 preferred, and specific examples thereof include alkylalkylene groups, for example,

alkylmethylene groups such as $-\text{CH}(\text{CH}_3)-$, $-\text{CH}(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_3)-$, and $-\text{C}(\text{CH}_2\text{CH}_3)_2-$; alkylethylene groups such as $-\text{CH}(\text{CH}_3)\text{CH}_2-$, $-\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2\text{CH}_2-$, $-\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2-$, and $-\text{C}(\text{CH}_2\text{CH}_3)_2\text{CH}_2-$; alkyltrimethylene groups such as $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-$, and $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$; and alkyltetramethylene groups such as $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2-$, and $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-$. As the alkyl group in the alkylalkylene group, a linear alkyl group having 1 to 5 carbon atoms is preferable.

[0155]

The linear or branched aliphatic hydrocarbon group may or may not have a substituent. Examples of the substituent include a fluorine atom, a fluorinated alkyl group having 1 to 5 carbon atoms, which has been substituted with a fluorine atom, and a carbonyl group.

[0156]

... Aliphatic hydrocarbon group containing ring in structure thereof

Examples of the aliphatic hydrocarbon group containing a ring in the structure thereof include a cyclic aliphatic hydrocarbon group which may have a substituent containing a hetero atom in the ring structure thereof (a group in which two hydrogen atoms have been removed from an aliphatic hydrocarbon ring), a group in which the cyclic aliphatic hydrocarbon group is bonded to the terminal of a linear or branched aliphatic hydrocarbon group, and a group in which the cyclic aliphatic hydrocarbon group is interposed in a linear or branched aliphatic hydrocarbon group. As the linear or branched aliphatic hydrocarbon group, the same groups as those described above can be mentioned.

The cyclic aliphatic hydrocarbon group preferably has 3 to 20 carbon atoms and more preferably 3 to 12 carbon atoms.

The cyclic aliphatic hydrocarbon group may be a polycyclic group or a monocyclic group. As the monocyclic alicyclic hydrocarbon group, a group in which two hydrogen atoms have been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane. As the polycyclic alicyclic hydrocarbon group, a group in which two hydrogen atoms have been removed from a polycycloalkane is preferable. As the polycycloalkane, a group having 7 to 12 carbon atoms is preferable. Examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane.

10 [0157]

The cyclic aliphatic hydrocarbon group may or may not have a substituent. Examples of the substituent include an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, and a carbonyl group.

The alkyl group as the substituent is preferably an alkyl group having 1 to 5 carbon atoms, and a methyl group, an ethyl group, a propyl group, an n-butyl group, or a tert-butyl group is most preferable.

The alkoxy group as the substituent is preferably an alkoxy group having 1 to 5 carbon atoms, more preferably a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group, or a tert-butoxy group, and still more preferably a methoxy group or an ethoxy group.

Examples of the halogen atom as the substituent include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom, and a fluorine atom is preferable.

Examples of the halogenated alkyl group as the substituent include groups in which part or all hydrogen atoms in the above-described alkyl groups have been substituted with the above-described halogen atoms.

In the cyclic aliphatic hydrocarbon group, some carbon atoms constituting the ring structure thereof may be substituted with a substituent containing a hetero atom. As the substituent containing a hetero atom, -O-, -C(=O)-O-, -S-, -S(=O)₂-, or -S(=O)₂-O- is preferable.

5 [0158]

·· Aromatic hydrocarbon group as Ya²¹

The aromatic hydrocarbon group is a hydrocarbon group having at least one aromatic ring.

The aromatic ring is not particularly limited as long as it is a cyclic conjugated system having $(4n + 2) \pi$ electrons, and may be monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, still more preferably 6 to 15 carbon atoms, and particularly preferably 6 to 12 carbon atoms. Here, the number of carbon atoms in a substituent is not included in the number of carbon atoms.

15 Specific examples of the aromatic ring include aromatic hydrocarbon rings such as benzene, naphthalene, anthracene, and phenanthrene; and aromatic hetero rings in which some carbon atoms constituting the above-described aromatic hydrocarbon rings have been substituted with hetero atoms. Examples of the hetero atom in the aromatic hetero rings include an oxygen atom, a sulfur atom, and a nitrogen atom. Specific examples of the aromatic hetero ring include a pyridine ring and a thiophene ring.

Specific examples of the aromatic hydrocarbon group include a group in which two hydrogen atoms have been removed from the above-described aromatic hydrocarbon ring or aromatic hetero ring (an arylene group or a heteroarylene group); a group in which two hydrogen atoms have been removed from an aromatic compound having two or more aromatic rings (such as biphenyl or fluorene); and a group in which one

hydrogen atom of a group (an aryl group or a heteroaryl group) obtained by removing one hydrogen atom from the above-described aromatic hydrocarbon ring or aromatic hetero ring has been substituted with an alkylene group (for example, a group obtained by further removing one hydrogen atom from an aryl group in an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group). The number of carbon atoms in the alkylene group bonded to the aryl group or the heteroaryl group is preferably in a range of 1 to 4, more preferably 1 or 2, and particularly preferably 1.

[0159]

With respect to the aromatic hydrocarbon group, the hydrogen atom which the aromatic hydrocarbon group has may be substituted with a substituent. For example, the hydrogen atom bonded to the aromatic ring in the aromatic hydrocarbon group may be substituted with a substituent. Examples of substituents include an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, and a hydroxyl group.

The alkyl group as the substituent is preferably an alkyl group having 1 to 5 carbon atoms, and a methyl group, an ethyl group, a propyl group, an n-butyl group, or a tert-butyl group is most preferable.

As the alkoxy group, the halogen atom, and the halogenated alkyl group as the substituents, the same groups as the above-described substituents for substituting a hydrogen atom which the cyclic aliphatic hydrocarbon group has can be mentioned.

[0160]

· Divalent linking group containing hetero atom

In a case where $Y_{a^{21}}$ represents a divalent linking group containing a hetero atom, preferred examples of the linking group include -O-, -C(=O)-O-, -O-C(=O)-, -C(=O)-, -O-C(=O)-O-, -C(=O)-NH-, -NH-, -NH-C(=NH)- (H may be substituted with a

substituent such as an alkyl group, an acyl group, or the like), -S-, -S(=O)₂-, -S(=O)₂-O-, and a group represented by General Formula: -Y²¹-O-Y²²-, -Y²¹-O-, -Y²¹-C(=O)-O-, -C(=O)-O-Y²¹-, -[Y²¹-C(=O)-O]_m-, -Y²²-, -Y²¹-O-C(=O)-Y²²- or -Y²¹-S(=O)₂-O-Y²²- [in the formulae, Y²¹ and Y²² each independently represents a divalent hydrocarbon group which may have a substituent, O represents an oxygen atom, and m'' represents an integer of 0 to 3].

In a case where the divalent linking group containing a hetero atom is -C(=O)-NH-, -C(=O)-NH-C(=O)-, -NH-, or -NH-C(=NH)-, H may be substituted with a substituent such as an alkyl group, an acyl group, or the like. The substituent (an alkyl group, an acyl group, or the like) preferably has 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms, and most preferably 1 to 5 carbon atoms.

In General Formula -Y²¹-O-Y²²-, -Y²¹-O-, -Y²¹-C(=O)-O-, -C(=O)-O-Y²¹-, -[Y²¹-C(=O)-O]_m-, -Y²²-, -Y²¹-O-C(=O)-Y²²-, or -Y²¹-S(=O)₂-O-Y²²-, Y²¹, and Y²² each independently represents a divalent hydrocarbon group which may have a substituent. Examples of the divalent hydrocarbon group include those (mentioned as the divalent hydrocarbon group which may have a substituent) in the description of the above-described divalent linking group as Y^{a21}.

As Y²¹, a linear aliphatic hydrocarbon group is preferable, a linear alkylene group is more preferable, a linear alkylene group having 1 to 5 carbon atoms is still more preferable, and a methylene group or an ethylene group is particularly preferable.

As Y²², a linear or branched aliphatic hydrocarbon group is preferable, and a methylene group, an ethylene group, or an alkylmethylene group is more preferable. The alkyl group in the alkylmethylene group is preferably a linear alkyl group having 1 to 5 carbon atoms, more preferably a linear alkyl group having 1 to 3 carbon atoms, and most preferably a methyl group.

In the group represented by Formula $-[Y^{21}-C(=O)-O]_m-Y^{22}$, m represents an integer of 0 to 3, preferably an integer of 0 to 2, more preferably 0 or 1, and particularly preferably 1. In other words, it is particularly preferable that the group represented by Formula $-[Y^{21}-C(=O)-O]_m-Y^{22}$ represent a group represented by Formula $-Y^{21}-C(=O)-O-Y^{22}$. Among these, a group represented by Formula $-(CH_2)_a-C(=O)-O-(CH_2)_b-$ is preferable. In the formula, a represents an integer of 1 to 10, preferably an integer of 1 to 8, more preferably an integer of 1 to 5, still more preferably 1 or 2, and most preferably 1. b represents an integer of 1 to 10, preferably an integer of 1 to 8, more preferably an integer of 1 to 5, still more preferably 1 or 2, and most preferably 1.

10 [0161]

Among the above, As Y^{21} , a single bond, an ester bond $[-C(=O)-O-]$, an ether bond $(-O-)$, a linear or branched alkylene group, or a combination of these is preferable.

[0162]

In Formula (a2-1), R^{21} represents a lactone-containing cyclic group, a $-SO_2-$ -containing cyclic group, or a carbonate-containing cyclic group.

Preferred examples of the lactone-containing cyclic group, the $-SO_2-$ -containing cyclic group, and the carbonate-containing cyclic group as R^{21} include groups each represented by General Formulae (a2-r-1) to (a2-r-7), groups each represented by General Formulae (a5-r-1) to (a5-r-4), and groups each represented by General Formulae (ax3-r-1) to (ax3-r-3) described above.

Among the examples, R^{21} is preferably a lactone-containing cyclic group or a $-SO_2-$ -containing cyclic group and more preferably groups each represented by General Formula (a2-r-1), (a2-r-2), (a2-r-6), or (a5-r-1). Specifically, groups each represented by any of Chemical Formulae (r-lc-1-1) to (r-lc-1-7), (r-lc-2-1) to (r-lc-2-18), (r-lc-6-1), (r-sl-1-1), and (r-sl-1-18) are more preferable.

[0163]

The constitutional unit (a2) which the component (A1) has may be one kind or may be two or more kinds.

In a case where the component (A1) has the constitutional unit (a2), the
5 proportion of the constitutional unit (a2) in the component (A1) is preferably in a range of 5% to 60% by mole, more preferably in a range of 10% to 60% by mole, still more preferably in a range of 20% to 55% by mole, and particularly preferably in a range of 30% to 50% by mole with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

10 In a case where the proportion of the constitutional unit (a2) is equal to or greater than the lower limit of the above-described preferred range, the effect obtained by allowing the component (A1) to contain the constitutional unit (a2) can be sufficiently achieved by the effect described above. In a case where the proportion of the constitutional unit (a2) is equal to or lower than the upper limit of the above-described
15 preferred range, balance with other constitutional units can be obtained, and various lithography characteristics are improved.

[0164]

In regard to constitutional unit (a3):

The component (A1) may further have, as necessary, a constitutional unit (a3)
20 (provided that a constitutional unit corresponding to the constitutional unit (a1) or the constitutional unit (a2) is excluded) containing an aliphatic hydrocarbon group having a polar group, in addition to the constitutional unit (a1). In a case where the component (A1) has the constitutional unit (a3), the hydrophilicity of the component (A) is increased, which contributes to an improvement in resolution. Further, acid diffusion
25 length can be appropriately adjusted.

[0165]

Examples of the polar group include a hydroxyl group, a cyano group, a carboxy group, or a hydroxyalkyl group in which some hydrogen atoms of the alkyl group have been substituted with fluorine atoms. Among these, a hydroxyl group is particularly
5 preferable.

Examples of the aliphatic hydrocarbon group include linear or branched hydrocarbon groups (preferably alkylene groups) having 1 to 10 carbon atoms, and cyclic aliphatic hydrocarbon groups (cyclic groups). The cyclic group may be a monocyclic group or a polycyclic group. For example, these cyclic groups can be selected
10 appropriately from the multitude of groups that have been proposed for the resins of resist compositions for ArF excimer lasers.

[0166]

In a case where the cyclic group is a monocyclic group, the monocyclic group preferably has 3 to 10 carbon atoms. Among the examples, constitutional units derived
15 from acrylic acid ester that includes an aliphatic monocyclic group containing a hydroxyl group, cyano group, carboxy group, or a hydroxyalkyl group in which some hydrogen atoms of the alkyl group have been substituted with fluorine atoms are particularly preferable. Examples of the monocyclic group include a group in which two or more hydrogen atoms have been removed from a monocycloalkane. Specific examples of the
20 monocyclic group include groups obtained by removing two or more hydrogen atoms from monocycloalkanes such as cyclopentane, cyclohexane, and cyclooctane. Among these monocyclic groups, a group in which two or more hydrogen atoms have been removed from cyclopentane or a group in which two or more hydrogen atoms have been removed from cyclohexane are industrially preferable.

25 [0167]

In a case where the cyclic group is a polycyclic group, the polycyclic group preferably has 7 to 30 carbon atoms. Among the examples, constitutional units derived from acrylic acid ester that includes an aliphatic polycyclic group containing a hydroxyl group, cyano group, carboxy group, or a hydroxyalkyl group in which some hydrogen atoms of the alkyl group have been substituted with fluorine atoms are particularly preferable. Examples of the polycyclic group include groups in which two or more hydrogen atoms have been removed from a bicycloalkane, tricycloalkane, tetracycloalkane, or the like. Specific examples thereof include groups in which two or more hydrogen atoms have been removed from a polycycloalkane such as adamantane, norbornane, isobornane, tricyclodecane or tetracyclododecane. Among these polycyclic groups, groups in which two or more hydrogen atoms have been removed from adamantane, groups in which two or more hydrogen atoms have been removed from norbornane or groups in which two or more hydrogen atoms have been removed from tetracyclododecane are preferred industrially.

[0168]

The constitutional unit (a3) is not particularly limited as long as the constitutional unit contains a polar group-containing aliphatic hydrocarbon group, and an optional constitutional unit may be used.

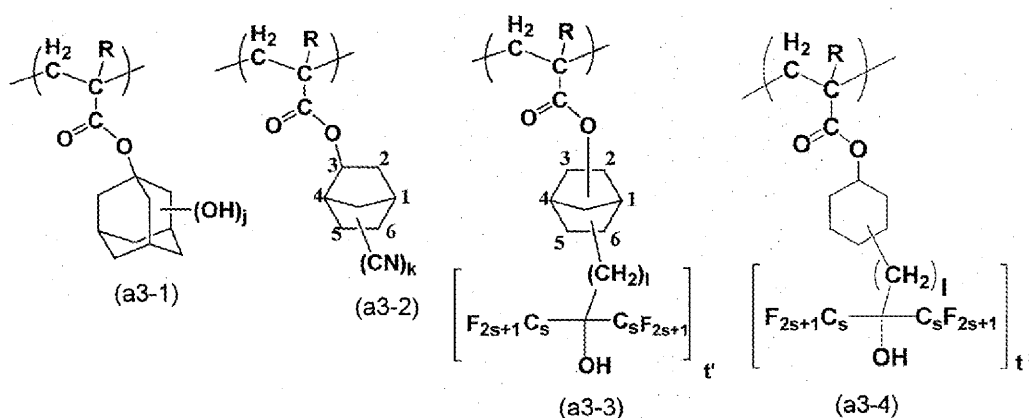
The constitutional unit (a3) is a constitutional unit derived from acrylic acid ester in which the hydrogen atom bonded to the carbon atom at the α -position may be substituted with a substituent, and a constitutional unit containing a polar group-containing aliphatic hydrocarbon group is preferable.

In a case where the hydrocarbon group in the aliphatic hydrocarbon group containing a polar group is a linear or branched hydrocarbon group having 1 to 10 carbon atoms, the constitutional unit (a3) is preferably a constitutional unit derived from a

hydroxyethyl ester of acrylic acid.

Further, as the constitutional unit (a3), in a case where the hydrocarbon group in the aliphatic hydrocarbon group containing a polar group is a polycyclic group, a constitutional unit represented by Formula (a3-1), a constitutional unit represented by Formula (a3-2), and a constitutional unit represented by Formula (a3-3) are preferable, and in a case where the hydrocarbon group is a monocyclic group, a constitutional unit represented by Formula (a3-4) is preferable.

[0169]



[In the formulae, R has the same definition as described above, j represents an integer of 1 to 3, k represents an integer of 1 to 3, t' represents an integer of 1 to 3, l represents an integer of 0 to 5, and s represents an integer of 1 to 3.]

[0170]

In Formula (a3-1), j preferably represents 1 or 2 and more preferably 1. In a case where j represents 2, it is preferable that the hydroxyl groups be bonded to the 3rd and 5th positions of the adamantyl group. In a case where j represents 1, it is preferable that the hydroxyl group be bonded to the 3-position of the adamantyl group. It is preferable that j represent 1, and it is particularly preferable that the hydroxyl group be bonded to the 3-position of the adamantyl group.

[0171]

In Formula (a3-2), k preferably represents 1. The cyano group is preferably bonded to the 5th or 6th position of the norbornyl group.

[0172]

5 In Formula (a3-3), it is preferable that t' represent 1. It is preferable that l represent 1. It is preferable that s represent 1. Further, it is preferable that a 2-norbornyl group or 3-norbornyl group be bonded to the terminal of the carboxy group of the acrylic acid. It is preferable that the fluorinated alkyl alcohol be bonded to the 5- or 6-position of the norbornyl group.

10 [0173]

In Formula (a3-4), it is preferable that t' represent 1 or 2. It is preferable that l represent 0 or 1. It is preferable that s represent 1. It is preferable that the fluorinated alkyl alcohol be bonded to the 3- or 5-position of the cyclohexyl group.

[0174]

15 The constitutional unit (a3) which the component (A1) has may be one kind or may be two or more kinds.

In a case where the component (A1) has the constitutional unit (a3), the proportion of the constitutional unit (a3) is preferably in a range of 1% to 30% by mole, more preferably in a range of 2% to 25% by mole, and still more preferably in a range of
20 5% to 20% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

In a case where the proportion of the constitutional unit (a3) is equal to or greater than the lower limit of the above-described preferred range, the effect obtained by allowing the component (A1) to contain the constitutional unit (a3) can be sufficiently
25 achieved by the effect described above. In a case where the proportion of the

constitutional unit (a2) is equal to or lower than the upper limit of the above-described preferred range, balance with other constitutional units can be obtained, and various lithography characteristics are improved.

[0175]

5 In regard to constitutional unit (a4):

The component (A1) may further have, in addition to the constitutional unit (a1), a constitutional unit (a4) containing an acid non-dissociable aliphatic cyclic group.

In a case where the component (A1) has the constitutional unit (a4), the dry etching resistance of the formed resist pattern is improved. Further, the hydrophobicity
10 of the component (A) increases. The improvement in hydrophobicity contributes to the improvement in resolution, resist pattern shape, and the like, particularly in the case of a solvent developing process. The “acid non-dissociable cyclic group” in the constitutional unit (a4) is a cyclic group that remains in the constitutional unit without being dissociated even when an acid acts in a case where the acid is generated in the
15 resist composition by exposure (for example, in a case where an acid is generated from the constitutional unit generating an acid upon exposure or the component (B)).

[0176]

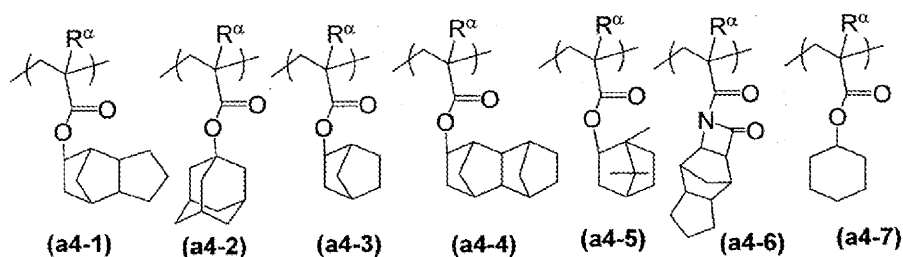
Examples of the constitutional unit (a4) preferably include a constitutional unit derived from an acrylate ester including an acid non-dissociable aliphatic cyclic group.
20 As the cyclic group, many cyclic groups conventionally known as cyclic groups used as a resin component of a resist composition for ArF excimer laser, KrF excimer laser (preferably KrF excimer laser), or the like can be used.

The cyclic group is particularly preferably at least one selected from a tricyclodecyl group, an adamantyl group, a tetracyclododecyl group, an isobornyl group,
25 and a norbornyl group, from the viewpoint of industrial availability. These polycyclic

groups may have, as a substituent, a linear or branched alkyl group having 1 to 5 carbon atoms.

Specific examples of the constitutional unit (a4) include constitutional units each represented by General Formulae (a4-1) to (a4-7).

5 [0177]



[In the formula, R^{α} is the same as above.]

[0178]

10 The constitutional unit (a4) which the component (A1) has may be one kind or may be two or more kinds.

In a case where the component (A1) has the constitutional unit (a4), the proportion of the constitutional unit (a4) is preferably in a range of 1% to 40% by mole and more preferably in a range of 5% to 20% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

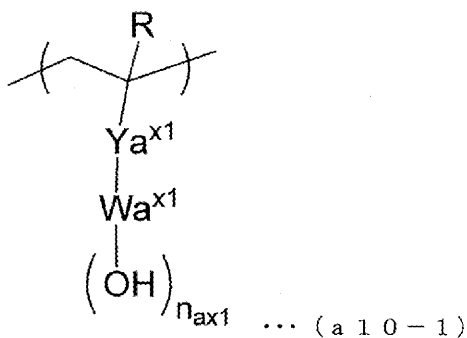
15 In a case where the proportion of the constitutional unit (a4) is equal to or greater than the lower limit of the preferred range, the effect obtained by allowing the component (A1) to contain the constitutional unit (a3) can be sufficiently achieved. In a case where the proportion of the constitutional unit (a4) is equal to or lower than the upper limit of the preferred range, the balance with other constitutional units is obtained
20 easily.

[0179]

In regard to constitutional unit (a10):

The constitutional unit (a10) is a constitutional unit represented by General Formula (a10-1).

[0180]



5

[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. $\text{Y}^{\text{a}^{\text{x}1}}$ represents a single bond or a divalent linking group. $\text{W}^{\text{a}^{\text{x}1}}$ represents an $(n_{\text{ax}1} + 1)$ -valent aromatic hydrocarbon group. $n_{\text{ax}1}$ represents an integer of 1 or more.]

10

[0181]

In Formula (a10-1), R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbons.

15

As the alkyl group having 1 to 5 carbon atoms as R, a linear or branched alkyl group having 1 to 5 carbon atoms is preferable, and specific examples thereof include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, and a neopentyl group.

20

The halogenated alkyl group having 1 to 5 carbon atoms as R is a group in which part or all hydrogen atoms of the above-described alkyl group having 1 to 5 carbon atoms have been substituted with halogen atoms. Examples of the halogen atom

include a fluorine atom, a chlorine atom, a bromine atom and, an iodine atom, and a fluorine atom is particularly preferable.

As R, a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a fluorinated alkyl group having 1 to 5 carbon atoms is preferable, and a hydrogen atom, a methyl group, or trifluoromethyl group is more preferable, a hydrogen atom or a methyl group is still more preferable, and a methyl group is particularly preferable in terms of industrial availability.

[0182]

In Formula (a10-1), Y^{x1} represents a single bond or a divalent linking group.

In the chemical formulae described above, the divalent linking group as Y^{x1} is not particularly limited, and suitable examples thereof include a divalent hydrocarbon group which may have a substituent and a divalent linking group having hetero atoms.

[0183]

· Divalent hydrocarbon group which may have substituent:

In a case where Y^{x1} represents a divalent hydrocarbon group which may have a substituent, the hydrocarbon group may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

[0184]

·· Aliphatic hydrocarbon group as Y^{x1}

The aliphatic hydrocarbon group indicates a hydrocarbon group that has no aromaticity. The aliphatic hydrocarbon group may be saturated or unsaturated. In general, it is preferable that the aliphatic hydrocarbon group be saturated. Examples of the aliphatic hydrocarbon group include a linear or branched aliphatic hydrocarbon group, and an aliphatic hydrocarbon group containing a ring in the structure thereof.

[0185]

... Linear or branched aliphatic hydrocarbon group

The linear aliphatic hydrocarbon group preferably has 1 to 10 carbon atoms, more preferably 1 to 6 carbon atoms, still more preferably 1 to 4 carbon atoms, and most preferably 1 to 3 carbon atoms.

5 The linear aliphatic hydrocarbon group is preferably a linear alkylene group, and specific examples thereof include a methylene group $[-CH_2-]$, an ethylene group $[-(CH_2)_2-]$, a trimethylene group $[-(CH_2)_3-]$, a tetramethylene group $[-(CH_2)_4-]$, and a pentamethylene group $[-(CH_2)_5-]$.

10 The branched aliphatic hydrocarbon group preferably has 2 to 10 carbon atoms, more preferably 3 to 6 carbon atoms, still more preferably 3 or 4 carbon atoms, and most preferably 3 carbon atoms.

As the branched aliphatic hydrocarbon group, a branched alkylene group is preferred, and specific examples thereof include alkylalkylene groups, for example, alkylmethylene groups such as $-CH(CH_3)-$, $-CH(CH_2CH_3)-$, $-C(CH_3)_2-$, $-C(CH_3)(CH_2CH_3)-$, $-C(CH_3)(CH_2CH_2CH_3)-$, and $-C(CH_2CH_3)_2-$; alkylethylene groups such as $-CH(CH_3)CH_2-$, $-CH(CH_3)CH(CH_3)-$, $-C(CH_3)_2CH_2-$, $-CH(CH_2CH_3)CH_2-$, and $-C(CH_2CH_3)_2CH_2-$; alkyltrimethylene groups such as $-CH(CH_3)CH_2CH_2-$, and $-CH_2CH(CH_3)CH_2-$; and alkyltetramethylene groups such as $-CH(CH_3)CH_2CH_2CH_2-$, and $-CH_2CH(CH_3)CH_2CH_2-$. As the alkyl group in the alkylalkylene group, a linear alkyl group having 1 to 5 carbon atoms is preferable.

15

20

[0186]

The linear or branched aliphatic hydrocarbon group may or may not have a substituent. Examples of the substituent include a fluorine atom, a fluorinated alkyl group having 1 to 5 carbon atoms, which has been substituted with a fluorine atom, and a carbonyl group.

25

[0187]

... Aliphatic hydrocarbon group containing ring in structure thereof

Examples of the aliphatic hydrocarbon group containing a ring in the structure thereof include a cyclic aliphatic hydrocarbon group which may have a substituent
5 containing a hetero atom in the ring structure thereof (a group in which two hydrogen atoms have been removed from an aliphatic hydrocarbon ring), a group in which the cyclic aliphatic hydrocarbon group is bonded to the terminal of a linear or branched aliphatic hydrocarbon group, and a group in which the cyclic aliphatic hydrocarbon group is interposed in a linear or branched aliphatic hydrocarbon group. As the linear
10 or branched aliphatic hydrocarbon group, the same groups as those described above can be mentioned.

The cyclic aliphatic hydrocarbon group preferably has 3 to 20 carbon atoms and more preferably 3 to 12 carbon atoms.

The cyclic aliphatic hydrocarbon group may be a polycyclic group or a
15 monocyclic group. As the monocyclic alicyclic hydrocarbon group, a group in which two hydrogen atoms have been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane. As the polycyclic alicyclic hydrocarbon group, a group in which two hydrogen atoms have been removed from a polycycloalkane is
20 preferable. As the polycycloalkane, a group having 7 to 12 carbon atoms is preferable. Examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane.

[0188]

The cyclic aliphatic hydrocarbon group may or may not have a substituent.

25 Examples of the substituent include an alkyl group, an alkoxy group, a halogen atom, a

halogenated alkyl group, a hydroxyl group, and a carbonyl group.

The alkyl group as the substituent is preferably an alkyl group having 1 to 5 carbon atoms, and a methyl group, an ethyl group, a propyl group, an n-butyl group, or a tert-butyl group is most preferable.

5 The alkoxy group as the substituent is preferably an alkoxy group having 1 to 5 carbon atoms, more preferably a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group, or a tert-butoxy group, and still more preferably a methoxy group or an ethoxy group.

10 Examples of the halogen atom as the substituent include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom, and a fluorine atom is preferable.

Examples of the halogenated alkyl group as the substituent include groups in which part or all hydrogen atoms in the above-described alkyl groups have been substituted with the above-described halogen atoms.

15 In the cyclic aliphatic hydrocarbon group, some carbon atoms constituting the ring structure thereof may be substituted with a substituent containing a hetero atom. As the substituent containing a hetero atom, -O-, -C(=O)-O-, -S-, -S(=O)₂-, or -S(=O)₂-O- is preferable.

[0189]

·· Aromatic hydrocarbon group as Ya^{x1}

20 The aromatic hydrocarbon group is a hydrocarbon group having at least one aromatic ring.

The aromatic ring is not particularly limited as long as it is a cyclic conjugated system having $(4n + 2) \pi$ electrons, and may be monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, 25 still more preferably 6 to 15 carbon atoms, and particularly preferably 6 to 12 carbon

atoms. Here, the number of carbon atoms in a substituent is not included in the number of carbon atoms.

Specific examples of the aromatic ring include aromatic hydrocarbon rings such as benzene, naphthalene, anthracene, and phenanthrene; and aromatic hetero rings in
5 which some carbon atoms constituting the above-described aromatic hydrocarbon rings have been substituted with hetero atoms. Examples of the hetero atom in the aromatic hetero rings include an oxygen atom, a sulfur atom, and a nitrogen atom. Specific examples of the aromatic hetero ring include a pyridine ring and a thiophene ring.

Specific examples of the aromatic hydrocarbon group include a group in which
10 two hydrogen atoms have been removed from the above-described aromatic hydrocarbon ring or aromatic hetero ring (an arylene group or a heteroarylene group); a group in which two hydrogen atoms have been removed from an aromatic compound having two or more aromatic rings (such as biphenyl or fluorene); and a group in which one hydrogen atom of a group (an aryl group or a heteroaryl group) obtained by removing
15 one hydrogen atom from the above-described aromatic hydrocarbon ring or aromatic hetero ring has been substituted with an alkylene group (for example, a group obtained by further removing one hydrogen atom from an aryl group in an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group). The number of carbon atoms in
20 the alkylene group bonded to the aryl group or the heteroaryl group is preferably in a range of 1 to 4, more preferably 1 or 2, and particularly preferably 1.

[0190]

With respect to the aromatic hydrocarbon group, the hydrogen atom which the aromatic hydrocarbon group has may be substituted with a substituent. For example,
25 the hydrogen atom bonded to the aromatic ring in the aromatic hydrocarbon group may

be substituted with a substituent. Examples of substituents include an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, and a hydroxyl group.

The alkyl group as the substituent is preferably an alkyl group having 1 to 5 carbon atoms, and a methyl group, an ethyl group, a propyl group, an n-butyl group, or a tert-butyl group is most preferable.

As the alkoxy group, the halogen atom, and the halogenated alkyl group as the substituents, the same groups as the above-described substituents for substituting a hydrogen atom which the cyclic aliphatic hydrocarbon group has can be mentioned.

[0191]

· Divalent linking group containing hetero atom

In a case where Y^{x1} represents a divalent linking group containing a hetero atom, preferred examples of the linking group include -O-, -C(=O)-O-, -O-C(=O)-, -C(=O)-, -O-C(=O)-O-, -C(=O)-NH-, -NH-, -NH-C(=NH)- (H may be substituted with a substituent such as an alkyl group, an acyl group, or the like), -S-, -S(=O)₂-, -S(=O)₂-O-, and a group represented by General Formula: $-Y^{21}-O-Y^{22}-$, $-Y^{21}-O-$, $-Y^{21}-C(=O)-O-$, $-C(=O)-O-Y^{21}-$, $-[Y^{21}-C(=O)-O]_{m''}-Y^{22}-$, $-Y^{21}-O-C(=O)-Y^{22}-$ or $-Y^{21}-S(=O)_2-O-Y^{22}-$ [in the formulae, Y^{21} and Y^{22} each independently represents a divalent hydrocarbon group which may have a substituent, O represents an oxygen atom, and m'' represents an integer of 0 to 3].

In a case where the divalent linking group containing a hetero atom is -C(=O)-NH-, -C(=O)-NH-C(=O)-, -NH-, or -NH-C(=NH)-, H may be substituted with a substituent such as an alkyl group, an acyl group, or the like. The substituent (an alkyl group, an acyl group, or the like) preferably has 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms, and most preferably 1 to 5 carbon atoms.

In General Formula $-Y^{21}-O-Y^{22}-$, $-Y^{21}-O-$, $-Y^{21}-C(=O)-O-$, $-C(=O)-O-Y^{21}-$, -

[Y²¹-C(=O)-O]_m"-Y²²-, -Y²¹-O-C(=O)-Y²²-, or -Y²¹-S(=O)₂-O-Y²²-, Y²¹, and Y²² each independently represents a divalent hydrocarbon group which may have a substituent. Examples of the divalent hydrocarbon group include those (mentioned as the divalent hydrocarbon group which may have a substituent) in the description of the above-

5 described divalent linking group as Ya^{x1}.

As Y²¹, a linear aliphatic hydrocarbon group is preferable, a linear alkylene group is more preferable, a linear alkylene group having 1 to 5 carbon atoms is still more preferable, and a methylene group or an ethylene group is particularly preferable.

As Y²², a linear or branched aliphatic hydrocarbon group is preferable, and a

10 methylene group, an ethylene group, or an alkylmethylene group is more preferable. The alkyl group in the alkylmethylene group is preferably a linear alkyl group having 1 to 5 carbon atoms, more preferably a linear alkyl group having 1 to 3 carbon atoms, and most preferably a methyl group.

In the group represented by Formula -[Y²¹-C(=O)-O]_m"-Y²²-, m" represents an

15 integer of 0 to 3, preferably an integer of 0 to 2, more preferably 0 or 1, and particularly preferably 1. In other words, it is particularly preferable that the group represented by Formula -[Y²¹-C(=O)-O]_m"-Y²²- represent a group represented by Formula -Y²¹-C(=O)-O-Y²²-. Among these, a group represented by Formula -(CH₂)_a'-C(=O)-O-(CH₂)_b'- is preferable. In the formula, a' represents an integer of 1 to 10, preferably an integer of 1

20 to 8, more preferably an integer of 1 to 5, still more preferably 1 or 2, and most preferably 1. b' represents an integer of 1 to 10, preferably an integer of 1 to 8, more preferably an integer of 1 to 5, still more preferably 1 or 2, and most preferably 1.

[0192]

Among the above, Ya^{x1} is preferably a single bond, an ester bond [-C(=O)-O-, -

25 O-C(=O)-], an ether bond (-O-), a linear or branched alkylene group, or a combination

thereof, more preferably a single bond, an ester bond [-C(=O)-O-, -O-C(=O)-] is more preferable, and a single bond is still more preferable.

[0193]

In Formula (a10-1), Wa^{x1} represents an $(n_{ax1} + 1)$ -valent aromatic hydrocarbon
5 group.

Examples of the aromatic hydrocarbon group as Wa^{x1} include a group obtained by removing $(n_{ax1} + 1)$ hydrogen atoms from an aromatic ring. The aromatic ring is not particularly limited as long as it is a cyclic conjugated system having $(4n + 2) \pi$ electrons, and may be monocyclic or polycyclic. The aromatic ring preferably has 5 to
10 30 carbon atoms, more preferably 5 to 20 carbon atoms, still more preferably 6 to 15 carbon atoms, and particularly preferably 6 to 12 carbon atoms. Specific examples of the aromatic ring include aromatic hydrocarbon rings such as benzene, naphthalene, anthracene, and phenanthrene; and aromatic hetero rings in which some carbon atoms constituting the above-described aromatic hydrocarbon rings have been substituted with
15 hetero atoms. Examples of the hetero atom in the aromatic hetero rings include an oxygen atom, a sulfur atom, and a nitrogen atom. Specific examples of the aromatic hetero ring include a pyridine ring and a thiophene ring.

Examples of the aromatic hydrocarbon group as Wa^{x1} also include a group obtained by removing $(n_{ax1} + 1)$ hydrogen atoms from an aromatic compound including
20 two or more aromatic rings (for example, biphenyl and fluorene).

Among them, Wa^{x1} is preferably a group obtained by removing $(n_{ax1} + 1)$ hydrogen atoms from benzene, naphthalene, anthracene, or biphenyl, more preferably a group obtained by removing $(n_{ax1} + 1)$ hydrogen atoms from benzene or naphthalene, and still more preferably a group obtained by removing $(n_{ax1} + 1)$ hydrogen atoms from
25 benzene.

[0194]

The aromatic hydrocarbon group as Wa^{x1} may or may not have a substituent, but preferably does not have a substituent. Examples of the substituent include an alkyl group, an alkoxy group, a halogen atom, and a halogenated alkyl group. Examples of the alkyl groups, the alkoxy groups, the halogen atoms, and the halogenated alkyl groups as the substituent include the same groups which are mentioned as the above-described substituents of the cyclic aliphatic hydrocarbon group as Ya^{x1} . In a case where Wa^{x1} is a group obtained by removing $(n_{ax1} + 1)$ hydrogen atoms from an aromatic ring, the substituent substitutes the hydrogen atoms, which are the removed $(n_{ax1} + 1)$ hydrogen atoms of the aromatic ring of the group. The substituent is preferably a linear or branched alkyl group having 1 to 5 carbon atoms, more preferably a linear or branched alkyl group having 1 to 3 carbon atoms, still more preferably an ethyl group or a methyl group, and particularly preferably a methyl group.

[0195]

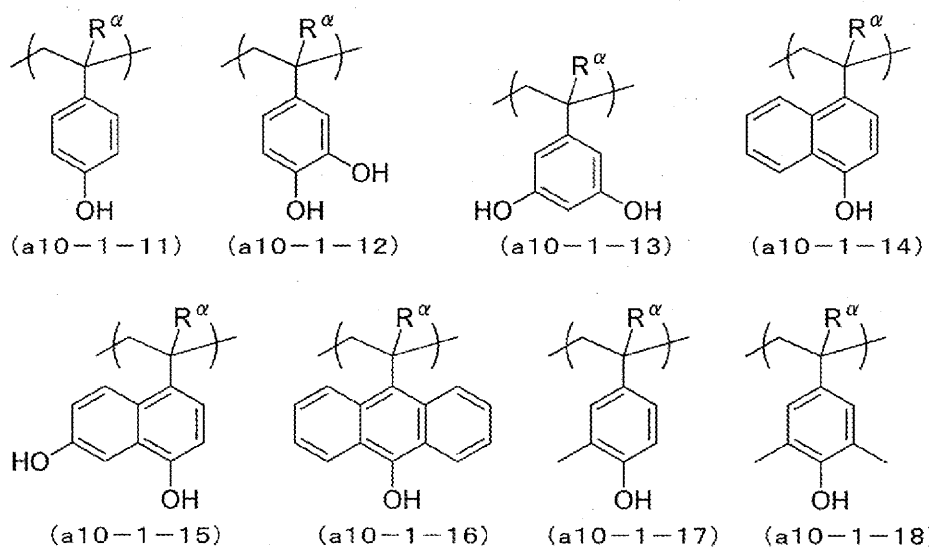
In the Formula (a10-1), n_{ax1} represents an integer of 1 or more, preferably an integer of 1 to 10, more preferably an integer of 1 to 5, still more preferably 1, 2, or 3, and particularly preferably 1 or 2. Among them, n_{ax1} is preferably 1.

[0196]

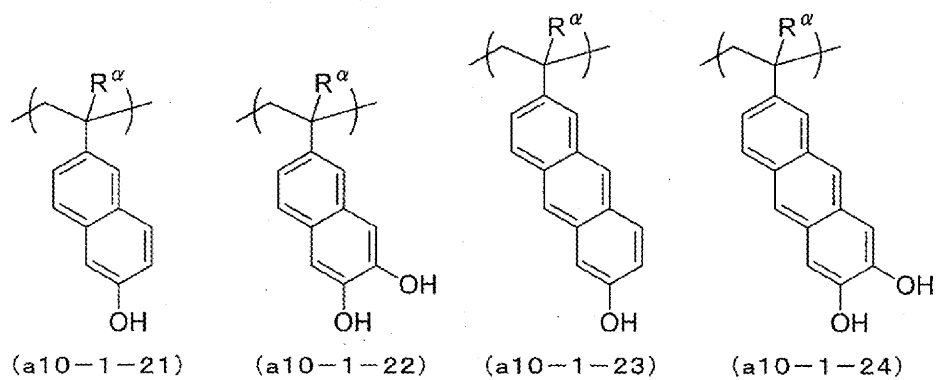
Specific examples of the constitutional unit (a10) represented by Formula (a10-1) are shown below.

In the formulae shown below, R^a represents a hydrogen atom, a methyl group, or a trifluoromethyl group.

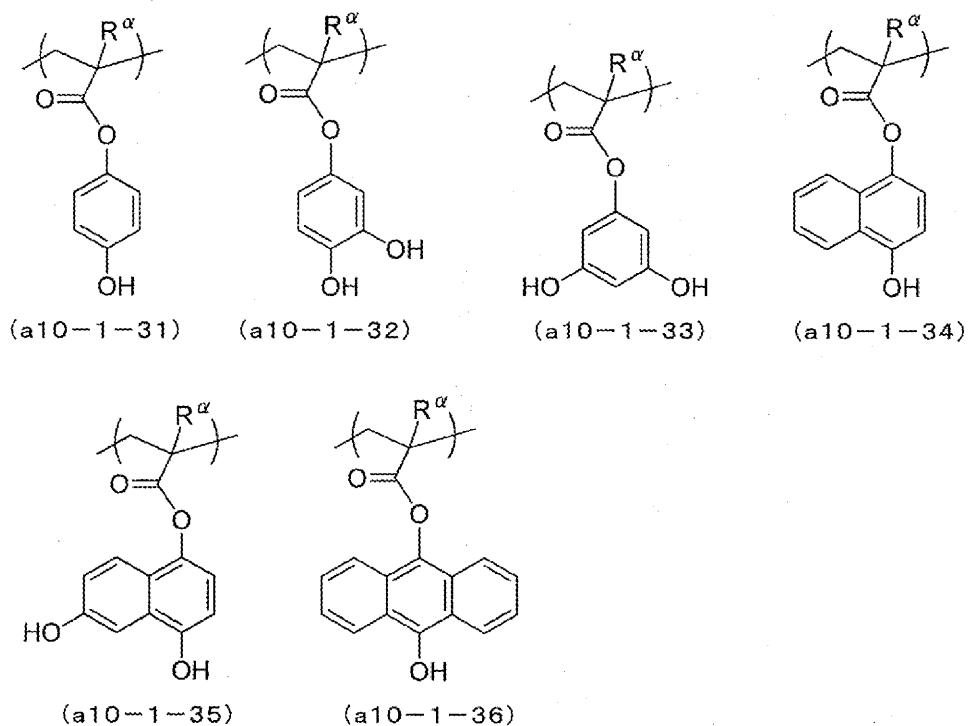
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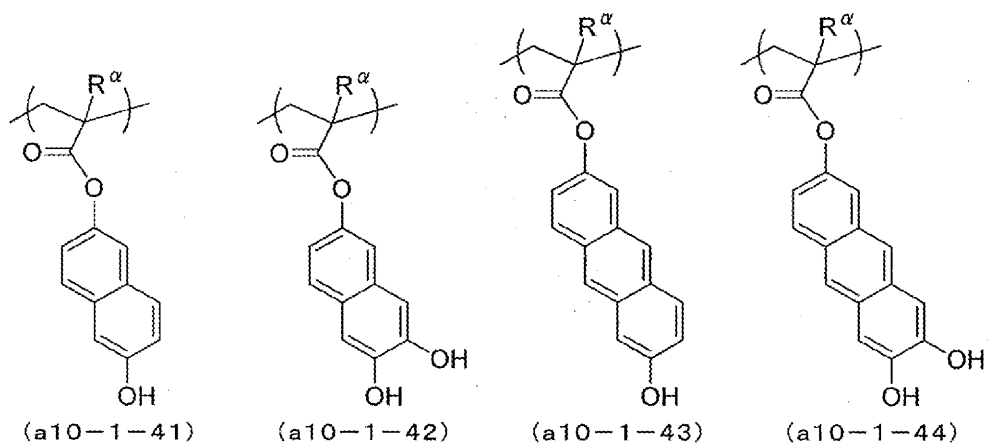
[0198]



[0199]



[0200]



[0201]

5 The constitutional unit (a10) which the component (A1) has may be one kind or may be two or more kinds.

In a case where the component (A1) has the constitutional unit (a10), the proportion of the constitutional unit (a10) in the component (A1) is preferably in a range

of 5% to 50% by mole, more preferably in a range of 5% to 40% by mole, and still more preferably in a range of 10% to 30% by mole with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

In a case where the proportion of the constitutional unit (a10) is equal to or more
5 than the lower limit, the sensitivity can be more easily increased. On the other hand, in a case where the proportion of the constitutional unit (a10) is equal to or lower than the upper limit, balance with other constitutional units is obtained easily.

[0202]

In regard to constitutional unit (st):

10 The constitutional unit (st) is a constitutional unit derived from styrene or a styrene derivative. A “constitutional unit derived from styrene” means a constitutional unit that is formed by the cleavage of an ethylenic double bond of styrene. A “constitutional unit derived from a styrene derivative” means a constitutional unit formed by the cleavage of an ethylenic double bond of a hydroxystyrene derivative.

15 [0203]

The “styrene derivative” means a compound in which at least a part of hydrogen atoms of styrene are substituted with a substituent. Examples of the styrene derivative include a derivative in which the hydrogen atom at the α -position of styrene is substituted with a substituent, a derivative in which one or more hydrogen atoms of the benzene ring
20 of styrene are substituted with a substituent, and a derivative in which the hydrogen at the α -position of styrene and one or more hydrogen atoms of the benzene ring are substituted with a substituent.

[0204]

As the substituent for substituting the hydrogen atom at the α -position of
25 styrene, an alkyl group having 1 to 5 carbon atoms or a halogenated alkyl group having 1

to 5 carbon atoms can be mentioned.

As the alkyl group having 1 to 5 carbon atoms, a linear or branched alkyl group having 1 to 5 carbon atoms is preferable, and specific examples thereof include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, and a neopentyl group.

The halogenated alkyl group having 1 to 5 carbon atoms is a group in which part or all hydrogen atoms in the alkyl group having 1 to 5 carbon atoms have been substituted with halogen atoms. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom and, an iodine atom, and a fluorine atom is particularly preferable. The substituent for substituting the hydrogen atom at the α -position of styrene is preferably an alkyl group having 1 to 5 carbon atoms or a fluorinated alkyl group having 1 to 5 carbon atoms, more preferably an alkyl group having 1 to 3 carbon atoms or a fluorinated alkyl group having 1 to 3 carbon atoms, and still more preferably a methyl group from the viewpoint of industrial availability.

[0205]

Examples of the substituent for substituting the hydrogen atom of the benzene ring of styrene include an alkyl group, an alkoxy group, a halogen atom, and a halogenated alkyl group.

The alkyl group as the substituent is preferably an alkyl group having 1 to 5 carbon atoms, and a methyl group, an ethyl group, a propyl group, an n-butyl group, or a tert-butyl group is most preferable.

The alkoxy group as the substituent is preferably an alkoxy group having 1 to 5 carbon atoms, more preferably a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group, or a tert-butoxy group, and still more preferably a methoxy group or an ethoxy group.

Examples of the halogen atom as the substituent include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom, and a fluorine atom is preferable.

Examples of the halogenated alkyl group as the substituent include groups in which part or all hydrogen atoms in the above-described alkyl groups have been substituted with the above-described halogen atoms.

The substituent for substituting the hydrogen atom of the benzene ring of styrene, an alkyl group having 1 to 5 carbon atoms is preferable, a methyl group or an ethyl group is more preferable, and a methyl group is still more preferable.

[0206]

The constitutional unit (st) is preferably a constitutional unit derived from styrene or a styrene derivative in which the hydrogen atom at the α -position of styrene is substituted with an alkyl group having 1 to 5 carbon atoms or a halogenated alkyl group having 1 to 5 carbon atoms, more preferably a constitutional unit derived from styrene, or a constitutional unit derived from a styrene derivative in which the hydrogen atom at the α -position of styrene is substituted with a methyl group, and still more preferably a constitutional unit derived from styrene.

[0207]

The constitutional unit (st) which the component (A1) has may be one kind or may be two or more kinds.

In a case where the component (A1) has the constitutional unit (st), the proportion of the constitutional unit (st) is preferably in a range of 1% to 30% by mole and more preferably in a range of 3% to 20% by mole with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

[0208]

The component (A1) contained in the resist composition may be used alone or in

combination of two or more kinds thereof.

In the resist composition of the present embodiment, the component (A1) contains a high-molecular-weight compound having a repeated structure of the constitutional unit (a1).

5 The preferred component (A1) contains a high-molecular-weight compound having a repeated structure of the constitutional unit (a1) and a constitutional unit other than the constitutional unit (a1). As the other constitutional units, the constitutional unit (a10), the constitutional unit (st), and the like can be mentioned.

10 In addition to the combination of the above two constitutional units, the constitutional units described above may be combined as a third constitutional unit or three or more constitutional units as appropriate in accordance with the desired effect. Examples of the combination of three or more constitutional units include a combination of the constitutional unit (a1), the constitutional unit (a10), and the constitutional unit (st).

15 Preferred examples of the component (A1) include: a high-molecular-weight compound having a repeated structure of the constitutional unit (a1) and the constitutional unit (a10); a high-molecular-weight compound having a repeated structure of the constitutional unit (a1) and the constitutional unit (st); and a high-molecular-weight compound having a repeated structure of the constitutional unit (a1), the constitutional unit (a10), and the constitutional unit (st).

[0209]

25 The component (A1) can be produced by dissolving, in a polymerization solvent, each monomer from which the constitutional unit is derived, adding thereto a radical polymerization initiator such as azobisisobutyronitrile (AIBN) or dimethyl azobisisobutyrate (for example, V-601) to perform polymerization.

Alternatively, the component (A1) can be produced by dissolving, in a polymerization solvent, a monomer from which the constitutional unit (a1) is derived and, as necessary, a monomer from which a constitutional unit other than the constitutional unit (a1) is derived, and adding thereto a radical polymerization initiator
5 such as described above to perform polymerization, and then performing a deprotection reaction.

Further, a $-C(CF_3)_2-OH$ group may be introduced into the terminal of the component (A1) during the polymerization using a chain transfer agent such as $HS-CH_2-CH_2-CH_2-C(CF_3)_2-OH$ together. As described above, a copolymer into which a
10 hydroxyalkyl group, formed by substitution of some hydrogen atoms in the alkyl group with fluorine atoms, has been introduced is effective for reducing development defects and reducing line edge roughness (LER: uneven irregularities of a line side wall).

[0210]

The weight-average molecular weight (M_w) (based on the polystyrene-equivalent value determined by gel permeation chromatography (GPC)) of the
15 component (A1), which is not particularly limited, is preferably in a range of 1,000 to 50,000, more preferably in a range of 2,000 to 30,000, and still more preferably in a range of 3,000 to 20,000.

In a case where M_w of the component (A1) is equal or lower than the upper
20 limit of the above-described range, the resist composition exhibits sufficient solubility in a solvent for a resist such that the resist composition can be used as a resist. On the other hand, in a case where M_w of the component (A1) is equal to or greater than the lower limit of the above-described range, dry etching resistance and the cross-sectional shape of the resist pattern become excellent.

25 Further, the dispersity (M_w/M_n) of the component (A1) is not particularly

limited, but is preferably in a range of 1.0 to 4.0, more preferably in a range of 1.0 to 3.0, and particularly preferably in a range of 1.0 to 2.0. Further, Mn represents the number-average molecular weight.

[0211]

5 · In regard to base material components other than component (A1)

In the resist composition of the present embodiment, a base material component having solubility in a developing solution, which is changed by action of an acid, which does not correspond to the component (A1), may be used in combination as the component (A). The base material component which does not correspond to the component (A1) is not particularly limited, many components conventionally known as base material components for a chemically amplified resist composition can be randomly selected, and one kind of high-molecular-weight compound or low-molecular-weight compound may be used alone or in combination of two or more kinds thereof.

[0212]

15 The proportion of the component (A1) in the component (A) is preferably 25% by mass or greater, more preferably 50% by mass or greater, still more preferably 75% by mass or greater, and may be 100% by mass with respect to the total mass of the component (A). In a case where the proportion is 25% by mass or more, a resist pattern having various excellent lithography characteristics can be easily formed.

20 [0213]

In the resist composition of the present embodiment, the content of the component (A) is preferably 20% by mass or more with respect to the total mass (100% by mass) of the resist composition. In a case where the content of the component (A) is 20% by mass or more, a thick resist film (for example, a film having a thickness of 5 μm or more) can be easily formed. The upper limit of the content of the component (A) is

25

not particularly limited as long as it has a concentration capable of forming a resist film, but may be, for example, 50 mass% or less. The content of the component (A) is preferably 20% to 50% by mass, more preferably 22% to 50% by mass, and still more preferably 25% to 50% by mass.

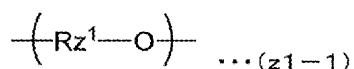
5 [0214]

<Component (Z)>

The component (Z) is a polyether compound having a weight-average molecular weight of 400 or more.

In the present specification, the “polyether compound” refers to a high-
 10 molecular-weight compound including a plurality of ether bonds (-O-) in the main chain. Examples of the component (Z) include a high-molecular-weight compound having a constitutional unit (z1) represented by General Formula (z1-1) shown below.

[0215]



15 [In the formula, Rz^1 represents a divalent hydrocarbon group which may have a substituent.]

[0216]

In General Formula (z1-1), Rz^1 represents a divalent hydrocarbon group which may have a substituent. The hydrocarbon group preferably has 1 to 15 carbon atoms,
 20 more preferably 1 to 10 carbon atoms, and still more preferably 1 to 6 carbon atoms. The hydrocarbon group may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group but is preferably an aliphatic hydrocarbon group. The aliphatic hydrocarbon group may be saturated or unsaturated but is preferably saturated.

Examples of the aliphatic hydrocarbon group include a linear or branched aliphatic hydrocarbon group and an aliphatic hydrocarbon group containing a ring in the structure thereof. Rz^1 is preferably a linear or branched aliphatic hydrocarbon group.

[0217]

- 5 The linear or branched aliphatic hydrocarbon group as Rz^1 is preferably a linear or branched alkylene group.

The linear alkylene group preferably has 1 to 10 carbon atoms, more preferably 1 to 6 carbon atoms, still more preferably 1 to 4 carbon atoms, and particularly preferably 2 to 3 carbon atoms. Specific examples of the linear alkylene group include a

10 methylene group $[-CH_2-]$, an ethylene group $[-(CH_2)_2-]$, a trimethylene group $[-(CH_2)_3-]$, a tetramethylene group $[-(CH_2)_4-]$, and a pentamethylene group $[-(CH_2)_5-]$.

The branched alkylene group preferably has 2 to 10 carbon atoms, more preferably 3 to 6 carbon atoms, still more preferably 3 or 4 carbon atoms, and particularly preferably 3 carbon atoms. Specific examples of the branched alkylene group include

15 alkylalkylene groups such as alkylmethylene groups such as $CH(CH_3)-$, $-CH(CH_2CH_3)-$, $-C(CH_3)_2-$, $-C(CH_3)(CH_2CH_3)-$, $-C(CH_3)(CH_2CH_2CH_3)-$, and $-C(CH_2CH_3)_2-$, alkylethylene groups such as $-CH(CH_3)CH_2-$, $-CH(CH_3)CH(CH_3)-$, $-C(CH_3)_2CH_2-$, $-CH(CH_2CH_3)CH_2-$, and $-C(CH_2CH_3)_2CH_2-$, alkyltrimethylene groups such as $-CH(CH_3)CH_2CH_2-$ and $-CH_2CH(CH_3)CH_2-$, and alkyltetramethylene groups such as $-CH(CH_3)CH_2CH_2CH_2-$ and $-CH_2CH(CH_3)CH_2CH_2-$. The alkyl group for the linear

20 alkylene group preferably has 1 to 5 carbon atoms, more preferably 1 to 3 carbon atoms, still more preferably 1 or 2 carbon atoms, and particularly preferably 1 carbon atom.

The alkyl group for the alkylalkylene group is preferably a linear alkyl group.

[0218]

- 25 The divalent hydrocarbon group as Rz^1 may or may not have a substituent, but

preferably does not have a substituent. Examples of the substituent which the divalent hydrocarbon group can have as Rz^1 include a hydroxyl group, an amino group, an alkoxy group, a halogen atom, a halogenated alkyl group, a carboxy group, and cyano group.

[0219]

- 5 Among them, Rz^1 is preferably an ethylene group ($-\text{CH}_2\text{CH}_2-$) or a methylethylene group $[-\text{CH}(\text{CH}_3)\text{CH}_2-]$.

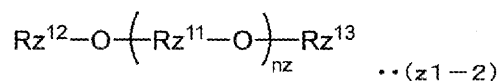
[0220]

- The constitutional unit (z1) which the component (Z) has may be one kind or may be two or more kinds. The constitutional unit (z1) preferably has an oxyalkylene skeleton and more preferably an oxyalkylene group. Preferred specific examples of the constitutional unit (z1) include: a constitutional unit composed of an oxyethylene group ($-\text{CH}_2\text{CH}_2\text{O}-$); and a constitutional unit composed of an oxypropylene group $[-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-]$.

[0221]

- 15 Preferred examples of the component (Z) include a high-molecular-weight compound (Z1-2) represented by General Formula (z1-2) shown below.

[0222]



- [In the formula, Rz^{11} represents a divalent hydrocarbon group which may have a substituent. nz represents an integer of 2 or more. A plurality of Rz^{11} may be the same or different from each other. Rz^{12} and Rz^{13} each independently represents a hydrogen atom, an alkyl group, an alkoxy group, an amino group, or a thiol group.]

[0223]

In General Formula (z1-2), Rz^{11} represents a divalent hydrocarbon group which may have a substituent. As the divalent hydrocarbon group as Rz^{11} , the same group as that mentioned in Rz^1 in General Formula (z1) can be mentioned. Rz^{11} is preferably a linear or branched alkylene group having 1 to 10 carbon atoms, more preferably a linear or branched alkylene group having 1 to 6 carbon atoms, still more preferably a linear or branched alkylene group having 2 to 4 carbon atoms, and particularly preferably an ethylene group or a methylethylene group.

A plurality of Rz^{11} may be the same or different from each other.

[0224]

10 In General Formula (z1-2), nz represents an integer of 2 or more. nz is preferably a numerical value such that the weight-average molecular weight of the high-molecular-weight compound (Z1-2) is 400 or more, and nz can vary depending on the kind of Rz^{11} . For example, in a case where Rz^{11} is an ethylene group ($-CH_2CH_2-$), nz is preferably an integer of 9 or more and more preferably an integer of 20 or more. For
15 example, in a case where Rz^{11} is a methylethylene group [$-CH(CH_3)CH_2-$], nz is preferably an integer of 7 or more and more preferably an integer of 15 or more. The upper limit of nz is not particularly limited, but examples thereof include 1,000 or less, 700 or less, 500 or less, and 400 or less.

[0225]

20 In General Formula (z1-2), Rz^{12} and Rz^{13} each independently represents a hydrogen atom, an alkyl group, an alkoxy group, an amino group, or a thiol group. The alkyl group or alkoxy group preferably has 1 to 10 carbon atoms, more preferably 1 to 6 carbon atoms, still more preferably 1 to 3 carbon atoms, and particularly preferably 1 to 2 carbon atoms. The alkyl group may be branched or linear but is preferably linear. The
25 alkyl group which the alkoxy group has may be branched or linear, but is preferably

linear.

Rz^{12} and Rz^{13} are preferably hydrogen atoms.

[0226]

Preferred specific examples of the component (Z) include polyalkylene glycols
5 such as a polyethylene glycol and a polypropylene glycol, and derivatives thereof.

Among them, the component (Z) is preferably a polyethylene glycol or a
polypropylene glycol.

[0227]

The weight-average molecular weight (Mw) (based on the polystyrene-
10 equivalent value determined by gel permeation chromatography) of the component (Z) is
400 or more. By setting the weight-average molecular weight of the component (Z) to
400 or more, it is possible to suppress the occurrence of cracking during resist pattern
formation. The Mw of the component (Z) is preferably 500 or more, more preferably
700 or more, still more preferably 800 or more, and particularly preferably 1,000 or
15 more. The upper limit of Mw of the component (Z) is not particularly limited but is
preferably 30,000 or less, more preferably 25,000 or less, and still more preferably
20,000 or less. The range of Mw of the component (Z) is, for example, 400 to 30,000,
500 to 30,000, 700 to 30,000, 800 to 30,000, and 1,000 to 30,000.

[0228]

20 In the resist composition according to the present embodiment, the component
(Z) may be used alone or in combination of two or more kinds thereof.

In the resist composition of the present embodiment, the content of the
component (Z) is 0.8 to 32 parts by mass with respect to 100 parts by mass of the
component (A). By setting the content of the component (Z) to be equal to or more than
25 the lower limit of the above range, it is possible to suppress the occurrence of cracking

during the resist pattern formation. Further, by setting the content of the component (Z) to be equal to or not less than the upper limit of the above range, it is possible to improve the resolution in the resist pattern formation. The content of the component (Z) is preferably 0.8 to 30 parts by mass, more preferably 1.0 to 25 parts by mass, still more preferably 1.5 to 20 parts by mass, and particularly preferably 2.0 to 15 parts by mass, with respect to 100 parts by mass of the component (A).

[0229]

<Other components>

The resist composition according to the present embodiment may further contain other components in addition to the component (A) and the component (Z) described above. Examples of the other components include a component (B), a component (D), a component (E), a component (F), and a component (S), which are described below.

[0230]

<<Acid generator component (B)>>

The resist composition of the present embodiment may further contain an acid generator component (B) (hereinafter, referred to as “component (B)”) generating an acid upon exposure, in addition to the component (A) and the component (Z).

The component (B) is not particularly limited, and those which have been proposed as an acid generator for a chemically amplified resist composition in the related art can be used.

Examples of these acid generators are numerous and include onium salt-based acid generators such as iodonium salts and sulfonium salts; oxime sulfonate-based acid generators; diazomethane-based acid generators such as bisalkyl or bisaryl sulfonyl diazomethanes and poly(bis-sulfonyl)diazomethanes; nitrobenzylsulfonate-based acid generators; iminosulfonate-based acid generators; and disulfone-based acid generators.

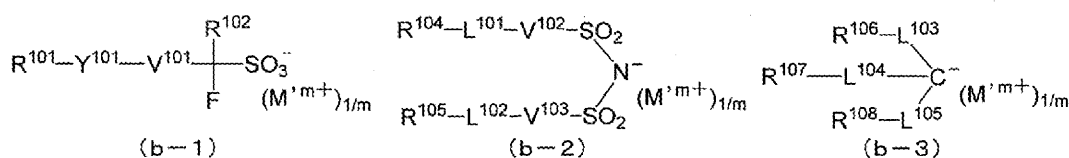
The component (B) preferably contains a compound (B1) composed of an onium salt (hereinafter, referred to as "component (B1)").

[0231]

· In regard to component (B1)

5 Examples of the component (B1) include a compound represented by General Formula (b-1) (hereinafter, also referred to as "component (b-1)"), a compound represented by General Formula (b-2) (hereinafter, also referred to as "component (b-2)"), and a compound represented by General Formula (b-3) (hereinafter, also referred to as "component (b-3)").

10 [0232]



[in the formulae, R^{101} and R^{104} to R^{108} each independently represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent, R^{104} and R^{105} may be bonded to each other to form a ring structure, R^{102} represents a fluorinated alkyl group having 1 to 5 carbon atoms, or a fluorine atom, Y^{101} represents a divalent linking group containing an oxygen atom or a single bond, V^{101} to V^{103} each independently represents a single bond, an alkylene group, or a fluorinated alkylene group, L^{101} and L^{102} each independently represents a single bond or an oxygen atom, and L^{103} to L^{105} each independently represents a single bond, -CO-, or -SO₂-. m represents an integer of 1 or greater, and M'^{m+} represents an m-valent onium cation.]

[0233]

{ Anion moiety }

· Anion in component (b-1)

In Formula (b-1), R^{101} represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which
5 may have a substituent.

[0234]

Cyclic group which may have substituent:

The cyclic group is preferably a cyclic hydrocarbon group, and the cyclic hydrocarbon group may be an aromatic hydrocarbon group or an aliphatic hydrocarbon
10 group. The aliphatic hydrocarbon group indicates a hydrocarbon group that has no aromaticity. The aliphatic hydrocarbon group may be saturated or unsaturated. In general, it is preferable that the aliphatic hydrocarbon group be saturated.

[0235]

The aromatic hydrocarbon group as R^{101} is a hydrocarbon group having an
15 aromatic ring. The aromatic hydrocarbon group preferably has 3 to 30 carbon atoms, more preferably 5 to 30, still more preferably 5 to 20, particularly preferably 6 to 15, and most preferably 6 to 10. Here, the number of carbon atoms in a substituent is not included in the number of carbon atoms.

Specific examples of the aromatic ring the aromatic hydrocarbon group has as
20 R^{101} include benzene, fluorene, naphthalene, anthracene, phenanthrene, biphenyl, or an aromatic hetero ring in which some carbon atoms constituting any of these aromatic rings have been substituted with hetero atoms. Examples of the hetero atom in the aromatic hetero rings include an oxygen atom, a sulfur atom, and a nitrogen atom.

Specific examples of the aromatic hydrocarbon group as R^{101} include a group in
25 which one hydrogen atom has been removed from the above-described aromatic ring (an

aryl group such as a phenyl group or a naphthyl group) and a group in which one hydrogen atom in the aromatic ring has been substituted with an alkylene group (an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, 1-naphthylethyl group, or a 2-naphthylethyl group). The
 5 alkylene group (an alkyl chain in the arylalkyl group) preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and particularly preferably 1 carbon atom.

[0236]

Examples of the cyclic aliphatic hydrocarbon group as R¹⁰¹ include aliphatic hydrocarbon groups containing a ring in the structure thereof.

10 Examples of the aliphatic hydrocarbon group containing a ring in the structure thereof include an alicyclic hydrocarbon group (a group in which one hydrogen atom has been removed from an aliphatic hydrocarbon ring), a group in which the alicyclic hydrocarbon group is bonded to the terminal of a linear or branched aliphatic hydrocarbon group, and a group in which the alicyclic hydrocarbon group is interposed
 15 in a linear or branched aliphatic hydrocarbon group.

The alicyclic hydrocarbon group preferably has 3 to 20 carbon atoms and more preferably 3 to 12 carbon atoms.

The alicyclic hydrocarbon group may be a polycyclic group or a monocyclic group. As the monocyclic alicyclic hydrocarbon group, a group in which one or more
 20 hydrogen atoms have been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane. As the polycyclic alicyclic hydrocarbon group, a group in which one or more hydrogen atoms have been removed from a polycycloalkane is preferable, and the number of carbon atoms of the polycycloalkane is
 25 preferably in a range of 7 to 30. Among polycycloalkanes, a polycycloalkane having a

bridged ring polycyclic skeleton, such as adamantane, norbornane, isobornane, tricyclodecane, or tetracyclododecane, and a polycycloalkane having a fused ring polycyclic skeleton, such as a cyclic group having a steroid skeleton are preferable.

[0237]

5 Among these examples, as the cyclic aliphatic hydrocarbon group as R^{101} , a group in which one or more hydrogen atoms have been removed from a monocycloalkane or a polycycloalkane is preferable, a group in which one hydrogen atom has been removed from a polycycloalkane is more preferable, an adamantyl group or a norbornyl group is particularly preferable, and an adamantyl group is most
10 preferable.

[0238]

The linear aliphatic hydrocarbon group which may be bonded to the alicyclic hydrocarbon group preferably has 1 to 10 carbon atoms, more preferably 1 to 6 carbon atoms, still more preferably 1 to 4 carbon atoms, and most preferably 1 to 3 carbon
15 atoms. The linear aliphatic hydrocarbon group is preferably a linear alkylene group, and specific examples thereof include a methylene group $[-CH_2-]$, an ethylene group $[-(CH_2)_2-]$, a trimethylene group $[-(CH_2)_3-]$, a tetramethylene group $[-(CH_2)_4-]$, and a pentamethylene group $[-(CH_2)_5-]$.

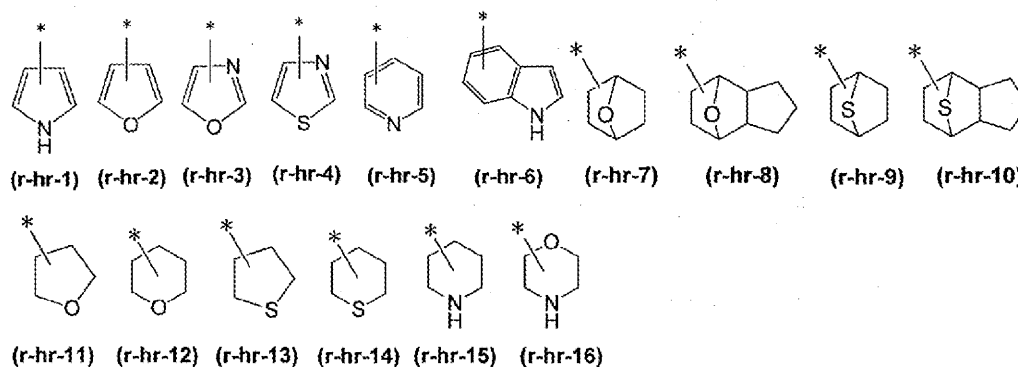
The branched aliphatic hydrocarbon group which may be bonded to the alicyclic
20 hydrocarbon group preferably has 2 to 10 carbon atoms, more preferably 3 to 6 carbon atoms, still more preferably 3 or 4 carbon atoms, and most preferably 3 carbon atoms. As the branched aliphatic hydrocarbon group, a branched alkylene group is preferred, and specific examples thereof include alkylalkylene groups, for example, alkylmethylene groups such as $-CH(CH_3)-$, $-CH(CH_2CH_3)-$, $-C(CH_3)_2-$, $-C(CH_3)(CH_2CH_3)-$, -
25 $C(CH_3)(CH_2CH_2CH_3)-$, and $-C(CH_2CH_3)_2-$; alkylethylene groups such as -

CH(CH₃)CH₂-, -CH(CH₃)CH(CH₃)-, -C(CH₃)₂CH₂-, -CH(CH₂CH₃)CH₂-, and -C(CH₂CH₃)₂-CH₂-; alkyltrimethylene groups such as -CH(CH₃)CH₂CH₂-, and -CH₂CH(CH₃)CH₂-, and alkyltetramethylene groups such as -CH(CH₃)CH₂CH₂CH₂-, and -CH₂CH(CH₃)CH₂CH₂-. As the alkyl group in the alkylalkylene group, a linear alkyl group having 1 to 5 carbon atoms is preferable.

[0239]

The cyclic hydrocarbon group as R¹⁰¹ may contain a hetero atom such as a hetero ring. Specific examples thereof include lactone-containing cyclic groups each represented by General Formulae (a2-r-1) to (a2-r-7), -SO₂--containing cyclic groups each represented by General Formulae (a5-r-1) to (a5-r-4), and other heterocyclic groups each represented by Chemical Formulae (r-hr-1) to (r-hr-16).

[0240]



[0241]

Examples of the substituent for the cyclic group as R¹⁰¹ include an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, a carbonyl group, and a nitro group. The alkyl group as the substituent is preferably an alkyl group having 1 to 5 carbon atoms, and a methyl group, an ethyl group, a propyl group, an n-butyl group, or a tert-butyl group is most preferable.

The alkoxy group as the substituent is preferably an alkoxy group having 1 to 5 carbon atoms, more preferably a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group, or a tert-butoxy group, and most preferably a methoxy group or an ethoxy group.

5 Examples of the halogen atom for the substituent include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom, and a fluorine atom is preferable.

Example of the above-described halogenated alkyl group as the substituent includes a group in which part or all hydrogen atoms in an alkyl group having 1 to 5 carbon atoms such as a methyl group, an ethyl group, a propyl group, an n-butyl group,
10 or a tert-butyl group have been substituted with the above-described halogen atoms.

The carbonyl group as the substituent is a group that substitutes a methylene group (-CH₂-) constituting the cyclic hydrocarbon group.

[0242]

Chain-like alkyl group which may have substituent:

15 The chain-like alkyl group as R¹⁰¹ may be linear or branched.

The linear alkyl group preferably has 1 to 20 carbon atoms, more preferably 1 to 15 carbon atoms, and most preferably 1 to 10 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decanyl group, an undecyl
20 group, a dodecyl group, a tridecyl group, an isotridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, an isohexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl group, an icosyl group, a hencosyl group, and a docosyl group.

The branched alkyl group preferably has 3 to 20 carbon atoms, more preferably
25 3 to 15, and most preferably 3 to 10. Specific examples thereof include a 1-methylethyl

group, a 1-methylpropyl group, a 2-methylpropyl group, a 1-methylbutyl group, a 2-methylbutyl group, a 3-methylbutyl group, a 1-ethylbutyl group, a 2-ethylbutyl group, a 1-methylpentyl group, a 2-methylpentyl group, a 3-methylpentyl group, and a 4-methylpentyl group.

5 [0243]

Chain-like alkenyl group which may have substituent:

A chain-like alkenyl group as R^{101} may be linear or branched, and the number of carbon atoms thereof is preferably in a range of 2 to 10, more preferably in a range of 2 to 5, still more preferably in a range of 2 to 4, and particularly preferably 3. Examples
10 of the linear alkenyl group include a vinyl group, a propenyl group (an allyl group), and a butynyl group. Examples of the branched alkenyl group include a 1-methylvinyl group, a 2-methylvinyl group, a 1-methylpropenyl group, and a 2-methylpropenyl group.

Among the examples, as the chain-like alkenyl group, a linear alkenyl group is preferable, a vinyl group or a propenyl group is more preferable, and a vinyl group is
15 particularly preferable.

[0244]

As the substituent for the chain-like alkyl group or alkenyl group as R^{101} , an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, a carbonyl group, a nitro group, an amino group, a cyclic group as R^{101} or the like can be used.

20 [0245]

Among the above examples, R^{101} is preferably a cyclic group which may have a substituent and more preferably a cyclic hydrocarbon group which may have a substituent. More specific examples of the cyclic hydrocarbon group include a phenyl group, a naphthyl group, a group in which one or more hydrogen atoms have been
25 removed from a polycycloalkane, lactone-containing cyclic groups each represented by

any of General Formulae (a2-r-1) to (a2-r-7), and -SO₂-containing cyclic groups each represented by any of General Formulae (a5-r-1) to (a5-r-4).

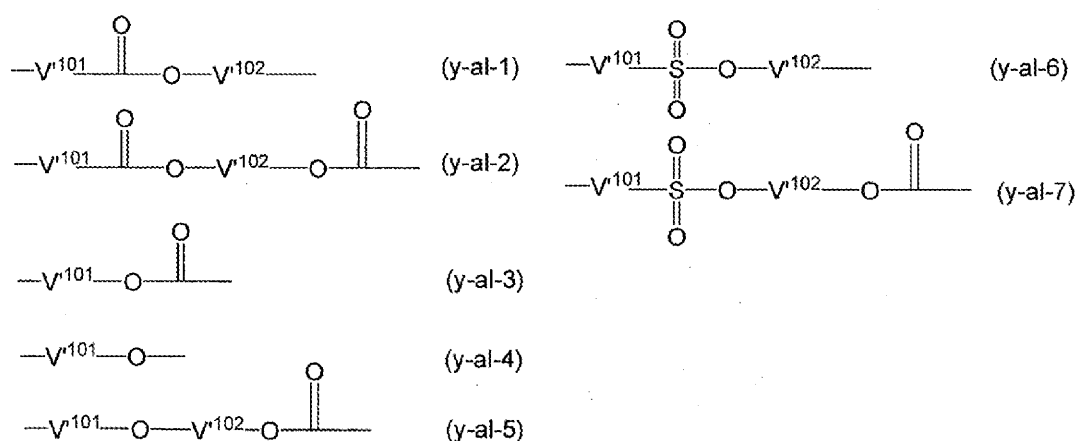
[0246]

In Formula (b-1), Y¹⁰¹ represents a single bond or a divalent linking group
5 containing an oxygen atom.

In a case where Y¹⁰¹ represents a divalent linking group containing an oxygen atom, Y¹⁰¹ may contain an atom other than an oxygen atom. Examples of atoms other than an oxygen atom include a carbon atom, a hydrogen atom, a sulfur atom, and a nitrogen atom.

10 Examples of divalent linking groups containing an oxygen atom include non-hydrocarbon oxygen atom-containing linking groups such as an oxygen atom (an ether bond; -O-), an ester bond (-C(=O)-O-), an oxycarbonyl group (-O-C(=O)-), an amide bond (-C(=O)-NH-), a carbonyl group (-C(=O)-), or a carbonate bond (-O-C(=O)-O-); and combinations of the above-described non-hydrocarbon oxygen atom-containing
15 linking groups with an alkylene group. Furthermore, a sulfonyl group (-SO₂-) may be linked to the combination. Examples of divalent linking groups containing an oxygen atom include linking groups each represented by General Formulae (y-al-1) to (y-al-7) shown below.

[0247]



[In the formulae, V^{101} represents a single bond or an alkylene group having 1 to 5 carbon atoms, and V^{102} represents a divalent saturated hydrocarbon group having 1 to 30 carbon atoms.]

5 [0248]

The divalent saturated hydrocarbon group as V^{102} is preferably an alkylene group having 1 to 30 carbon atoms, more preferably an alkylene group having 1 to 10 carbon atoms, and still more preferably an alkylene group having 1 to 5 carbon atoms.

[0249]

10 The alkylene group as V^{101} and V^{102} may be a linear alkylene group or a branched alkylene group, and a linear alkylene group is preferable.

Specific examples of the alkylene group as V^{101} and V^{102} include a methylene group $[-\text{CH}_2-]$; an alkylmethylene group such as $-\text{CH}(\text{CH}_3)-$, $-\text{CH}(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_3)-$, or $-\text{C}(\text{CH}_2\text{CH}_3)_2-$; an ethylene group $[-\text{CH}_2\text{CH}_2-]$; an alkylethylene group such as $-\text{CH}(\text{CH}_3)\text{CH}_2-$, $-\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2\text{CH}_2-$, or $-\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2-$; a trimethylene group (n-propylene group) $[-\text{CH}_2\text{CH}_2\text{CH}_2-]$; an alkyltrimethylene group such as $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-$ or $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$; a tetramethylene group $[-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-]$; an alkyltetramethylene

group such as $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-$; and a pentamethylene group $[-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-]$.

Further, a part of a methylene group in the alkylene group as V^{101} and V^{102} may be substituted with a divalent aliphatic cyclic group having 5 to 10 carbon atoms.

- 5 The aliphatic cyclic group is preferably a divalent group in which one hydrogen atom has been removed from the cyclic aliphatic hydrocarbon group (a monocyclic aliphatic hydrocarbon group or a polycyclic aliphatic hydrocarbon group) as Ra'^3 in Formula (a1-r-1), and a cyclohexylene group, a 1,5-adamantylene group, or a 2,6-adamantylene group is more preferable.

10 [0250]

Y^{101} preferably represents a divalent linking group containing an ester bond or a divalent linking group containing an ether bond and more preferably linking groups each represented by Formulae (y-al-1) to (y-al-5).

[0251]

- 15 In Formula (b-1), V^{101} represents a single bond, an alkylene group, or a fluorinated alkylene group. The alkylene group and the fluorinated alkylene group as V^{101} preferably have 1 to 4 carbon atoms. Examples of the fluorinated alkylene group as V^{101} include a group in which part or all hydrogen atoms in the alkylene group as V^{101} have been substituted with fluorine atoms. Among these examples, as V^{101} , a single
20 bond or a fluorinated alkylene group having 1 to 4 carbon atoms is preferable.

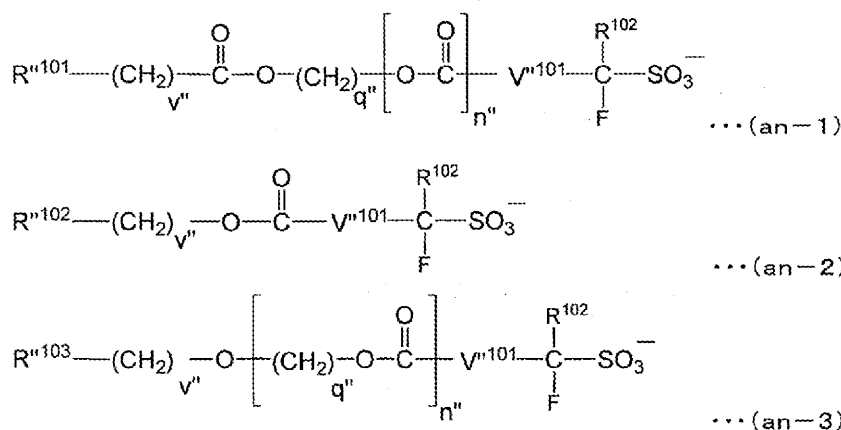
[0252]

In Formula (b-1), R^{102} represents a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms. R^{102} preferably represents a fluorine atom or a perfluoroalkyl group having 1 to 5 carbon atoms and more preferably a fluorine atom.

25 [0253]

As a specific example of the anion moiety represented by Formula (b-1), in a case where Y¹⁰¹ represents a single bond, a fluorinated alkylsulfonate anion such as a trifluoromethanesulfonate anion or a perfluorobutanesulfonate anion can be mentioned; and in a case where Y¹⁰¹ represents a divalent linking group containing an oxygen atom, anions represented by Formulae (an-1) to (an-3) shown below can be mentioned.

[0254]



[In the formula, R''¹⁰¹ represents an aliphatic cyclic group which may have a substituent, monovalent heterocyclic groups each represented by each of Chemical Formulae (r-hr-1) to (r-hr-6), or a chain-like alkyl group which may have a substituent. R''¹⁰² is an aliphatic cyclic group which may have a substituent, lactone-containing cyclic groups each represented by General Formulae (a2-r-1), (a2-r-3) to (a2-r-7), -or SO₂--containing cyclic groups each represented by General Formulae (a5-r-1) to (a5-r-4). R''¹⁰³ represents an aromatic cyclic group which may have a substituent, an aliphatic cyclic group which may have a substituent, or a chain-like alkenyl group which may have a substituent. V''¹⁰¹ represents a single bond, an alkylene group having 1 to 4 carbon atoms, or a fluorinated alkylene group having 1 to 4 carbon atoms. R¹⁰² represents a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms. v'' each

independently represents an integer of 0 to 3, q'' each independently represents an integer of 0 to 20, and n'' represents 0 or 1.]

[0255]

As the aliphatic cyclic group as R''^{101} , R''^{102} , and R''^{103} which may have a
 5 substituent, the same groups as the cyclic aliphatic hydrocarbon group as R^{101} in Formula (b-1) described above are preferable. As the substituent, the same group as the substituent which may substitute the cyclic aliphatic hydrocarbon group as R^{101} in Formula (b-1) can be mentioned.

[0256]

10 As the aromatic cyclic group as R''^{103} in Formula (b-1), which may have a substituent, the same groups as the aromatic hydrocarbon group for the cyclic hydrocarbon group represented by R^{101} in Formula (b-1) described above are preferable. As the substituent, the same groups as the substituents which may substitute the aromatic hydrocarbon group as R^{101} in Formula (b-1) can be mentioned.

15 [0257]

As the chain-like alkyl group as R''^{101} which may have a substituent, the same groups mentioned as the chain-like alkyl groups represented by R^{101} in Formula (b-1) are preferable.

20 As the chain-like alkenyl group as R''^{103} which may have a substituent, the same groups mentioned as the chain-like alkenyl groups represented by R^{101} in Formula (b-1) are preferable.

[0258]

· Anion in component (b-2)

In Formula (b-2), R^{104} and R^{105} each independently represents a cyclic group
 25 which may have a substituent, a chain-like alkyl group which may have a substituent or a

chain-like alkenyl group which may have a substituent, and has the same definition as that for R^{101} in Formula (b-1). R^{104} and R^{105} may be bonded to each other to form a ring.

As R^{104} and R^{105} , a chain-like alkyl group which may have a substituent is preferable, and a linear or branched alkyl group or a linear or branched fluorinated alkyl group is more preferable.

The chain-like alkyl group preferably has 1 to 10 carbon atoms, more preferably 1 to 7 carbon atoms, and still more preferably 1 to 3 carbon atoms. It is preferable that the number of carbon atoms in the chain-like alkyl group as R^{104} and R^{105} be small because the solubility in a solvent for a resist is also excellent in this range of the number of carbon atoms. Further, in the chain-like alkyl group as R^{104} and R^{105} , it is preferable that the number of hydrogen atoms substituted with fluorine atoms be as large as possible because the acid strength increases and the transparency to high energy radiation of 250 nm or less or electron beams is improved. The proportion of fluorine atoms in the chain-like alkyl group, that is, the fluorination ratio is preferably in a range of 70% to 100% and more preferably in a range of 90% to 100%, and it is most preferable that the chain-like alkyl group is a perfluoroalkyl group in which all hydrogen atoms be substituted with fluorine atoms.

In Formula (b-2), V^{102} and V^{103} each independently represents a single bond, an alkylene group, or a fluorinated alkylene group, and has the same definition as that for V^{101} in Formula (b-1).

In Formula (b-2), L^{101} and L^{102} each independently represents a single bond or an oxygen atom.

[0259]

· Anion in component (b-3)

In Formula (b-3), R^{106} to R^{108} each independently represents a cyclic group which may have a substituent or a chain-like alkyl group which may have a substituent or a chain-like alkenyl group which may have a substituent, and has the same definition as that for R^{101} in Formula (b-1).

5 In Formula (b-3), L^{103} to L^{105} each independently represents a single bond, -CO-, or -SO₂-.

[0260]

Among the above, as the anion moiety of the component (B), an anion of the component (b-1) is preferable. Among the above examples, a fluorinated alkyl
 10 sulfonate anion or an anion represented by any of General Formulae (an-1) to (an-3) is more preferable, and a fluorinated alkyl sulfonate anion or an anion represented by any of General Formula (an-1) and (an-2) is still more preferable.

[0261]

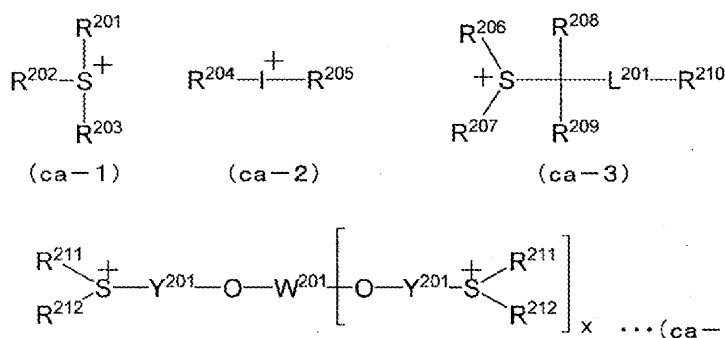
{ Cation moiety }

15 In Formulae (b-1), (b-2), and (b-3), M^{m+} represents an m-valent onium cation. Among them, a sulfonium cation and an iodonium cation are preferable. m represents an integer of 1 or more.]

[0262]

As the preferred cation moiety $((M^{m+})_{1/m})$, organic cations each represented by
 20 General Formulae (ca-1) to (ca-4) can be mentioned.

[0263]



[In the formula, R^{201} to R^{207} and R^{211} to R^{212} each independently represents an aryl group, an alkyl group, or an alkenyl group, each of which may have a substituent.

R^{201} to R^{203} , R^{206} to R^{207} , and R^{211} to R^{212} may be bonded to each other to form a ring

5 together with the sulfur atoms in the formulae. R^{208} and R^{209} each independently

represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms. R^{210}

represents an aryl group which may have a substituent, an alkyl group which may have a substituent, an alkenyl group which may have a substituent, or a $-\text{SO}_2$ -containing cyclic group which may have a substituent. L^{201} represents $-\text{C}(=\text{O})-$ or $-\text{C}(=\text{O})-\text{O}-$. Y^{201} s

10 each independently represents an arylene group, an alkylene group, or an alkenylene group. x represents 1 or 2. W^{201} represents an $(x+1)$ -valent linking group.]

[0264]

In General Formulae (ca-1) to (ca-4), examples of the aryl group as R^{201} to R^{207} , R^{211} , and R^{212} include an unsubstituted aryl group having 6 to 20 carbon atoms, and a

15 phenyl group or a naphthyl group is preferable.

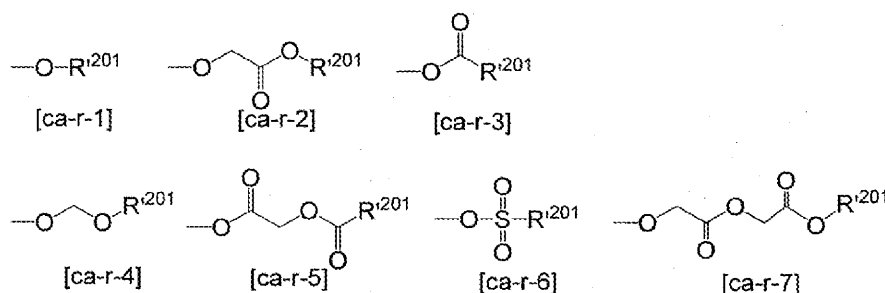
The alkyl group as R^{201} to R^{207} , R^{211} , and R^{212} is a chain-like or cyclic alkyl group, and the number of carbon atoms thereof is preferably in a range of 1 to 30.

The alkenyl group as R^{201} to R^{207} , R^{211} , and R^{212} preferably has 2 to 10 carbon atoms.

20 Examples of the substituent which may be included in R^{201} to R^{207} and R^{210} to

R²¹² include an alkyl group, a halogen atom, a halogenated alkyl group, a carbonyl group, a cyano group, an amino group, an aryl group, and groups each represented by General Formulae (ca-r-1) to (ca-r-7) shown above.

[0265]



5

[In the formulae, R²⁰¹ s each independently represents a hydrogen atom, a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent.]

[0266]

10

Cyclic group which may have substituent:

The cyclic group is preferably a cyclic hydrocarbon group, and the cyclic hydrocarbon group may be an aromatic hydrocarbon group or an aliphatic hydrocarbon group. The aliphatic hydrocarbon group indicates a hydrocarbon group that has no aromaticity. The aliphatic hydrocarbon group may be saturated or unsaturated. In general, it is preferable that the aliphatic hydrocarbon group be saturated.

15

[0267]

The aromatic hydrocarbon group as R²⁰¹ is a hydrocarbon group having an aromatic ring. The aromatic hydrocarbon group preferably has 3 to 30 carbon atoms, more preferably 5 to 30 carbon atoms, still more preferably 5 to 20 carbon atoms, particularly preferably 6 to 15 carbon atoms, and most preferably 6 to 10 carbon atoms.

20

Here, the number of carbon atoms in a substituent is not included in the number of carbon atoms.

Specific examples of the aromatic ring which the aromatic hydrocarbon group has as R'²⁰¹ include benzene, fluorene, naphthalene, anthracene, phenanthrene, biphenyl, or an aromatic hetero ring in which some carbon atoms constituting any of these aromatic rings have been substituted with hetero atoms. Examples of the hetero atom in the aromatic hetero rings include an oxygen atom, a sulfur atom, and a nitrogen atom.

Specific examples of the aromatic hydrocarbon group as R'²⁰¹ include a group in which one hydrogen atom has been removed from the above-described aromatic ring (an aryl group such as a phenyl group or a naphthyl group) and a group in which one hydrogen atom in the aromatic ring has been substituted with an alkylene group (an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, 1-naphthylethyl group, or a 2-naphthylethyl group). The alkylene group (an alkyl chain in the arylalkyl group) preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and particularly preferably 1 carbon atom.

[0268]

Examples of the cyclic aliphatic hydrocarbon group as R'²⁰¹ include aliphatic hydrocarbon groups containing a ring in the structure thereof.

Examples of the aliphatic hydrocarbon group containing a ring in the structure thereof include an alicyclic hydrocarbon group (a group in which one hydrogen atom has been removed from an aliphatic hydrocarbon ring), a group in which the alicyclic hydrocarbon group is bonded to the terminal of a linear or branched aliphatic hydrocarbon group, and a group in which the alicyclic hydrocarbon group is interposed in a linear or branched aliphatic hydrocarbon group.

The alicyclic hydrocarbon group preferably has 3 to 20 carbon atoms and more

preferably 3 to 12 carbon atoms.

The alicyclic hydrocarbon group may be a polycyclic group or a monocyclic group. As the monocyclic alicyclic hydrocarbon group, a group in which one or more hydrogen atoms have been removed from a monocycloalkane is preferable. The
 5 monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane. As the polycyclic alicyclic hydrocarbon group, a group in which one or more hydrogen atoms have been removed from a polycycloalkane is preferable, and the number of carbon atoms of the polycycloalkane is preferably in a range of 7 to 30. Among polycycloalkanes, a polycycloalkane having a
 10 bridged ring polycyclic skeleton, such as adamantane, norbornane, isobornane, tricyclodecane, or tetracyclododecane, and a polycycloalkane having a fused ring polycyclic skeleton, such as a cyclic group having a steroid skeleton are preferable.

[0269]

Among these examples, as the cyclic aliphatic hydrocarbon group as R'²⁰¹, a
 15 group in which one or more hydrogen atoms have been removed from a monocycloalkane or a polycycloalkane is preferable, a group in which one hydrogen atom has been removed from a polycycloalkane is more preferable, an adamantyl group or a norbornyl group is particularly preferable, and an adamantyl group is most preferable.

20 [0270]

The linear or branched aliphatic hydrocarbon group which may be bonded to the alicyclic hydrocarbon group preferably has 1 to 10 carbon atoms, more preferably 1 to 6 carbon atoms, still more preferably 1 to 4 carbon atoms, and particularly preferably 1 to 3 carbon atoms.

25 The linear aliphatic hydrocarbon group is preferably a linear alkylene group, and

specific examples thereof include a methylene group $[-\text{CH}_2-]$, an ethylene group $[-(\text{CH}_2)_2-]$, a trimethylene group $[-(\text{CH}_2)_3-]$, a tetramethylene group $[-(\text{CH}_2)_4-]$, and a pentamethylene group $[-(\text{CH}_2)_5-]$.

As the branched aliphatic hydrocarbon group, a branched alkylene group is preferred, and specific examples thereof include alkylalkylene groups, for example, alkylmethylene groups such as $-\text{CH}(\text{CH}_3)-$, $-\text{CH}(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_3)-$, and $-\text{C}(\text{CH}_2\text{CH}_3)_2-$; alkylethylene groups such as $-\text{CH}(\text{CH}_3)\text{CH}_2-$, $-\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2\text{CH}_2-$, $-\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2-$, and $-\text{C}(\text{CH}_2\text{CH}_3)_2\text{CH}_2-$; alkyltrimethylene groups such as $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-$, and $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$; and alkyltetramethylene groups such as $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2-$, and $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-$. As the alkyl group in the alkylalkylene group, a linear alkyl group having 1 to 5 carbon atoms is preferable.

[0271]

The cyclic hydrocarbon group as R'^{201} may contain a hetero atom such as a hetero ring. Specific examples thereof include lactone-containing cyclic groups each represented by General Formulae (a2-r-1) to (a2-r-7), $-\text{SO}_2-$ -containing cyclic groups each represented by General Formulae (a5-r-1) to (a5-r-4), and other heterocyclic groups each represented by Chemical Formulae (r-hr-1) to (r-hr-16).

[0272]

Examples of the substituent for the cyclic group as R'^{201} include an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, a carbonyl group, and a nitro group.

The alkyl group as the substituent is preferably an alkyl group having 1 to 5 carbon atoms, and a methyl group, an ethyl group, a propyl group, an n-butyl group, or a tert-butyl group is most preferable.

The alkoxy group as the substituent is preferably an alkoxy group having 1 to 5 carbon atoms, more preferably a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group, or a tert-butoxy group, and most preferably a methoxy group or an ethoxy group.

5 Examples of the halogen atom for the substituent include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom, and a fluorine atom is preferable.

Example of the above-described halogenated alkyl group as the substituent includes a group in which part or all hydrogen atoms in an alkyl group having 1 to 5 carbon atoms such as a methyl group, an ethyl group, a propyl group, an n-butyl group,
10 or a tert-butyl group have been substituted with the above-described halogen atoms.

The carbonyl group as the substituent is a group that substitutes a methylene group (-CH₂-) constituting the cyclic hydrocarbon group.

[0273]

Chain-like alkyl group which may have substituent:

15 The chain-like alkyl group as R²⁰¹ may be linear or branched.

The linear alkyl group preferably has 1 to 20 carbon atoms, more preferably 1 to 15 carbon atoms, and most preferably 1 to 10 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decanyl group, an undecyl
20 group, a dodecyl group, a tridecyl group, an isotridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, an isohexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl group, an icosyl group, a hencosyl group, and a docosyl group.

The branched alkyl group preferably has 3 to 20 carbon atoms, more preferably
25 3 to 15 carbon atoms, and most preferably 3 to 10 carbon atoms. Specific examples

thereof include a 1-methylethyl group, a 1-methylpropyl group, a 2-methylpropyl group, a 1-methylbutyl group, a 2-methylbutyl group, a 3-methylbutyl group, a 1-ethylbutyl group, a 2-ethylbutyl group, a 1-methylpentyl group, a 2-methylpentyl group, a 3-methylpentyl group, and a 4-methylpentyl group.

5 [0274]

Chain-like alkenyl group which may have substituent:

Such a chain-like alkenyl group as R'^{201} may be linear or branched, preferably has 2 to 10 carbon atoms, more preferably 2 to 5 carbon atoms, still more preferably 2 to 4 carbon atoms, and particularly preferably 3 carbon atoms. Examples of the linear
 10 alkenyl group include a vinyl group, a propenyl group (an allyl group), and a butynyl group. Examples of the branched alkenyl group include a 1-methylvinyl group, a 2-methylvinyl group, a 1-methylpropenyl group, and a 2-methylpropenyl group.

Among the examples, as the chain-like alkenyl group, a linear alkenyl group is preferable, a vinyl group or a propenyl group is more preferable, and a vinyl group is
 15 particularly preferable.

[0275]

As the substituent for the chain-like alkyl group or alkenyl group as R'^{201} , an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, a carbonyl group, a nitro group, an amino group, a cyclic group as R'^{201} or the like may be used.

20 [0276]

As the cyclic group which may have a substituent, the chain-like alkyl group which may have a substituent, or the chain-like alkenyl group which may have a substituent, as R'^{201} , a group that is the same as the acid-dissociable group represented by above-described Formula (a1-r-2) can be mentioned as the cyclic group which may have
 25 a substituent or the chain-like alkyl group which may have a substituent, in addition to

the groups described above.

[0277]

Among the examples, as R'^{201} , a cyclic group which may have a substituent is preferable, and a cyclic hydrocarbon group which may have a substituent is more preferable. More specific examples of the cyclic hydrocarbon group include a phenyl group, a naphthyl group, a group in which one or more hydrogen atoms have been removed from a polycycloalkane, lactone-containing cyclic groups each represented by any of General Formulae (a2-r-1) to (a2-r-7), and $-SO_2$ -containing cyclic groups each represented by any of General Formulae (a5-r-1) to (a5-r-4).

[0278]

In General Formulae (ca-1) to (ca-4), R^{201} to R^{203} , R^{206} and R^{207} , and R^{211} and R^{212} are bonded to each other to form a ring with a sulfur atom in the formula, these groups may be bonded to one another via a hetero atom such as a sulfur atom, an oxygen atom or a nitrogen atom, or a functional group such as a carbonyl group, $-SO-$, $-SO_2-$, $-SO_3-$, $-COO-$, $-CONH-$ or $-N(R_N)-$ (here, R_N represents an alkyl group having 1 to 5 carbon atoms). As a ring to be formed, a ring containing the sulfur atom in the formula in the ring skeleton thereof is preferably a 3- to 10-membered ring and most preferably a 5- to 7-membered ring including the sulfur atom. Specific examples of the ring to be formed include a thiophene ring, a thiazole ring, a benzothiophene ring, a thianthrene ring, a benzothiophene ring, a dibenzothiophene ring, a 9H-thioxanthene ring, a thioxanthone ring, a thianthrene ring, a phenoxathiin ring, a tetrahydrothiophenium ring, and a tetrahydrothiopyranium ring.

[0279]

R^{208} and R^{209} each independently represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms and is preferably a hydrogen atom or an alkyl group having 1

to 3 carbon atoms. In a case where R^{208} and R^{209} each represents an alkyl group, R^{208} and R^{209} may be bonded with each other to form a ring.

[0280]

R^{210} represents an aryl group which may have a substituent, an alkyl group
5 which may have a substituent, an alkenyl group which may have a substituent, or a $-SO_2-$ containing cyclic group which may have a substituent.

Examples of the aryl group as R^{210} include an unsubstituted aryl group having 6 to 20 carbon atoms, and a phenyl group or a naphthyl group is preferable.

The alkyl group as R^{210} , a chain-like or cyclic alkyl group having 1 to 30 carbon
10 atoms is preferable.

The alkenyl group as R^{210} preferably has 2 to 10 carbon atoms. The $-SO_2-$ containing cyclic group which may have a substituent, as R^{210} , is preferably a “ $-SO_2-$ containing polycyclic group”, and is a group represented by General Formula (a5-r-1) is more preferable.

15 [0281]

Y^{201} s each independently represents an arylene group, an alkylene group, or an alkenylene group.

Examples of the arylene group as Y^{201} include groups in which one hydrogen atom has been removed from an aryl group mentioned as the aromatic hydrocarbon group
20 represented by R^{101} in Formula (b-1) described above.

Examples of the alkylene group and alkenylene group as Y^{201} include groups in which one hydrogen atom has been removed from the chain-like alkyl group or the chain-like alkenyl group as R^{101} in Formula (b-1) described above.

[0282]

25 In Formula (ca-4), x represents 1 or 2.

W^{201} represents an $(x + 1)$ -valent linking group, that is, a divalent or trivalent linking group.

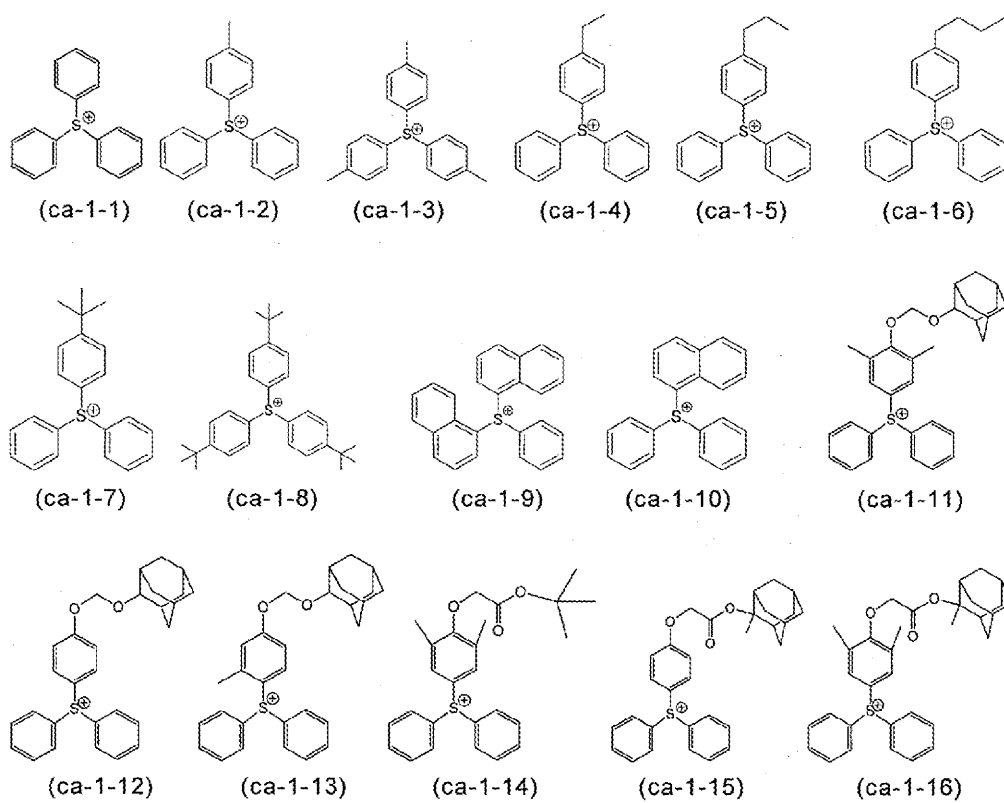
As the divalent linking group represented by W^{201} , a divalent hydrocarbon group which may have a substituent is preferable, and as examples thereof, the same divalent hydrocarbon groups (which may have a substituent) as those described above represented by Y^{21} in General Formula (a2-1) can be mentioned. The divalent linking group as W^{201} may be linear, branched or cyclic, and cyclic is more preferable. Among these, an arylene group having two carbonyl groups, each bonded to the terminal thereof is preferable. Examples of the arylene group include a phenylene group and a naphthylene group, and a phenylene group is particularly preferable.

As the trivalent linking group as W^{201} , a group in which one hydrogen atom has been removed from the above-described divalent linking group as W^{201} and a group in which the divalent linking group has been bonded to another divalent linking group can be mentioned. The trivalent linking group as W^{201} is preferably a group in which two carbonyl groups are bonded to an arylene group.

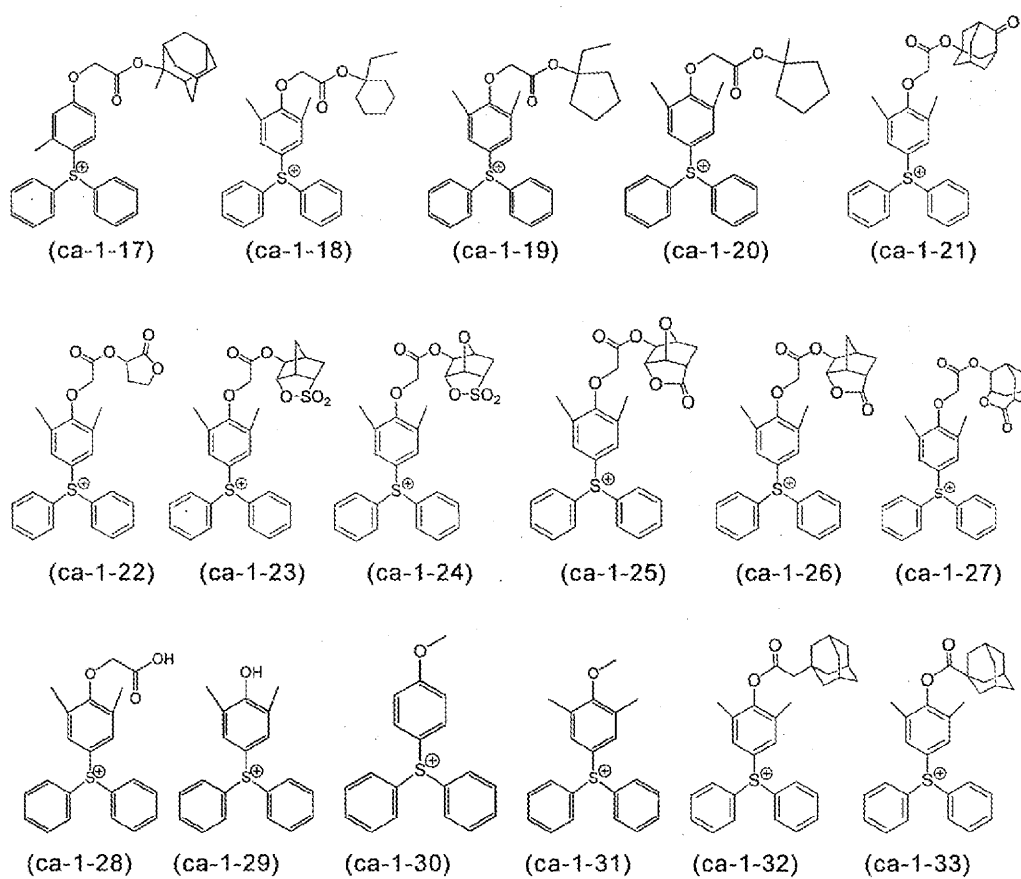
[0283]

Specific examples of suitable cations each represented by Formula (ca-1) include cations each represented by Chemical Formulae (ca-1-1) to (ca-1-70) shown below.

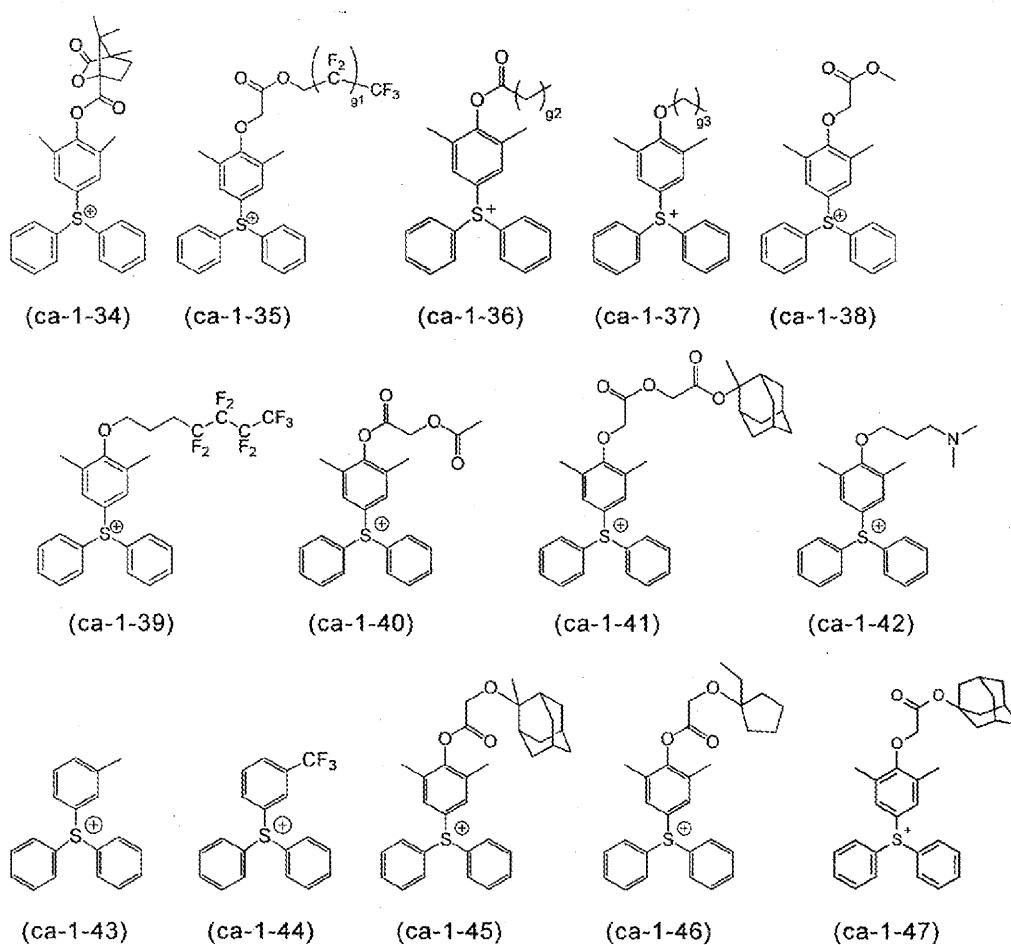
[0284]



[0285]

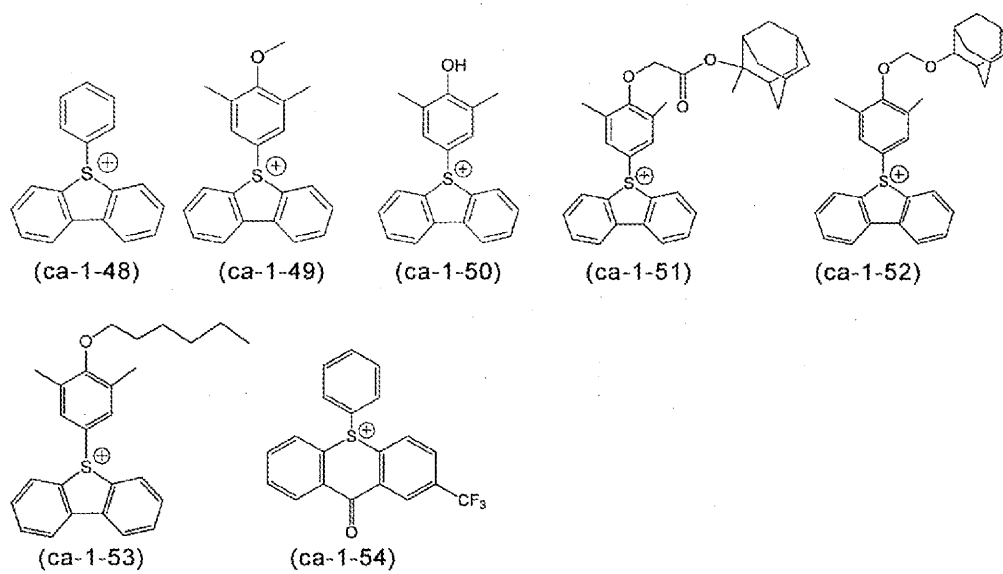


[0286]

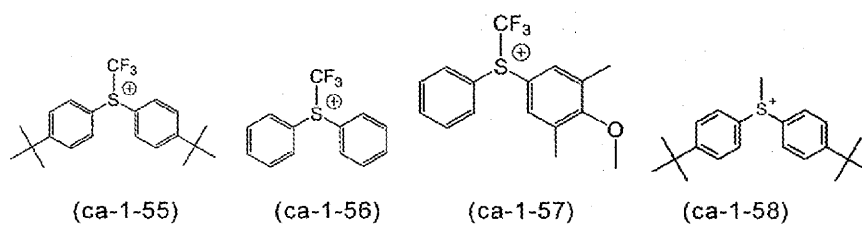


[In the formula, g1, g2, and g3 represent the numbers of repetitions, g1 is an integer of 1 to 5, g2 is an integer of 0 to 20, and g3 is an integer of 0 to 20.]

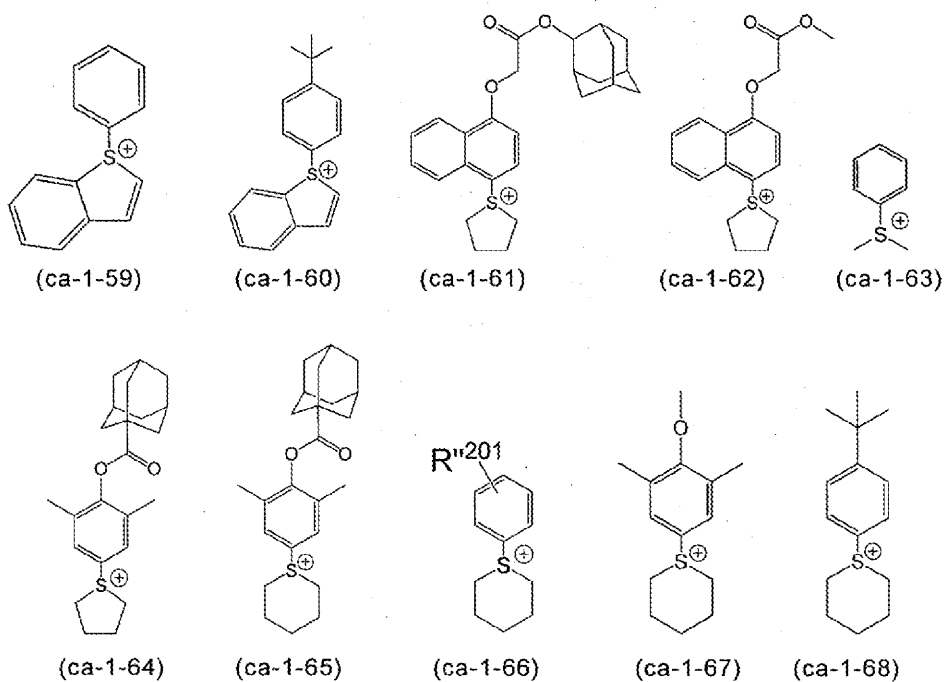
[0287]



[0288]



[0289]



[In the formula, R^{201} represents a hydrogen atom or a substituent, and the substituent is the same as the substituent that R^{201} to R^{207} and R^{210} to R^{212} may have.]

[0290]

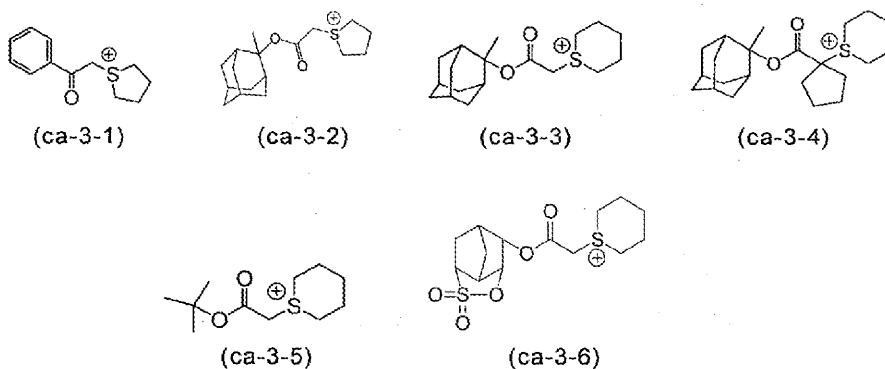
5 Specific examples of suitable cations represented by Formula (ca-2) include a diphenyliodonium cation and a bis(4-tert-butylphenyl)iodonium cation.

[0291]

Specific examples of the suitable cations each represented by Formula (ca-3) include cations each represented by Formulae (ca-3-1) and (ca-3-6) shown below.

10

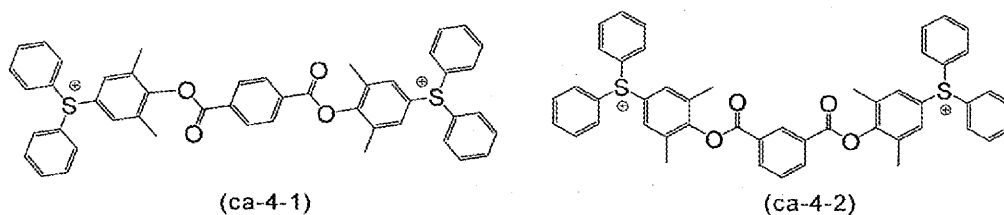
[0292]



[0293]

Specific examples of the suitable cations each represented by Formula (ca-4) include cations each represented by Formulae (ca-4-1) and (ca-4-2) shown below.

5 [0294]



[0295]

Among the above cations, as the cation moiety $((M^{m+})_{1/m})$, a cation represented by General Formula (ca-1) is preferable. From the viewpoint that the transparency is maintained in a thick resist film, in General Formula (ca-1), it is preferable that at least one of R^{202} to R^{203} preferably be an alkyl or alkenyl group, more preferable that two or more of R^{202} to R^{203} be alkyl groups or alkenyl groups, and still more preferable that two or more of R^{202} to R^{203} be alkyl groups. In a case where two or more of R^{202} to R^{203} are an alkyl group or an alkenyl group, two of them may be bonded to each other to form a ring together with the sulfur atom in the formula. The cation represented by General Formula (ca-1) is preferably a cation represented by Formulae (ca-1-55) to (ca-1-68) and

more preferably a cation represented by Formulae (ca-1-63) to (ca-1-68).

[0296]

· In regard to component (B2)

The component (B) may contain an acid generator component (hereinafter,
5 referred to as “component (B2)”) which does not correspond to the component (B1).

The component (B2) is not particularly limited as long as it generates an acid upon exposure and does not correspond to the component (B1), and can be randomly selected from known components. Examples of the component (B2) are numerous and include; oxime sulfonate-based acid generators; diazomethane-based acid generators such as
10 bisalkyl or bisaryl sulfonyl diazomethanes and poly(bis-sulfonyl)diazomethanes; nitrobenzylsulfonate-based acid generators; iminosulfonate-based acid generators; and disulfone-based acid generators.

[0297]

In the resist composition according to the present embodiment, the component
15 (B) may be used alone or in combination of two or more kinds thereof.

In a case where the resist composition contains the component (B), the content of the component (B) in the resist composition is preferably less than 50 parts by mass, more preferably in a range of 1 to 40 parts by mass, and still more preferably in a range of 5 to 25 parts by mass with respect to 100 parts by mass of the component (A).

20 In a case where the content of the component (B) is set to be in the preferred range described above, pattern formation can be satisfactorily performed. Further, in a case where each component of the resist composition is dissolved in an organic solvent, the above range is preferable since a uniform solution is easily obtained and the storage stability of the resist composition is improved.

25 [0298]

<Base component (D)>>

The resist composition of the present embodiment may further contain, in addition to the components (A) and (Z), a base component (component (D)) that traps (that is, controls the diffusion of an acid) an acid generated by exposure. The
 5 component (D) functions as a quencher (an acid diffusion-controlling agent) which traps the acid generated in the resist composition upon exposure.

Examples of the component (D) include a photodecomposable base (D1) having an acid diffusion-controlling activity (hereinafter, referred to as the “component (D1)”) which is lost by the decomposition by exposure and a nitrogen-containing organic
 10 compound (D2) (hereinafter, referred to as a “component (D2)”) which does not correspond to the component (D1). Among these, the nitrogen-containing organic compound (D2) (component (D2)) is preferable from the viewpoint of maintaining sensitivity in a thick resist film. As the component (D2), a chain-like alkylamine is more preferable from the viewpoint of maintaining transparency in a thick resist film.

15 [0299]

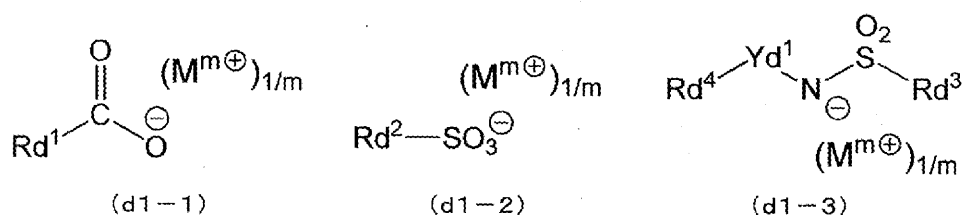
· In regard to component (D1)

In a case where a resist composition containing the component (D1) is obtained, the contrast between the light-exposed portion and the light-unexposed portion of the resist film can be further improved at the time of the formation of a resist pattern. The
 20 component (D1) is not particularly limited as long as the component is decomposed upon exposure and loses the acid diffusion controllability, and one or more compounds selected from the group consisting of a compound represented by General Formula (d1-1) (hereinafter, referred to as a “component (d1-1)”), a compound represented by General Formula (d1-2) (hereinafter, referred to as a “component (d1-2)”), and a compound
 25 represented by General Formula (d1-3) (hereinafter, referred to as a “component (d1-3)”)

are preferable.

At the light-exposed portion of the resist film, the components (d1-1) to (d1-3) are decomposed and then lose the acid diffusion controllability (basicity), and thus the components (d1-1) to (d1-3) cannot act as a quencher, whereas the components (d1-1) to
5 (d1-3) act as a quencher at the light-unexposed portion of the resist film.

[0300]



[In the formulae, Rd¹ to Rd⁴ represent cyclic groups which may have a substituent, chain-like alkyl groups which may have a substituent, or chain-like alkenyl groups which may have a substituent. Here, the carbon atom adjacent to the S atom as
10 Rd² in Formula (d1-2) has no fluorine atom bonded thereto. Yd¹ represents a single bond or a divalent linking group. m represents an integer of 1 or greater, and each M^{m+} independently represents an m-valent organic cation.]

[0301]

15 {Component (d1-1)}

·· Anion moiety

In Formula (d1-1), Rd¹ represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent, and examples thereof are the same as those described
20 above as R²⁰¹.

Among these, as the group as Rd¹, an aromatic hydrocarbon group which may

have a substituent, an aliphatic cyclic group which may have a substituent and a chain-like alkyl group which may have a substituent are preferable. Examples of the substituent which these groups may have include a hydroxyl group, an oxo group, an alkyl group, an aryl group, a fluorine atom, a fluorinated alkyl group, lactone-containing cyclic groups each represented by any of General Formulae (a2-r-1) to (a2-r-7), an ether bond, an ester bond, and a combination thereof. In a case where an ether bond or an ester bond is included as the substituent, the substituent may be bonded via an alkylene group, and linking groups each represented by any of Formulae (y-al-1) to (y-al-5) are preferable as the substituent.

As the aromatic hydrocarbon group, a phenyl group, a naphthyl group, and a polycyclic structure (a polycyclic structure including a bicyclooctane skeleton and a ring structure other than the bicyclooctane skeleton) including a bicyclooctane skeleton can be suitably mentioned.

As the aliphatic cyclic group, a group in which one or more hydrogen atoms have been removed from a polycycloalkane such as adamantane, norbornane, isobornane, tricyclodecane and tetracyclododecane is more preferable.

The chain-like alkyl group preferably has 1 to 10 carbon atoms, and specific examples thereof include a linear alkyl group such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, or a decyl group, and a branched alkyl group such as a 1-methylethyl group, a 1-methylpropyl group, a 2-methylpropyl group, a 1-methylbutyl group, a 2-methylbutyl group, a 3-methylbutyl group, a 1-ethylbutyl group, a 2-ethylbutyl group, a 1-methylpentyl group, a 2-methylpentyl group, a 3-methylpentyl group, or a 4-methylpentyl group.

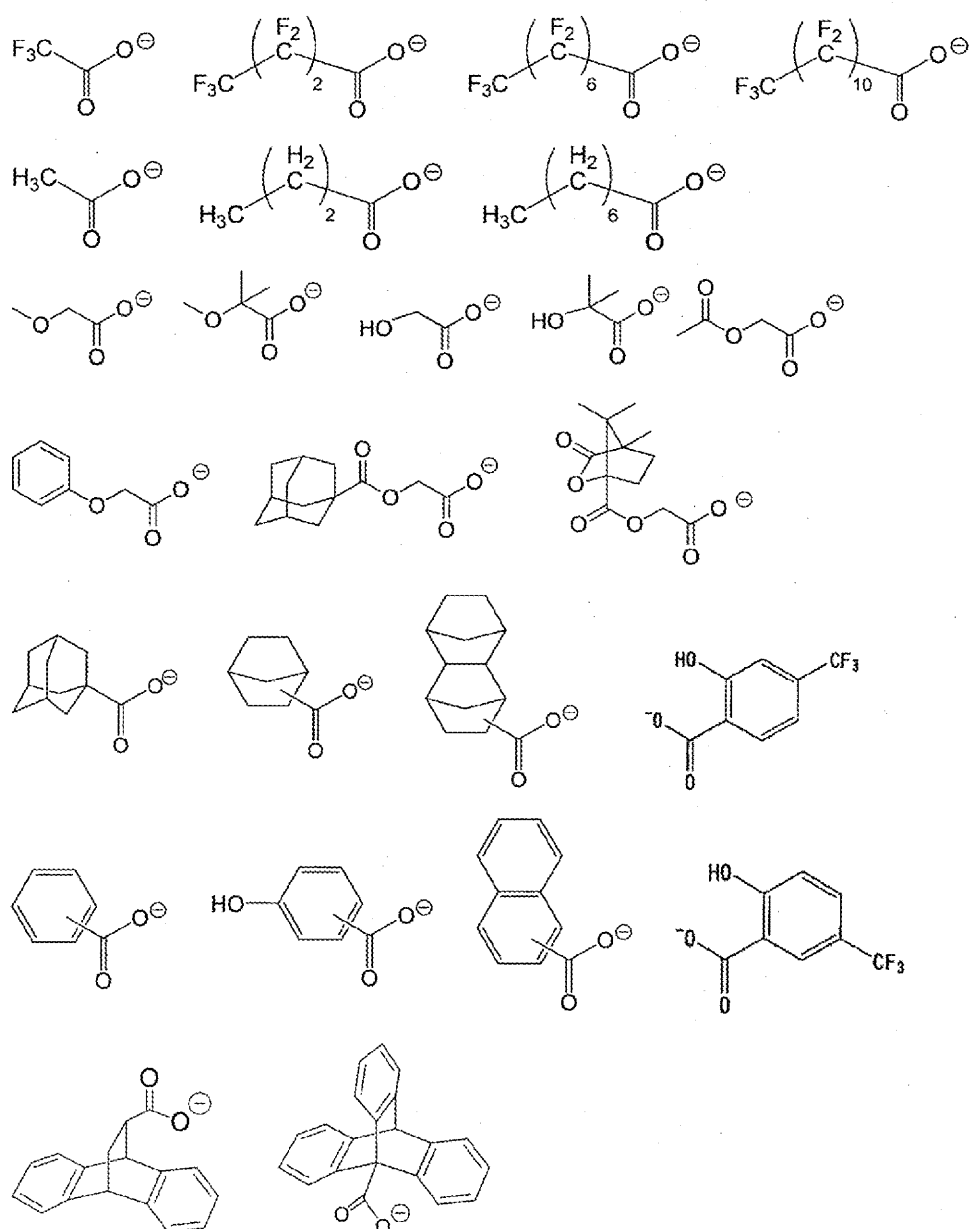
In a case where the chain-like alkyl group is a fluorinated alkyl group having a fluorine atom or a fluorinated alkyl group as a substituent, the fluorinated alkyl group preferably has 1 to 11 carbon atoms, more preferably 1 to 8 carbon atoms, and still more preferably 1 to 4 carbon atoms. The fluorinated alkyl group may contain an atom other than a fluorine atom. Examples of the atom other than a fluorine atom include an oxygen atom, a sulfur atom, and a nitrogen atom.

As Rd¹, a fluorinated alkyl group in which part or all hydrogen atoms constituting a linear alkyl group have been substituted with fluorine atom(s) is preferable, and a fluorinated alkyl group in which all of the hydrogen atoms constituting a linear alkyl group have been substituted with fluorine atoms (a linear perfluoroalkyl group) is particularly preferable.

[0303]

Specific examples of the preferred anion moiety for the component (d1-1) are shown below.

[0304]



[0305]

.. Cation moiety

In Formula (d1-1), M^{m+} represents an m-valent organic cation.

- 5 The organic cations of M^{m+} are preferably the same as those each represented by General Formulae (ca-1) to (ca-4), the cations each represented by General Formula (ca-1) are preferable, and cations each represented by Formulae (ca-1-1) to (ca-1-70) are more preferable.

The component (d1-1) may be used alone or in combination of two or more kinds thereof.

[0306]

{ Component (d1-2) }

5 ··· Anion moiety

In Formula (d1-2), Rd^2 represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent, and examples thereof are the same as those described above as R'^{201} .

10 Here, the carbon atom adjacent to the S atom in Rd^2 has no fluorine atom bonded thereto (the carbon atom adjacent to the sulfur atom in Rd^2 is not substituted with a fluorine atom). As a result, the anion of the component (d1-2) becomes an appropriately weak acid anion, thereby improving the quenching ability of the component (D).

15 As Rd^2 , a chain-like alkyl group which may have a substituent or an aliphatic cyclic group which may have a substituent is preferable. The chain-like alkyl group preferably has 1 to 10 carbon atoms and more preferably 3 to 10 carbon atoms. As the aliphatic cyclic group, a group in which one or more hydrogen atoms have been removed from adamantane, norbornane, isobornane, tricyclodecane, or tetracyclododecane (which
20 may have a substituent) and a group in which one or more hydrogen atoms have been removed from camphor are more preferable.

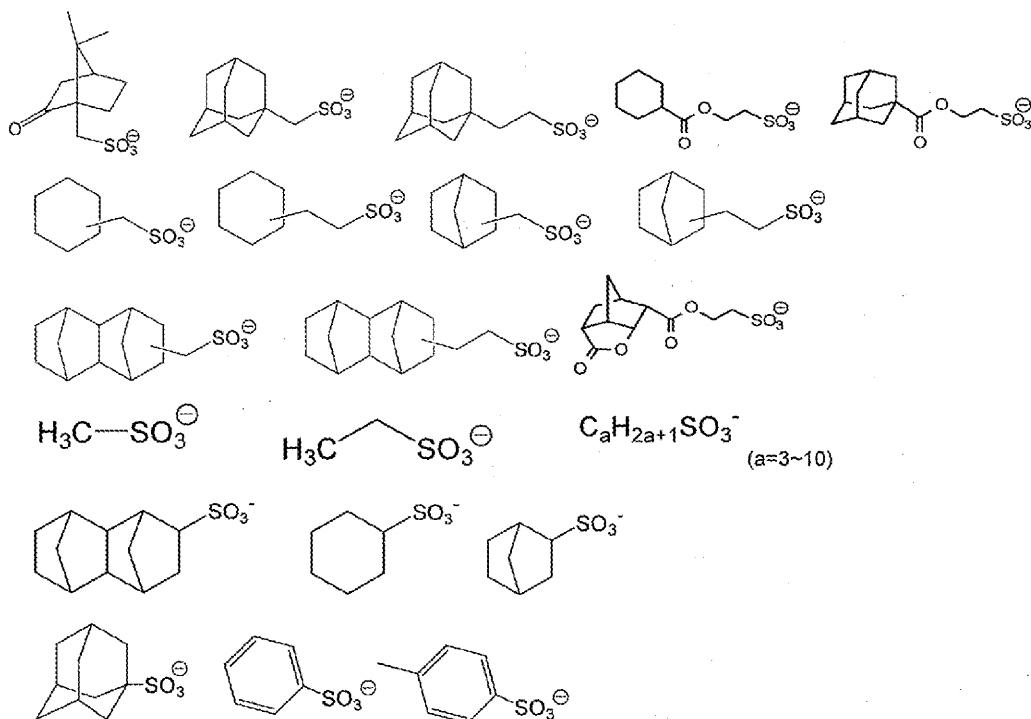
The hydrocarbon group as Rd^2 may have a substituent. As the substituent, the same groups as the substituents which may be included in the hydrocarbon group (such as an aromatic hydrocarbon group, an aliphatic cyclic group, or a chain-like alkyl group)
25 as Rd^1 in Formula (d1-1) can be mentioned.

[0309]

The component (d1-2) may be used alone or in combination of two or more kinds thereof.

[0310]

.. Anion moiety



In Formula (d1-3), Rd^3 represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent, and the same groups as those described above as R'^{201} can be mentioned, and a cyclic group containing a fluorine atom, a chain-like alkyl group, or a chain-like alkenyl group is preferable. Among these, a fluorinated alkyl group is preferable, and the same fluorinated alkyl groups as those described above as Rd^1 are more preferable.

[0311]

In Formula (d1-3), Rd^4 represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent, and examples thereof are the same as those described above as R'^{201} .

Among these, an alkyl group which may have a substituent, an alkoxy group which may have a substituent, an alkenyl group which may have a substituent, or a cyclic group which may have a substituent is preferable.

The alkyl group as Rd^4 is preferably a linear or branched alkyl group having 1 to 5 carbon atoms, and specific examples thereof include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, and a neopentyl group. Some hydrogen atoms in the alkyl group as Rd^4 may be substituted with a hydroxyl group, a cyano group, or the like.

The alkoxy group as Rd^4 is preferably an alkoxy group having 1 to 5 carbon atoms, and specific examples of the alkoxy group having 1 to 5 carbon atoms include a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group, and a tert-butoxy group. Among these, a methoxy group and an ethoxy group are preferable.

[0312]

As the alkenyl group as Rd^4 , the same group as the alkenyl group described above as R'^{201} can be mentioned, and a vinyl group, a propenyl group (an allyl group), a 1-methylpropenyl group, and a 2-methylpropenyl group are preferable. These groups
 5 may have an alkyl group having 1 to 5 carbon atoms or a halogenated alkyl group having 1 to 5 carbon atoms as a substituent.

[0313]

As the cyclic group as Rd^4 , the same group as the cyclic group described above as R'^{201} can be mentioned. Among these, as the cyclic group, an alicyclic group in
 10 which one or more hydrogen atoms have been removed from a cycloalkane such as cyclopentane, cyclohexane, adamantane, norbornane, isobornane, tricyclodecane or tetracyclododecane or an aromatic group such as a phenyl group or a naphthyl group is preferable. In a case where Rd^4 represents an alicyclic group, the resist composition can be satisfactorily dissolved in an organic solvent, thereby improving lithography
 15 characteristics. In a case where Rd^4 is an aromatic group, the resist composition is excellent in light absorption efficiency and thus has good sensitivity and lithography characteristics in lithography using EUV or the like as a light source for exposure.

[0314]

In Formula (d1-3), Yd^1 represents a single bond or a divalent linking group.
 20 The divalent linking group as Yd^1 is not particularly limited, and examples thereof include a divalent hydrocarbon group (an aliphatic hydrocarbon group or an aromatic hydrocarbon group) which may have a substituent and a divalent linking group containing a hetero atom. The divalent linking groups are the same as those described above as the divalent hydrocarbon group which may have a substituent and the divalent
 25 linking group containing a hetero atom described above as the divalent linking group as

Ya²¹ in Formula (a2-1).

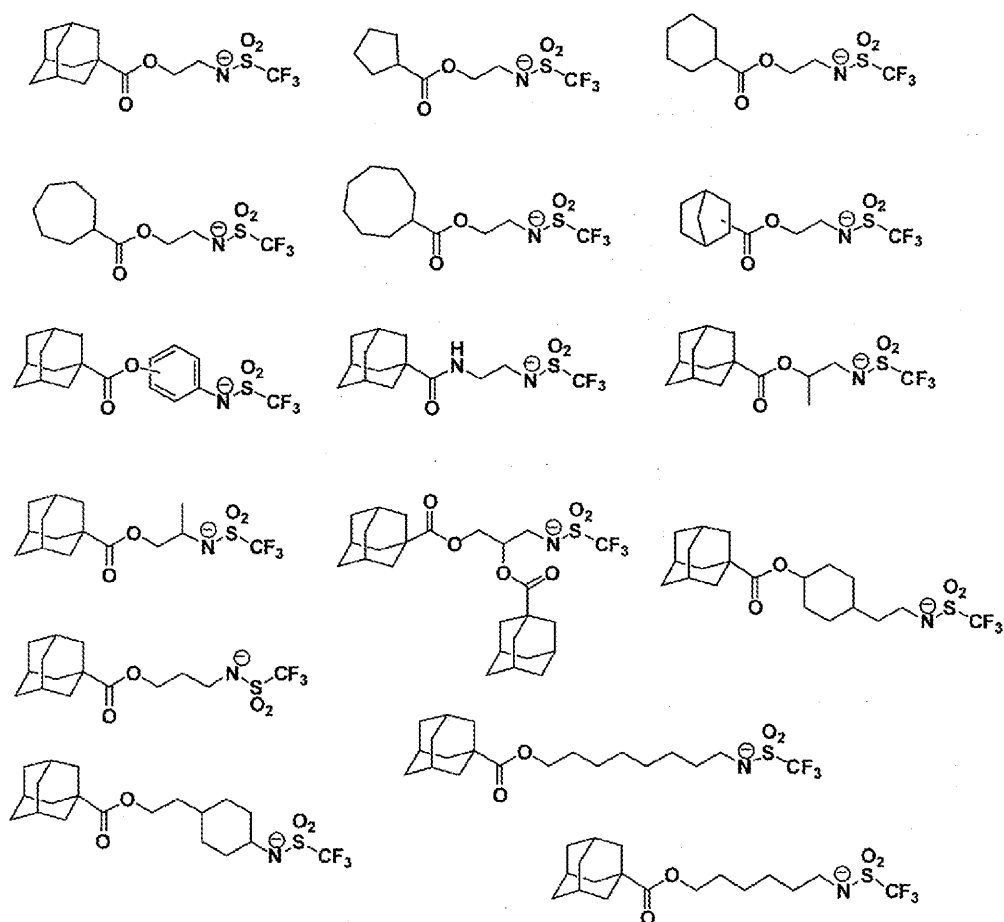
As Yd¹, a carbonyl group, an ester bond, an amide bond, an alkylene group, or a combination of these is preferable. As the alkylene group, a linear or branched alkylene group is more preferable, and a methylene group or an ethylene group is still more

5 preferable.

[0315]

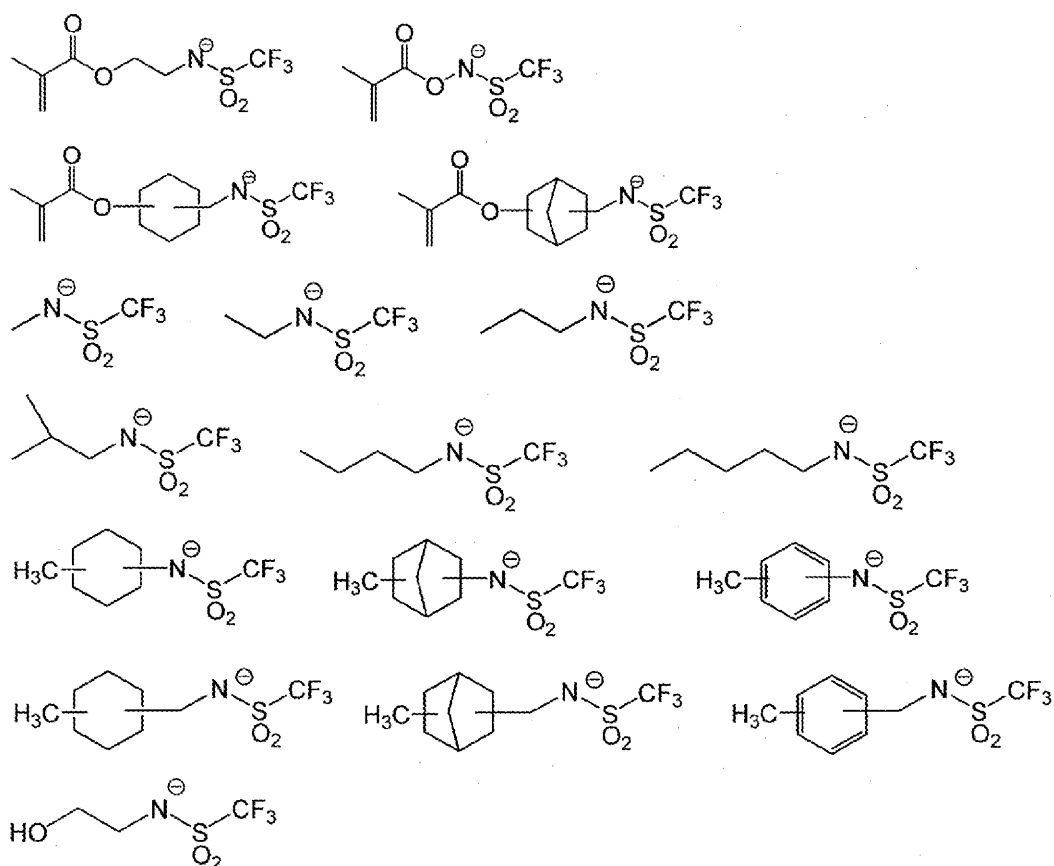
Specific examples of the preferred anion moiety for the component (d1-3) are shown below.

[0316]



10

[0317]



[0318]

·· Cation moiety

In Formula (d1-3), M^{m+} represents an m-valent organic cation and has the same
 5 definition as that for M^{m+} in Formula (d1-1).

The component (d1-3) may be used alone or in combination of two or more
 kinds thereof.

[0319]

As the component (D1), only one of the above-described components (d1-1) to
 10 (d1-3) or a combination of two or more kinds thereof may be used.

In a case where the resist composition contains the component (D1), the content
 of the component (D1) in the resist composition is preferably less than 0.5 to 20 parts by

mass, more preferably in a range of 1 to 15 parts by mass, and still more preferably in a range of 5 to 10 parts by mass with respect to 100 parts by mass of the component (A).

In a case where the content of the component (D1) is equal to or greater than the preferred lower limit, excellent lithography characteristics and an excellent resist pattern shape are easily obtained. On the other hand, in a case where the content of the component (D1) is equal to or lower than the upper limit, the sensitivity can be maintained satisfactorily and the throughput is also excellent.

[0320]

Method of producing component (D1):

The production methods of the components (d1-1) and (d1-2) are not particularly limited, and the components (d1-1) and (d1-2) can be produced by known methods.

Further, the method of producing the component (d1-3) is not particularly limited, and the component (d1-3) can be produced in the same manner as disclosed in United States Patent Application, Publication No. 2012-0149916.

[0321]

· In regard to component (D2)

The component (D) preferably contains a nitrogen-containing organic compound component (hereinafter, referred to as a “component (D2)”) which does not correspond to the above-mentioned component (D1).

The component (D2) is not particularly limited as long as it acts as an acid diffusion-controlling agent and does not correspond to the component (D1), and any known compound may be used. Among the above, aliphatic amines are preferable, and among the aliphatic amines, a secondary aliphatic amine or a tertiary aliphatic amine is more preferable.

An aliphatic amine is an amine having one or more aliphatic groups, and the aliphatic groups preferably have 1 to 12 carbon atoms.

Examples of these aliphatic amines include amines in which at least one hydrogen atom of ammonia (NH_3) has been substituted with an alkyl group or hydroxyalkyl group having 12 or fewer carbon atoms (alkylamines or alkylalcoholamines) and cyclic amines.

Specific examples of alkylamines and alkylalcoholamines include monoalkylamines such as n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, and n-decylamine; dialkylamines such as diethylamine, di-n-propylamine, di-n-heptylamine, di-n-octylamine, and dicyclohexylamine; trialkylamines such as trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, tri-n-hexylamine, tri-n-pentylamine, tri-n-heptylamine, tri-n-octylamine, tri-n-nonylamine, tri-n-decylamine, and tri-n-dodecylamine; and alkyl alcohol amines such as diethanolamine, triethanolamine, diisopropanolamine, triisopropanolamine, di-n-octanolamine, and tri-n-octanolamine. Among these, trialkylamines of 5 to 10 carbon atoms are preferable, and tri-n-pentylamine and tri-n-octylamine are particularly preferable.

[0322]

Examples of the cyclic amine include heterocyclic compounds containing a nitrogen atom as a hetero atom. The heterocyclic compound may be a monocyclic compound (aliphatic monocyclic amine), or a polycyclic compound (aliphatic polycyclic amine).

Specific examples of the aliphatic monocyclic amine include piperidine and piperazine. The aliphatic polycyclic amine preferably has 6 to 10 carbon atoms, and specific examples thereof include 1, 5-diazabicyclo[4.3.0]-5-nonene, 1,8-diazabicyclo[5.4.0]-7-undecene, hexamethylenetetramine, and 1,4-

diazabicyclo[2.2.2]octane.

[0323]

Examples of other aliphatic amines include tris(2-methoxymethoxyethyl)amine, tris{2-(2-methoxyethoxy)ethyl}amine, tris{2-(2-methoxyethoxymethoxy)ethyl}amine, tris{2-(1-methoxyethoxy)ethyl}amine, tris{2-(1-ethoxyethoxy)ethyl}amine, tris{2-(1-ethoxypropoxy)ethyl}amine, tris[2-{2-(2-hydroxyethoxy)ethoxy}ethyl]amine and triethanolamine triacetate, and triethanolamine triacetate is preferable.

[0324]

In addition, as the component (D2), an aromatic amine may be used.

Examples of aromatic amines include 4-dimethylaminopyridine, pyrrole, indole, pyrazole, imidazole, and derivatives thereof, tribenzylamine, 2,6-diisopropylaniline, and N-tert-butoxycarbonylpyrrolidine.

[0325]

As the component (D2), an aliphatic amine is preferable, a chain-like aliphatic amine is more preferable, and a chain-like alkylamine is still more preferable, from the viewpoint of maintaining transparency in a thick resist film. The chain-like alkyl group which the chain-like alkylamine group has preferably has 5 to 10 carbon atoms. Among them, a dialkylamine or trialkylamine having a linear alkyl group having 5 to 10 carbon atoms is preferable, and a trialkylamine is more preferable.

[0326]

The component (D2) may be used alone or in combination of two or more kinds thereof. In a case where the resist composition contains the component (D2), the content of the component (D2) in the resist composition is typically in a range of 0.01 to 5 parts by mass with respect to 100 parts by mass of the component (A). By setting the content within the above range, the resist pattern shape, the post-exposure temporal

stability, and the like are improved.

[0327]

<<At least one compound (E) selected from the group consisting of organic carboxylic acid, phosphorus oxo acid, and derivatives thereof>>

5 For the purpose of preventing any deterioration in sensitivity, and improving the resist pattern shape and the post-exposure temporal stability, the resist composition of the present embodiment may contain at least one compound (E) (hereinafter referred to as the component (E)) selected from the group consisting of an organic carboxylic acid, and a phosphorus oxo acid and a derivative thereof.

10 Examples of suitable organic carboxylic acids include acetic acid, malonic acid, citric acid, malic acid, succinic acid, benzoic acid, and salicylic acid.

 Examples of phosphorus oxo acid include phosphoric acid, phosphonic acid, and phosphinic acid. Among these, phosphonic acid is particularly preferable.

 Examples of phosphorus oxo acid derivatives include esters in which a hydrogen
15 atom in the above-described oxo acids is substituted with a hydrocarbon group.

 Examples of the hydrocarbon group include an alkyl group having 1 to 5 carbon atoms and an aryl group having 6 to 15 carbon atoms.

 Examples of phosphoric acid derivatives include phosphoric acid esters such as di-n-butyl phosphate and diphenyl phosphate.

20 Examples of phosphonic acid derivatives include phosphonic acid esters such as dimethyl phosphonate, di-n-butyl phosphonate, phenylphosphonic acid, diphenyl phosphonate, and dibenzyl phosphonate.

 Examples of phosphinic acid derivatives include phosphinic acid esters and phenylphosphinic acid.

25 In the resist composition according to the present embodiment, the component

(E) may be used alone or in combination of two or more kinds thereof.

In a case where the resist composition contains the component (E), the content of the component (E) is typically in a range of 0.01 to 5 parts by mass with respect to 100 parts by mass of the component (A).

5 [0328]

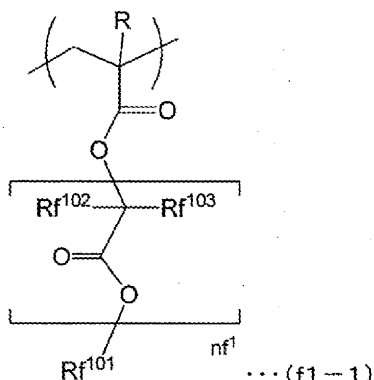
<<Fluorine additive component (F)>>

The resist composition of the present embodiment may further include a fluorine additive (hereinafter, referred to as a "component (F)") in order to impart water repellency to the resist film or to improve lithography characteristics.

10 As the component (F), a fluorine-containing high-molecular-weight compound described in Japanese Unexamined Patent Application, First Publication No. 2010-002870, Japanese Unexamined Patent Application, First Publication No. 2010-032994, Japanese Unexamined Patent Application, First Publication No. 2010-277043, Japanese Unexamined Patent Application, First Publication No. 2011-13569, and Japanese
15 Unexamined Patent Application, First Publication No. 2011-128226 can be mentioned.

Specific examples of the component (F) include polymers having a constitutional unit (f1) represented by General Formula (f1-1) shown below. This polymer is preferably a polymer (homopolymer) consisting of a constitutional unit (f1) represented by Formula (f1-1) shown below; a copolymer of the constitutional unit (f1) and the constitutional unit (a1); and a copolymer of the constitutional unit (f1), a constitutional unit derived from acrylic acid or methacrylic acid, and the above-described constitutional unit (a1). As the constitutional unit (a1) to be copolymerized with the constitutional unit (f1), a constitutional unit derived from 1-ethyl-1-cyclooctyl (meth)acrylate and a constitutional unit derived from 1-methyl-1-adamantyl
20 (meth)acrylate are preferable.

[0329]



[In the formula, R has the same definition as described above. Rf^{102} and Rf^{103} each independently represents a hydrogen atom, a halogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms, and Rf^{102} and Rf^{103} may be the same as or different from each other. nf^1 represents an integer of 1 to 5. Rf^{101} represents an organic group containing a fluorine atom.]

[0330]

In Formula (f1-1), R bonded to the carbon atom at the α -position has the same definition as described above. As R, a hydrogen atom or a methyl group is preferable.

In Formula (f1-1), examples of the halogen atom as Rf^{102} and Rf^{103} include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom, and a fluorine atom is particularly preferable. Examples of the alkyl group having 1 to 5 carbon atoms as Rf^{102} and Rf^{103} include those described above as the alkyl group having 1 to 5 carbon atoms as R, and a methyl group or an ethyl group is preferable. Specific examples of the halogenated alkyl group having 1 to 5 carbon atoms as Rf^{102} and Rf^{103} include groups in which part or all hydrogen atoms of the above-described alkyl groups of 1 to 5 carbon atoms have been substituted with halogen atoms. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom and, an iodine atom, and a

fluorine atom is particularly preferable. Among these examples, as Rf^{f102} and Rf^{f103} , a hydrogen atom, a fluorine atom, or an alkyl group having 1 to 5 carbon atoms is preferable, and a hydrogen atom, a fluorine atom, a methyl group, or an ethyl group is more preferable.

- 5 In Formula (f1-1), nf^1 represents an integer of 1 to 5, preferably an integer of 1 to 3, and more preferably an integer of 1 or 2.

[0331]

In Formula (f1-1), Rf^{f101} represents an organic group containing a fluorine atom and is preferably a hydrocarbon group containing a fluorine atom.

- 10 The hydrocarbon group containing a fluorine atom may be linear, branched, or cyclic, and preferably has 1 to 20 carbon atoms, more preferably 1 to 15 carbon atoms, and particularly preferably 1 to 10 carbon atoms.

- In addition, in the hydrocarbon group containing a fluorine atom, 25% or more of the hydrogen atoms in the hydrocarbon group are preferably fluorinated, more
15 preferably 50% or more are fluorinated, and particularly preferably 60% or more are fluorinated since the hydrophobicity of the resist film at the time of immersion exposure increases.

- Among these, as Rf^{f101} , a fluorinated hydrocarbon group having 1 to 6 carbon atoms is more preferable, and a trifluoromethyl group, $-CH_2-CF_3$, $-CH_2-CF_2-CF_3$, -
20 $CH(CF_3)_2$, $-CH_2-CH_2-CF_3$, and $-CH_2-CH_2-CF_2-CF_2-CF_2-CF_3$ are still more preferable.

[0332]

- The weight-average molecular weight (Mw) (based on the polystyrene-equivalent value determined by gel permeation chromatography) of the component (F) is preferably in a range of 1,000 to 50,000, more preferably in a range of 5,000 to 40,000,
25 and most preferably in a range of 10,000 to 30,000. In a case where the weight-average

molecular weight is equal or lower than the upper limit of the above-described range, the resist composition exhibits sufficiently satisfactory solubility in a solvent for a resist to be used as a resist. On the other hand, in a case where the weight-average molecular weight is equal to or greater than the lower limit of the above-described range, water
5 repellency of the resist film is excellent.

Further, the dispersity (M_w/M_n) of the component (F) is preferably in a range of 1.0 to 5.0, more preferably in a range of 1.0 to 3.0, and most preferably in a range of 1.0 to 2.5.

[0333]

10 In the resist composition according to the present embodiment, the component (F) may be used alone or in combination of two or more kinds thereof.

In a case where the resist composition contains the component (F), the content of the component (F) is typically in a range of 0.5 to 10 parts by mass, with respect to 100 parts by mass of the component (A).

15 [0334]

<<Organic solvent component (S)>>

The resist composition of the present embodiment may be produced by dissolving the resist materials in an organic solvent (hereinafter, referred to as a “component (S)”).

20 The component (S) may be any organic solvent which can dissolve the respective components to be used to obtain a uniform solution, and optional organic solvent can be appropriately selected from those which are conventionally known as solvents for a chemically amplified resist composition and then used.

Examples of the component (S) include lactones such as γ -butyrolactone;
25 ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl-n-pentyl ketone,

methyl isopentyl ketone, and 2-heptanone; polyhydric alcohols, such as ethylene glycol, diethylene glycol, propylene glycol and dipropylene glycol; compounds having an ester bond, such as ethylene glycol monoacetate, diethylene glycol monoacetate, propylene glycol monoacetate, and dipropylene glycol monoacetate; polyhydric alcohol derivatives
5 including compounds having an ether bond, such as a monoalkylether (such as monomethylether, monoethylether, monopropylether or monobutylether) or monophenylether of any of these polyhydric alcohols or compounds having an ester bond (among these, propylene glycol monomethyl ether acetate (PGMEA) and propylene glycol monomethyl ether (PGME) are preferable); cyclic ethers such as dioxane; esters
10 such as methyl lactate, ethyl lactate (EL), methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate, and ethyl ethoxypropionate; aromatic organic solvents such as anisole, ethylbenzylether, cresylmethylether, diphenylether, dibenzylether, phenetole, butylphenylether, ethylbenzene, diethylbenzene, pentylbenzene, isopropylbenzene, toluene, xylene, cymene and mesitylene; and
15 dimethylsulfoxide (DMSO).

In the resist composition according to the present embodiment, the component (S) may be used alone or as a mixed solvent of two or more kinds thereof. Among these, PGMEA, PGME, γ -butyrolactone, EL, and cyclohexanone are preferable.

[0335]

20 Further, a mixed solvent obtained by mixing PGMEA with a polar solvent is also preferable as the component (S). The blending ratio (mass ratio) of the mixed solvent can be appropriately determined, taking into consideration the compatibility of the PGMEA with the polar solvent, but is preferably in the range of 1:9 to 9:1 and more preferably in a range of 2:8 to 8:2.

25 More specifically, in a case where EL or cyclohexanone is blended as the polar

solvent, the PGMEA:EL or cyclohexanone mass ratio is preferably in a range of 1:9 to 9:1 and more preferably in a range of 2:8 to 8:2. Alternatively, in a case where PGME is blended as the polar solvent, the PGMEA:PGME mass ratio is preferably in a range of 1:9 to 9:1, more preferably in a range of 2:8 to 8:2, and still more preferably in a range of 3:7 to 7:3. Furthermore, a mixed solvent of PGMEA, PGME, and cyclohexanone is also preferable.

Further, as the component (S), a mixed solvent of at least one selected from PGMEA and EL and γ -butyrolactone is also preferable. In this case, as the mixing ratio, the mass ratio of the former to the latter is preferably in a range of 70:30 to 95:5.

10 [0336]

The amount of the component (S) to be used is set such that the concentration of solid content of the resist composition is 25% by mass or more. In the present specification, the solid content in the resist composition refers to components other than the component (S). The concentration of solid content of the resist composition is
15 calculated by the following expression.

Concentration of solid content (% by mass) = total mass of components other than component (S) / total mass of resist composition $\times$ 100

[0337]

For example, in a case where the resist composition consists of the component
20 (A), the component (Z), the component (B), the component (D), and the component (S), the concentration of solid content (% by mass) = [(the component (A) + the component (Z) + the component (B) + the component (D))/(the component (A) + the component (Z) + the component (B) + the component (D) + the component (S))] $\times$ 100.

[0338]

25 In a case where the resist composition is applied onto a substrate to form a resist

film, a thick resist film (for example, a film having a thickness of 5 μm or more, and preferably 7 μm or more) can be formed by setting the concentration of solid content of the resist composition to 25% by mass or more. The concentration of solid content of the resist composition is not particularly limited as long as it is 25% by mass or more, and can be appropriately determined depending on the desired film thickness of the resist film. Generally, the higher the concentration of the solid content, the thicker the resist film.

The upper limit of the concentration of solid content of the resist composition is not particularly limited as long as the concentration is a concentration in which the solid content can be dissolved. The concentration of solid content of the resist composition is, for example, 60% by mass or less, preferably 55% by mass or less, and more preferably 50% by mass or less.

The range of the concentration of solid content of the resist composition is, for example, 25% to 60% by mass, 25% to 55% by mass, or 25% to 50% by mass.

[0339]

As desired, other miscible additives can also be added to the resist composition of the present embodiment. The resist composition may further contain, as desired, miscible additives such as an additive resin, a dissolution inhibitor, a plasticizer, a stabilizer, a colorant, a halation prevention agent, and a dye for improving the performance of the resist film.

[0340]

After dissolving the resist material in the component (S), the resist composition of the present embodiment may be subjected to removal of impurities and the like by using a porous polyimide film, a porous polyamideimide film, or the like. For example, the resist composition may be filtered using a filter made of a porous polyimide film, a

filter made of a porous polyamideimide film, or a filter made of a porous polyimide film and a porous polyamideimide film. Examples of the porous polyimide film and the porous polyamideimide film include those described in Japanese Unexamined Patent Application, First Publication No. 2016-155121.

5 [0341]

The resist composition of the present embodiment described above has a concentration of solid content of 25% by mass or more and contains a polyether compound having a weight-average molecular weight of 400 or more at a predetermined proportion.

10 In the resist composition of the present embodiment, since the concentration of solid content of the resist composition is 25% by mass or more, a thick resist film (for example, a film having a thickness of 5 μm or more) is formed in a case where the resist composition is applied onto a substrate to form a resist film. In a case of such a thick resist film, in conventional resist composition, cracking easily occurs in the resist pattern.

15 Further, since it is difficult for light to reach the bottom of the film in the conventional resist composition, it is difficult to maintain sensitivity during exposure, and it is difficult to form a resist pattern having a good shape.

In the resist composition of the present embodiment, by containing a polyether compound having a weight-average molecular weight of 400 or more at a predetermined

20 proportion, it is possible to achieve both cracking resistance and high resolution. It is speculated that this is because the presence of the polyether compound in the resist film formed using the resist composition alleviates stress of the resist film. In addition, by setting the blending amount of the polyether compound within a predetermined range, it is possible to suppress a decrease in resolution.

25 [0342]

(Method of forming resist pattern)

The method of forming a resist pattern according to the second aspect of the present invention is a method including a step of forming a resist film on a supporting body using the resist composition according to the embodiment described above, a step
5 of exposing the resist film, and a step of developing the exposed resist film to form a resist pattern.

Examples of one embodiment of such a method of forming a resist pattern include a method of forming a resist pattern performed as described below.

[0343]

10 First, the resist composition of the above-described embodiment is applied onto a supporting body with a spinner or the like, and a baking (post-apply baking (PAB)) treatment is performed, for example, at a temperature condition of 80°C to 150°C for 40 to 120 seconds, preferably for 60 to 90 seconds to form a resist film.

Following the selective exposure performed on the resist film by, for example,
15 exposure through a mask (mask pattern) having a predetermined pattern formed on the mask by using an exposure apparatus such as an electron beam lithography apparatus and an EUV exposure apparatus, or direct irradiation of the resist film for drawing with an electron beam without using a mask pattern, baking treatment (post-exposure baking (PEB)) is performed, for example, under a temperature condition of 80°C to 150°C for 40
20 to 120 seconds and preferably 60 to 90 seconds.

Next, the resist film is subjected to a developing treatment. The developing treatment is performed using an alkali developing solution in a case of an alkali developing process, and a developing solution containing an organic solvent (organic developing solution) in a case of a solvent developing process.

25 [0344]

After the developing treatment, it is preferable to conduct a rinse treatment. As the rinse treatment, water rinsing using pure water is preferable in a case of an alkali developing process, and rinsing using a rinse solution containing an organic solvent is preferable in a case of a solvent developing process.

5 In a case of a solvent developing process, after the developing treatment or the rinsing, the developing solution or the rinse liquid remaining on the pattern can be removed by a treatment using a supercritical fluid.

After the developing treatment or the rinse treatment, drying is conducted. As desired, baking treatment (post-baking) can be performed following the developing
10 treatment.

In this manner, a resist pattern can be formed.

[0345]

The supporting body is not specifically limited and a conventionally known supporting body can be used. For example, substrates for electronic components, and
15 such substrates having wiring patterns formed thereon can be used. Specific examples of the material of the substrate include metals such as silicon wafer, copper, chromium, iron and aluminum; and glass. Suitable materials for the wiring pattern include copper, aluminum, nickel, and gold.

Further, as the supporting body, any supporting body having the above-described
20 substrate on which an inorganic and/or organic film is provided may be used. As the inorganic film, an inorganic antireflection film (inorganic BARC) can be used. As the organic film, an organic antireflection film (organic BARC) and an organic film such as a lower-layer organic film used in a multilayer resist method can be used.

Here, the multilayer resist method is a method in which at least one layer of an
25 organic film (lower-layer organic film) and at least one layer of a resist film (upper-layer

resist film) are provided on a substrate, and a resist pattern formed on the upper-layer resist film is used as a mask to conduct patterning of the lower-layer organic film. This method is considered as being capable of forming a pattern with a high aspect ratio.

More specifically, in the multilayer resist method, a desired thickness can be ensured by the lower-layer organic film, and as a result, the thickness of the resist film can be reduced, and an extremely fine pattern with a high aspect ratio can be formed.

The multilayer resist method is classified into a method in which a double-layer structure consisting of an upper-layer resist film and a lower-layer organic film is formed (double-layer resist method), and a method in which a multilayer structure having at least three layers consisting of an upper-layer resist film, a lower-layer organic film and at least one intermediate layer (thin metal film or the like) provided between the upper-layer resist film and the lower-layer organic film (triple-layer resist method).

[0346]

In the method of forming a resist pattern according to the present embodiment, since the resist composition of the above-described embodiment is used, a thick resist film is formed in step (i). The thickness of the resist film is preferably 5 μm or more, more preferably 7 μm or more, and still more preferably 8 μm or more. The upper limit of the film thickness of the resist film is, for example, 30 μm or less. The range of the film thickness of the resist film formed in the step (i) is, for example, 5 to 30 μm , preferably 7 to 20 μm , more preferably 7 to 15 μm , and still more preferably 8 to 12 μm . The film thickness of the resist film can be adjusted by controlling the concentration of solid content of the resist composition used in step (i). That is, the higher the concentration of solid content of the resist composition, the thicker the resist film can be formed.

[0347]

The wavelength to be used for exposure is not particularly limited and the exposure can be performed using radiation such as an ArF excimer laser, a KrF excimer laser, an F₂ excimer laser, extreme ultraviolet (EUV) rays, vacuum ultraviolet (VUV) rays, electron beams (EB), X-rays, and soft X-rays. The resist composition is highly useful for KrF excimer laser, ArF excimer laser, EB, or EUV, more useful for KrF excimer laser or ArF excimer laser, and particularly useful for KrF excimer laser. That is, the method of forming a resist pattern according to the present embodiment is a particularly useful method in a case where the step of exposing the resist film includes an operation of exposing the resist film to KrF excimer laser light.

[0348]

The exposure of the resist film can be a general exposure (dry exposure) performed in air or an inert gas such as nitrogen, or liquid immersion exposure (liquid immersion lithography).

In liquid immersion lithography, the region between the resist film and the lens at the lowermost point of the immersion exposure apparatus is pre-filled with a solvent (liquid immersion medium) that has a larger refractive index than the refractive index of air, and the exposure (immersion exposure) is performed in this state.

As the liquid immersion medium, a solvent that exhibits a refractive index larger than the refractive index of air but smaller than the refractive index of the resist film to be exposed is preferable. The refractive index of the solvent is not particularly limited as long as it satisfies the above-described requirements.

Examples of the solvent which exhibits a refractive index that is larger than the refractive index of air but smaller than the refractive index of the resist film include water, fluorine-based inert liquids, silicone-based solvents, and hydrocarbon-based solvents.

Specific examples of the fluorine-based inert liquids include liquids containing a fluorine-based compound such as $C_3HCl_2F_5$, $C_4F_9OCH_3$, $C_4F_9OC_2H_5$ or $C_5H_3F_7$ as the main component, and the boiling point is preferably in a range of 70° to 180°C and more preferably in a range of 80° to 160°C. A fluorine-based inert liquid having a boiling point in the above-described range is advantageous in that the removal of the immersion medium after the exposure can be performed by a simple method.

As a fluorine-based inert liquid, a perfluoroalkyl compound in which all of the hydrogen atoms of the alkyl group are substituted with fluorine atoms is particularly preferable. Examples of these perfluoroalkyl compounds include perfluoroalkylether compounds and perfluoroalkylamine compounds.

Specifically, an example of a suitable perfluoroalkylether compound is perfluoro(2-butyl-tetrahydrofuran) (boiling point of 102°C), and an example of a suitable perfluoroalkylamine compound is perfluorotributylamine (boiling point of 174°C).

As the immersion medium, water is preferable in terms of cost, safety, environment, and versatility.

[0349]

As an example of the alkali developing solution used for a developing treatment in an alkali developing process, a 0.1 to 10% by mass aqueous solution of tetramethylammonium hydroxide (TMAH) can be mentioned.

As the organic solvent contained in the organic developing solution used for a developing treatment in a solvent developing process, any of the conventional organic solvents can be used which are capable of dissolving the component (A) (prior to exposure). Specific examples of the organic solvent include polar solvents such as ketone solvents, ester solvents, alcohol solvents, nitrile solvents, amide solvents, and ether solvents, and hydrocarbon solvents.

A ketone solvent is an organic solvent containing C-C(=O)-C in the structure thereof. An ester solvent is an organic solvent containing C-C(=O)-O-C in the structure thereof. An alcohol solvent is an organic solvent containing an alcoholic hydroxyl group in the structure thereof. An "alcoholic hydroxyl group" indicates a hydroxyl group bonded to a carbon atom of an aliphatic hydrocarbon group. A nitrile solvent is an organic solvent containing a nitrile group in the structure thereof. An amide solvent is an organic solvent containing an amide group in the structure thereof. An ether solvent is an organic solvent containing C-O-C in the structure thereof.

Some organic solvents have a plurality of the functional groups which characterize the above-described solvents in the structure thereof. In such a case, the organic solvent can be classified as any type of solvent having a characteristic functional group. For example, diethylene glycol monomethylether can be classified as an alcohol solvent or an ether solvent.

A hydrocarbon solvent consists of a hydrocarbon which may be halogenated and does not have any substituent other than a halogen atom. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom, and a fluorine atom is preferable.

As the organic solvent contained in the organic developing solution, among these, a polar solvent is preferable, and ketone solvents, ester solvents, and nitrile solvents are preferable.

[0350]

Examples of ketone solvents include 1-octanone, 2-octanone, 1-nonanone, 2-nonanone, acetone, 4-heptanone, 1-hexanone, 2-hexanone, diisobutyl ketone, cyclohexanone, methylcyclohexanone, phenylacetone, methyl ethyl ketone, methyl isobutyl ketone, acetylacetone, acetonylacetone, ionone, diacetonylalcohol,

acetylcarbinol, acetophenone, methyl naphthyl ketone, isophorone, propylenecarbonate, γ -butyrolactone and methyl amyl ketone (2-heptanone). Among these examples, methyl amyl ketone (2-heptanone) is preferable as a ketone solvent.

[0351]

- 5 Examples of ester solvents include methyl acetate, butyl acetate, ethyl acetate, isopropyl acetate, amyl acetate, isoamyl acetate, ethyl methoxyacetate, ethyl ethoxyacetate, ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene glycol monobutyl ether acetate, ethylene glycol monophenyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monopropyl ether acetate, diethylene glycol monophenyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, 2-methoxybutyl acetate, 3-methoxybutyl acetate, 4-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, 3-ethyl-3-methoxybutyl acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, 2-ethoxybutyl acetate, 4-ethoxybutyl acetate, 4-propoxybutyl acetate, 2-methoxypentyl acetate, 3-methoxypentyl acetate, 4-methoxypentyl acetate, 2-methyl-3-methoxypentyl acetate, 3-methyl-3-methoxypentyl acetate, 3-methyl-4-methoxypentyl acetate, 4-methyl-4-methoxypentyl acetate, propylene glycol diacetate, methyl formate, ethyl formate, butyl formate, propyl formate, ethyl lactate, butyl lactate, propyl lactate, ethyl carbonate, propyl carbonate, butyl carbonate, methyl pyruvate, ethyl pyruvate, propyl pyruvate, butyl pyruvate, methyl acetoacetate, ethyl acetoacetate, methyl propionate, ethyl propionate, propyl propionate, isopropyl propionate, methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, methyl-3-methoxypropionate, ethyl-3-methoxypropionate, ethyl-3-ethoxypropionate, and propyl-3-methoxypropionate. Among these examples, as an ester solvent, butyl acetate is preferable.
- 10
- 15
- 20
- 25

[0352]

Examples of nitrile solvents include acetonitrile, propionitrile, valeronitrile, butyronitrile, and the like.

[0353]

5 As desired, the organic developing solution may have a conventional additive blended. Examples of the additive include surfactants. The surfactant is not particularly limited, and for example, an ionic or non-ionic fluorine and/or a silicone-based surfactant can be used. As the surfactant, a non-ionic surfactant is preferable, and a non-ionic fluorine surfactant or a non-ionic silicone-based surfactant is more
10 preferable.

In a case where a surfactant is blended, the amount of the surfactant to be blended is typically 0.001% to 5 % by mass, preferably 0.005% to 2% by mass, and more preferably 0.01% to 0.5% by mass with respect to the total amount of the organic developing solution.

15 [0354]

The developing treatment can be performed by a conventional developing method. Examples thereof include a method in which the supporting body is immersed in the developing solution for a predetermined time (a dip method), a method in which the developing solution is cast upon the surface of the supporting body by surface tension
20 and maintained for a predetermined period (a puddle method), a method in which the developing solution is sprayed onto the surface of the supporting body (spray method), and a method in which the developing solution is continuously ejected from a developing solution-ejecting nozzle while scanning at a constant rate to apply the developing solution to the supporting body while rotating the substrate at a constant rate (dynamic
25 dispense method).

[0355]

As the organic solvent contained in the rinse liquid used in the rinse treatment after the developing treatment in a case of a solvent developing process, an organic solvent hardly dissolving the resist pattern can be suitably selected and used, among the organic solvents mentioned as inorganic solvents that are used for the organic developing solution. In general, at least one kind of solvent selected from the group consisting of a hydrocarbon solvent, a ketone solvent, an ester solvent, an alcohol solvent, an amide solvent, and an ether solvent is used. Among these, at least one kind of solvent selected from the group consisting of a hydrocarbon solvent, a ketone solvent, an ester solvent, an alcohol solvent, and an amide solvent is preferable, more preferably at least one kind of solvent selected from the group consisting of an alcohol solvent and an ester solvent, and an alcohol solvent is particularly preferable.

The alcohol solvent used for the rinse liquid is preferably a monohydric alcohol of 6 to 8 carbon atoms, and the monohydric alcohol may be linear, branched, or cyclic. Specific examples thereof include 1-hexanol, 1-heptanol, 1-octanol, 2-hexanol, 2-heptanol, 2-octanol, 3-hexanol, 3-heptanol, 3-octanol, 4-octanol, and benzyl alcohol. Among these, 1-hexanol, 2-heptanol, and 2-hexanol are preferable, and 1-hexanol and 2-hexanol are more preferable.

As the organic solvent, one kind of solvent may be used alone, or two or more kinds of solvents may be used in combination. Further, an organic solvent other than the above-described examples or water may be mixed together. However, in consideration of the development characteristics, the amount of water to be blended in the rinse liquid is preferably 30% by mass or less, more preferably 10% by mass or less, still more preferably 5% by mass or less, and most preferably 3% by mass or less with respect to the total amount of the rinse liquid.

A known additive can be blended with the rinse solution as necessary.

Examples of the additive include surfactants. As the surfactant, the same surfactant as those described above can be mentioned, a non-ionic surfactant is preferable, and a non-ionic fluorine surfactant or a non-ionic silicone-based surfactant is more preferable.

5 In a case where a surfactant is blended, the amount of the surfactant to be blended is typically 0.001% to 5 % by mass, preferably 0.005% to 2% by mass, and more preferably 0.01% to 0.5% by mass with respect to the total amount of the rinse liquid.

[0356]

The rinse treatment using a rinse liquid (washing treatment) can be performed
10 by a conventional rinse method. Examples of the rinse treatment method include a method in which the rinse liquid is continuously applied to the supporting body while rotating it at a constant rate (rotational coating method), a method in which the supporting body is immersed in the rinse liquid for a predetermined time (dip method), and a method in which the rinse liquid is sprayed onto the surface of the supporting body
15 (spray method).

[0357]

According to the method of forming a resist pattern according to the present embodiment described above, since the resist composition according to the first aspect described above is used, it is possible to form a resist pattern having few cracks and high
20 resolution.

[0358]

Such a method of forming a resist pattern is useful for manufacturing a three-dimensional structure device.

Examples

25 [0359]

Hereinafter, the present invention will be described in more detail based on examples, but the present invention is not limited to these examples.

[0360]

<Preparation of resist composition>

5 (Examples 1 to 18 and Comparative Examples 1 to 7)

Each of the components shown in Tables 1 to 3 was mixed and dissolved to prepare a resist composition of each Example.

[0361]

[Table 1]

	Component (A)	Component (B)	Component (D)	Component (Z)		Component (S)	Concentration of solid contents (% by mass)
				Component (Z1)	Component (Z2)		
Example 1	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-2 [5.0]	-	(S)-1 [331]	25.0
Example 2	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-2 [5.0]	-	(S)-1 [214]	35.0
Example 3	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-2 [5.0]	-	(S)-1 [110.5]	50.0
Example 4	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-2 [1.0]	-	(S)-1 [198]	35.0
Example 5	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-2 [15.0]	-	(S)-1 [224]	35.0
Example 6	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-2 [30.0]	-	(S)-1 [251]	35.0
Example 7	(A)-1 [100]	(B)-2 [5.0]	(D)-1 [0.5]	(Z1)-2 [5.0]	-	(S)-1 [214]	35.0
Example 8	(A)-1 [100]	(B)-3 [5.0]	(D)-1 [0.5]	(Z1)-2 [5.0]	-	(S)-1 [214]	35.0
Example 9	(A)-1 [100]	(B)-4 [5.0]	(D)-1 [0.5]	(Z1)-2 [5.0]	-	(S)-1 [214]	35.0
Example 10	(A)-1 [100]	(B)-5 [5.0]	(D)-1 [0.5]	(Z1)-2 [5.0]	-	(S)-1 [214]	35.0
Example 11	(A)-1 [100]	(B)-6 [5.0]	(D)-1 [0.5]	(Z1)-2 [5.0]	-	(S)-1 [214]	35.0

[0362]

[Table 2]

	Component (A)	Component (B)	Component (D)	Component (Z)		Component (S)	Concentration of solid contents (% by mass)
				Component (Z1)	Component (Z2)		
Example 12	(A)-1 [100]	(B)-3 [5.0]	(D)-1 [0.5]	(Z1)-1 [5.0]	-	(S)-1 [214]	35.0
Example 13	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-3 [5.0]	-	(S)-1 [214]	35.0
Example 14	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-4 [5.0]	-	(S)-1 [214]	35.0
Example 15	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-5 [5.0]	-	(S)-1 [214]	35.0
Example 16	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-6 [5.0]	-	(S)-1 [214]	35.0
Example 17	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-7 [5.0]	-	(S)-1 [214]	35.0
Example 18	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-8 [5.0]	-	(S)-1 [214]	35.0

[0363]

[Table 3]

	Component (A)	Component (B)	Component (D)	Component (Z)		Component (S)	Concentration of solid contents (% by mass)
				Component (Z1)	Component (Z2)		
Comparative Example 1	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	-	-	(S)-1 [196]	35.0
Comparative Example 2	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-1 [0.5]	-	(S)-1 [197]	35.0
Comparative Example 3	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	(Z1)-1 [35.0]		(S)-1 [261]	35.0
Comparative Example 4	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	-	(Z2)-1 [5.0]	(S)-1 [214]	35.0
Comparative Example 5	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	-	(Z2)-2 [5.0]	(S)-1 [214]	35.0
Comparative Example 6	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	-	(Z2)-3 [5.0]	(S)-1 [214]	35.0
Comparative Example 7	(A)-1 [100]	(B)-1 [5.0]	(D)-1 [0.5]	-	(Z2)-4 [5.0]	(S)-1 [214]	35.0

5

[0364]

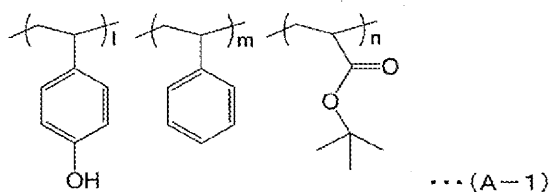
In Tables 1 to 3, each abbreviation has the following meaning. The numerical values in the brackets are blending amounts (parts by mass). The concentration of solid content was calculated according to the following expression, the concentration of solid

content (% by mass) = [(the component (A) + the component (B) + the component (D) + the component (Z))/(the component (A) + the component (B) + the component (D) + the component (Z) + the component (S))] $\times$ 100.

[0365]

- 5 (A)-1: a high-molecular-weight compound represented by Chemical Formula (A-1). The standard polystyrene-equivalent weight-average molecular weight (M_w) determined by GPC measurement and the molecular weight dispersity (M_w/M_n) are respectively 10,000 and 1.4. The copolymer compositional ratio (the ratio (molar ratio) among constitutional units in the structural formula) determined by ^{13}C -NMR is $l/m/n =$
- 10 60/15/25.

[0366]



[0367]

- (B)-1: an acid generator composed of a compound represented by Chemical
- 15 Formula (B-1).

(B)-2: an acid generator composed of a compound represented by Chemical

Formula (B-2).

(B)-3: an acid generator composed of a compound represented by Chemical

Formula (B-3).

- 20 (B)-4: an acid generator composed of a compound represented by Chemical
- Formula (B-4).

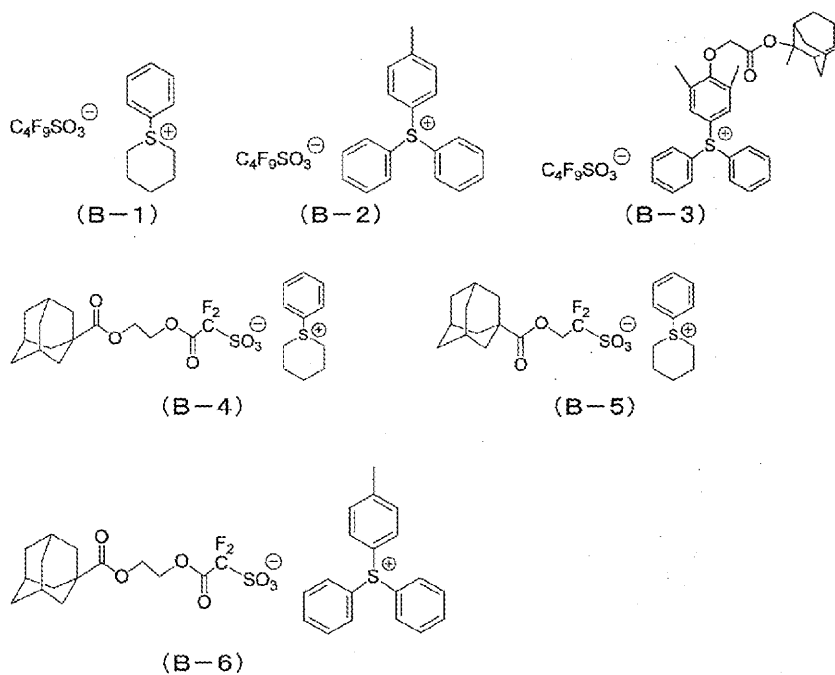
(B)-5: an acid generator composed of a compound represented by Chemical

Formula (B-5).

(B)-6: an acid generator composed of a compound represented by Chemical

Formula (B-6).

[0368]



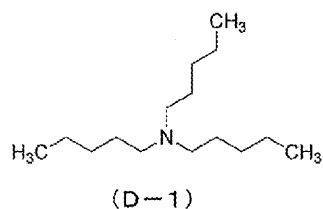
5

[0369]

(D)-1: a photodecomposable base composed of a compound represented by

Chemical Formula (D-1).

[0370]



10

[0371]

(Z1)-1: polypropylene glycol. The standard polystyrene-equivalent weight-

average molecular weight (Mw) determined by GPC measurement is 400.

(Z1)-2: polypropylene glycol. The standard polystyrene-equivalent weight-average molecular weight (Mw) determined by GPC measurement is 1,000.

(Z1)-3: polypropylene glycol. The standard polystyrene-equivalent weight-average molecular weight (Mw) determined by GPC measurement is 3,000.

(Z1)-4: polypropylene glycol. The standard polystyrene-equivalent weight-average molecular weight (Mw) determined by GPC measurement is 4,000.

(Z1)-5: polyethylene glycol. The standard polystyrene-equivalent weight-average molecular weight (Mw) determined by GPC measurement is 1,000.

(Z1)-6: polyethylene glycol. The standard polystyrene-equivalent weight-average molecular weight (Mw) determined by GPC measurement is 4,000.

(Z1)-7: polyethylene glycol. The standard polystyrene-equivalent weight-average molecular weight (Mw) determined by GPC measurement is 8,000.

(Z1)-8: polyethylene glycol. The standard polystyrene-equivalent weight-average molecular weight (Mw) determined by GPC measurement is 20,000.

[0372]

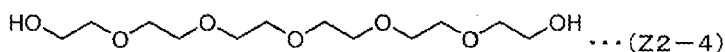
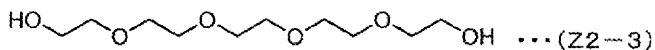
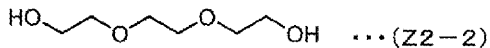
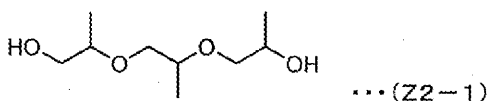
(Z2)-1: a compound represented by Chemical Formula (Z2-1). molecular weight: 193.

(Z2)-2: a compound represented by Chemical Formula (Z2-2). molecular weight: 164.

(Z2)-3: a compound represented by Chemical Formula (Z2-3). molecular weight: 238.

(Z2)-4: a compound represented by Chemical Formula (Z2-4). molecular weight: 282.

[0373]



[0374]

(S)-1: a mixed solvent of propylene glycol monomethyl ether/propylene glycol monomethyl ether acetate = 4/1 (mass ratio)

5 [0375]

<Formation of resist pattern>

Step (i):

The resist composition of

each example was applied using a spinner onto an 8-inch silicon wafer that had been
10 treated with hexamethyldisilazane (HMDS) at 110°C for 60 seconds. The coated wafer
was subjected to a pre-baking (PAB) treatment on a hot plate at a temperature of 160°C
for 120 seconds so that the coated wafer was dried to form a resist film having a film
thickness of 12 μm .

Step (ii):

15 Next, the resist film was selectively irradiated with a KrF excimer laser (248 nm) by a KrF exposure apparatus NSR-S203B (manufactured by Nikon Corporation; numerical aperture (NA) = 0.60, $\sigma = 0.68$) through a mask pattern (binary mask).

Thereafter, a post-exposure baking (PEB) treatment was performed on the resist film at 110°C for 90 seconds.

Step (iii):

Subsequently, alkali development was performed under the conditions of 23°C and 60 seconds using a 2.38% by mass tetramethylammonium hydroxide (TMAH) aqueous solution "NMD-3" (trade name, manufactured by TOKYO OHKA KOGYO CO., LTD.) as a developing solution.

Then, post-baking was performed at 100°C for 60 seconds.

As a result, an isolated space pattern having a space width of 1 to 3 μm was formed.

[0376]

[Evaluation of cracking resistance]

The silicon wafer on which the isolated space pattern was formed by the above <Formation of resist pattern> was placed in the chamber of a scanning electron microscope S-9380 (manufactured by Hitachi High-Tech Corporation), and vacuum-treated for 60 seconds under a pressure of 0.0001 Pa. The silicon wafer after the vacuum treatment was observed using an optical microscope, and the number of cracks was counted. The number of cracks was evaluated based on the following evaluation criteria. The results are shown in Tables 4 and 5 as "Cracks".

Evaluation criteria

A: 0 cracks

B: 1 to 5 cracks

C: 6 or more cracks

[0377]

[Evaluation of resolution]

In <Formation of resist pattern> described above, an optimum exposure dose E_{op} ($\mu\text{C}/\text{cm}^2$) for forming an isolated space pattern of 3 μm was determined. Then,

using the optimum exposure amount E_{op} as the exposure amount, an isolated space pattern of 1 μm was formed by <Formation of resist pattern>. The pattern shape of the isolated space pattern of 1 μm was observed using a scanning electron microscope S-9380 (manufactured by Hitachi High-Tech Corporation) and evaluated based on the following evaluation criteria. This is shown in Tables 4 and 5 as "Resolution".

Evaluation criteria

A: The pattern is definitely formed up to the substrate.

B: Trailing shape is slightly observed.

C: The pattern is not completely imprinted.

[0378]

[Table 4]

	Cracks	Resolution
Example 1	A	A
Example 2	A	A
Example 3	A	A
Example 4	B	A
Example 5	A	A
Example 6	A	B
Example 7	A	A
Example 8	A	A
Example 9	A	A
Example 10	A	A
Example 11	A	A
Example 12	B	A
Example 13	A	A
Example 14	A	A
Example 15	A	A
Example 16	A	A
Example 17	A	A
Example 18	A	A

[0379]

[Table 5]

	Cracks	Resolution
Comparative Example 1	C	A
Comparative Example 2	C	A
Comparative Example 3	A	C
Comparative Example 4	C	A
Comparative Example 5	C	A
Comparative Example 6	C	A
Comparative Example 7	C	A

[0380]

From the results shown in Tables 4 and 5, the resist compositions of Examples 1 to 17 were good in both crack resistance and resolution. On the other hand, the resist compositions of Comparative Examples 1 to 7 were not good in crack resistance and resolution.

While preferred embodiments of the invention have been described and illustrated above, it should be understood that these are exemplary of the invention and are not to be considered as limiting. Additions, omissions, substitutions, and other modifications can be made without departing from the spirit or scope of the present invention. Accordingly, the invention is not to be considered as being limited by the foregoing description, and is only limited by the scope of the appended claims.

What is claimed is:

1. A resist composition generating an acid upon exposure and having solubility in a developing solution, which is changed by action of an acid, the resist composition

5 comprising:

a base material component (A) having solubility in a developing solution, which is changed by action of an acid; and

a polyether compound having a weight-average molecular weight of 400 or more,

10 wherein a content of the polyether compound is 0.8 to 32 parts by mass with respect to 100 parts by mass of the base material component (A), and

a concentration of solid content of the resist composition is 25% by mass or more.

15 2. The resist composition according to claim 1, further comprising:

an acid generator component (B) generating an acid upon exposure,

wherein the acid generator component (B) contains a compound (B1) including an onium salt.

20 3. A method of forming a resist pattern, comprising:

a step of forming a resist film on a supporting body using the resist composition according to Claim 1 or 2;

a step of exposing the resist film; and

a step of developing the exposed resist film to form a resist pattern.