

RESIST COMPOSITION AND METHOD OF FORMING RESIST PATTERN

TECHNICAL FIELD

[0001]

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

 Priority is claimed on Japanese Patent Application No. 2019-217161, filed November 29, 2019, and Japanese Patent Application No. 2020-156373, filed September 17, 2020, the contents of which are incorporated herein by reference.

10

DESCRIPTION OF RELATED ART

[0002]

 In lithography techniques, for example, a resist film composed of a resist material is formed on a substrate, and the resist film is subjected to selective exposure, followed by
15 development, thereby forming a resist pattern having a predetermined shape on the resist film. A resist material in which the exposed portions of the resist film become soluble in a developing solution is called a positive-type, and a resist material in which the exposed portions of the resist film become insoluble in a developing solution is called a negative-type.

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 exposure light source. Conventionally, ultraviolet radiation typified by g-line and i-line radiation has been used, but nowadays
25 KrF excimer lasers and ArF excimer lasers are used in mass production. Furthermore, research is also being conducted into lithography techniques that use an exposure light source having a wavelength shorter (energy higher) than these excimer lasers, such as electron beam (EB), extreme ultraviolet radiation (EUV), and X ray.

[0003]

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

 As a resist material that satisfies these conditions, a chemically amplified

composition is used, which includes a base material component that exhibits a changed solubility in a developing solution under the action of acid and an acid-generator component that generates acid upon exposure.

For example, in the case where the developing solution is an alkali developing solution (alkali developing process), a chemically amplified positive resist which contains, as a base component (base resin), a resin which exhibits increased solubility in an alkali developing solution under action of acid, and an acid generator is typically used. If a resist film formed using such a resist composition is selectively exposed at the time of forming a resist pattern, in exposed areas, acid is generated from the acid generator component, and the polarity of the base resin increases by the action of the generated acid, thereby making the exposed areas of the resist film soluble in the alkali developing solution. Thus, by conducting alkali developing, the unexposed portions of the resist film remain to form a positive resist pattern.

On the other hand, when such a base resin is applied to a solvent developing process using a developing solution containing an organic solvent (organic developing solution), the solubility of the exposed portions in an organic developing solution is decreased. As a result, the unexposed portions of the resist film are dissolved and removed by the organic developing solution, and a negative resist pattern in which the exposed portions of the resist film are remaining is formed. Such a solvent developing process for forming a negative-tone resist composition is sometimes referred to as "negative-tone developing process".

[0004]

So far, as the base resin of the chemically amplified resist composition, for example, a resin PHS resin in which polyhydroxystyrene (PHS) or the hydroxyl group thereof is protected by an acid dissociable dissolution inhibiting group that exhibits high transparent with respect to KrF excimer laser (248 nm) has been used. Further, for example, for ArF excimer laser (193 nm), a resin ((meth)acrylic resin) in which the hydroxyl group in the carboxy group of (meth)acrylic acid is protected by an acid dissociable dissolution inhibiting group has been used (for example, see Patent Literature 1).

As the acid dissociable dissolution inhibiting group, the so-called acetal group such as a chain ether group (e.g., 1-ethoxyethyl group) or a cyclic ether group (e.g., tetrahydropyranyl group), a tertiary alkyl group (e.g., a tert-butyl group), and a tertiary alkoxycarbonyl group (e.g., tert-butoxycarbonyl group) has been mainly used.

[0005]

In addition, a wide variety of acid generator components used in the chemically amplified resist composition have been proposed so far, for example, onium salt-based acid generators such as iodonium salt and sulfonium salt, oxime sulfonate-based acid generators, 5 diazomethane-based acid generators, nitrobenzyl sulfonate-based acid generators, iminosulfonate-based acid generators, and disulfon-based acid generators are known.

Among these examples, onium salt-based acid generators are widely used, and those having onium ions such as triphenylsulfonium in the cation portion are mainly used. As the anion moiety of such onium salt-based acid generator, generally, an alkyl sulfonic 10 acid ion or a fluorinated alkyl sulfonic acid ion in which a part or all of the hydrogen atom of the alkyl group is replaced with a fluorine atom is used.

[0006]

Meanwhile, currently, along with the high integration of LSI and the high speed of communication, an increase in memory capacity is required, and further miniaturization 15 of patterns is rapidly progressing. However, although lithography using an electron beam or EUV aims to form a fine pattern of several tens of nanometers, there are still many problems such as low productivity, and there is a limit to the technique by microfabrication.

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

DOCUMENTS OF RELATED ART

[Patent Literature]

[0007]

25 [Patent Literature 1] Japanese Unexamined Patent Application, First Publication No. 2003-241385

SUMMARY OF THE INVENTION

[0008]

30 In the manufacture of the above-mentioned three-dimensional structure device, a thick resist film having a film thickness higher than that of the conventional one, for example, having a film thickness of 5 μm or more is formed on the surface of the workpiece to form a resist pattern, followed by etching or the like. In the case where a chemically

amplified resist composition is used, as the film thickness of the resist film becomes larger, it becomes difficult to maintain the sensitivity during exposure, and the resolution by developing is deteriorated, such that it becomes difficult to obtain a pattern having a desired shape. Another problem is that the thicker the resist film is, the more likely it is that cracks
5 will occur in the resist pattern.

[0009]

The present invention takes the above circumstances into consideration, with an object of providing a resist composition which is capable of forming a thick film resist film, which is unlikely to cause occurrence of cracks, and which exhibits good sensitivity; and
10 a method of forming a resist pattern using the resist composition.

[0010]

For solving the above-mentioned problems, the present invention employs the following aspects.

A first aspect of the present invention is a resist composition which generates acid
15 upon exposure and exhibits changed solubility in a developing solution under action of acid, the resist composition including a base component (A) which exhibits changed solubility in a developing solution under action of acid, and an ion liquid (Z), wherein a solid content of the resist composition is 25% by weight or more.

[0011]

A second aspect of the present invention is a method of forming a resist pattern,
20 including: using a resist composition according to the first aspect to form a resist film, exposing the resist film, and developing the exposed resist film to form a resist pattern.

[0012]

According to the present invention, there are provided a resist composition which
25 is capable of forming a thick film resist film, which is unlikely to cause occurrence of cracks, and which exhibits good sensitivity; and a method of forming a resist pattern using the resist composition.

DETAILED DESCRIPTION OF THE INVENTION

[0013]

30 In the present description and claims, the term “aliphatic” is a relative concept used in relation to the term “aromatic”, and defines a group or compound that has no aromaticity.

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

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

A “halogenated alkyl group” is a group in which part or all of the hydrogen atoms of an alkyl group is substituted with a halogen atom. 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 which part or all of the hydrogen atoms of an alkyl group or an alkylene group have been substituted with a fluorine atom.

The term “structural unit” refers to a monomer unit that contributes to the formation of a polymeric compound (resin, polymer, copolymer).

The case of describing “may have a substituent” includes both of the case where the hydrogen atom (-H) is substituted with a monovalent group and the case where the methylene group (-CH₂-) 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 term “base component” refers to an organic compound capable of forming a film, and is preferably an organic compound having a molecular weight of 500 or more. When the organic compound has a molecular weight of 500 or more, the film-forming ability is improved, and a resist pattern of nano level can be easily formed. The organic compound used as the base component is broadly classified into non-polymers and polymers. In general, as a non-polymer, any of those which have a molecular weight in the range of 500 to less than 4,000 is used. Hereafter, a “low molecular weight compound” refers to a non-polymer having a molecular weight in the range of 500 to less than 4,000. As a polymer, any of those which have a molecular weight of 1,000 or more is generally used. Hereafter, a “resin” or a “polymer” refers to a polymer having a molecular weight of 1,000 or more. As the molecular weight of the polymer, the weight average molecular weight in terms of the polystyrene equivalent value determined by gel permeation chromatography (GPC) is used.

[0015]

A “structural unit derived from an acrylate ester” refers to a structural unit that is formed by the cleavage of the ethylenic double bond of an acrylate ester.

An “acrylate ester” refers to 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.

The acrylate ester may have the hydrogen atom bonded to the carbon atom on the α -position substituted with a substituent. The substituent (R^{a0}) that substitutes the hydrogen atom bonded to the carbon atom on the α -position is an atom other than hydrogen or a group, and examples thereof include an alkyl group of 1 to 5 carbon atoms and a halogenated alkyl group of 1 to 5 carbon atoms. Further, an acrylate ester having the hydrogen atom bonded to the carbon atom on the α -position substituted with a substituent (R^{a0}) in which the substituent has been substituted with a substituent containing an ester bond (e.g., an itaconic acid diester), or an acrylic acid having the hydrogen atom bonded to the carbon atom on the α -position substituted with a substituent (R^{a0}) in which the substituent has been substituted with a hydroxyalkyl group or a group in which the hydroxy group within a hydroxyalkyl group has been modified (e.g., α -hydroxyalkyl acrylate ester) can be mentioned as an acrylate ester having the hydrogen atom bonded to the carbon atom on the α -position substituted with a substituent. A carbon atom on the α -position of an acrylate ester refers to the carbon atom bonded to the carbonyl group, unless specified otherwise.

Hereafter, an acrylate ester having the hydrogen atom bonded to the carbon atom on the α -position substituted with a substituent is sometimes referred to as “ α -substituted acrylate ester”. Further, acrylate esters and α -substituted acrylate esters are collectively referred to as “(α -substituted) acrylate ester”.

[0016]

A “structural unit derived from hydroxystyrene” refers to a structural unit that is formed by the cleavage of the ethylenic double bond of hydroxystyrene. A “structural unit derived from a hydroxystyrene derivative” refers to a structural unit that is formed by the cleavage of the 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 hydroxy

group has been substituted with an organic group and may have the hydrogen atom on the α -position substituted with a substituent; and hydroxystyrene which has a substituent other than a hydroxy group bonded to the benzene ring and may have the hydrogen atom on the α -position substituted with a substituent. Here, the α -position (carbon atom on the α -position) refers to the carbon atom having the benzene ring bonded thereto, unless specified otherwise.

As the substituent which substitutes the hydrogen atom on the α -position of hydroxystyrene, the same substituents as those described above for the substituent on the α -position of the aforementioned α -substituted acrylate ester can be mentioned.

[0017]

A “structural unit derived from vinylbenzoic acid or a vinylbenzoic acid derivative” refers to a structural unit that is formed by the cleavage of the ethylenic 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 benzoic acid in which the hydrogen atom of the carboxy group has been substituted with an organic group and may have the hydrogen atom on the α -position substituted with a substituent; and benzoic acid which has a substituent other than a hydroxy group and a carboxy group bonded to the benzene ring and may have the hydrogen atom on the α -position substituted with a substituent. Here, the α -position (carbon atom on the α -position) refers to the carbon atom having the benzene ring bonded thereto, unless specified otherwise.

[0018]

As the alkyl group as a substituent on 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 on the α -position include groups in which part or all of the hydrogen atoms of the aforementioned “alkyl group as the substituent on 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 desirable.

Specific examples of the hydroxyalkyl group as the substituent on the α -position include groups in which part or all of the hydrogen atoms of the aforementioned "alkyl group as the substituent on the α -position" are substituted with a hydroxy group. The
5 number of hydroxy groups within the hydroxyalkyl group is preferably 1 to 5, and most preferably 1.

[0019]

In the present specification and claims, some structures represented by chemical formulae may have an asymmetric carbon, such that an enantiomer or a diastereomer may
10 be present. In such a case, the one formula represents all isomers. The isomers may be used individually, or in the form of a mixture.

[0020]

(Resist composition)

The resist composition according to a first aspect of the present invention is a
15 resist composition which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid, the resist composition including a base component (A) which exhibits changed solubility in a developing solution under action of acid (hereafter, also referred to as "component (A)"), and an ion liquid (Z) (hereafter, also referred to as "component (Z)"). The solid content of the resist composition according to
20 the present embodiment is 25% by weight or more.

When a resist film is formed using such a resist composition, a thick-film resist film (for example, a film thickness of 5 μm or more) may be formed.

[0021]

When a resist film is formed using the resist composition according to the present
25 embodiment, and the resist film is selectively exposed, acid is generated at exposed portions of the resist film, and the solubility of the component (A) in a developing solution is changed by the action of the acid. On the other hand, at unexposed portions of the resist film, the solubility of the component (A) in a developing solution is unchanged. As a result, difference is generated between the exposed portions of the resist film and the unexposed
30 portions of the resist film in terms of solubility in a developing solution. Therefore, by subjecting the resist film to development, the exposed portions of the resist film are dissolved and removed to form a positive-tone resist pattern in the case of a positive resist, whereas the unexposed portions of the resist film are dissolved and removed to form a

negative-tone resist pattern in the case of a negative resist.

[0022]

In the present specification, a resist composition which forms a positive resist pattern by dissolving and removing the exposed portions of the resist film is called a positive resist composition, and a resist composition which forms a negative resist pattern by dissolving and removing the unexposed portions of the resist film is called a negative resist composition. The resist composition of the present embodiment may be either a positive resist composition or a negative resist composition. Further, the resist composition of the present embodiment may be used in an alkali developing process using an alkali developing solution in the developing treatment in a case of forming a resist pattern or may be used in a solvent developing process using a developing solution containing an organic solvent (organic developing solution) in the developing treatment.

[0023]

The resist composition of the present embodiment is capable of generating acid upon exposure. The acid may be generated from the component (A) upon exposure, or the acid may be generated from an additive component other than the component (A) upon exposure.

In the present embodiment, the resist composition may be a resist composition (1) containing an acid generator component (B) which generates acid upon exposure (hereafter, referred to as "component (B)"); a resist composition (2) in which the component (A) is a component which generates acid upon exposure; or a resist composition (3) in which the component (A) is a component which generates acid upon exposure, and further containing an acid generator component (B). That is, when the resist composition of the present invention is the aforementioned resist composition (2) or (3), the component (A) is a "base component which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid". In the case where the component (A) is a base component which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid, the component (A1) described later is preferably a polymeric compound which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid. As the polymeric compound, a resin having a structural unit which generates acid upon exposure can be used. As the structural unit which generates acid upon exposure, a conventional structural unit can be used. The resist composition of the present embodiment is preferably the aforementioned

resist composition (1).

[0024]

<Component (A)>

In the resist composition according to the present embodiment, the component
5 (A) preferably contains a resin component (A1) (hereafter, referred to as "component (A1)") which exhibits changed solubility in a developing solution by the action of acid. By using the component (A1), the polarity of the base component before and after exposure is changed. Therefore, a good development contrast may be achieved not only in an alkali developing process, but also in a solvent developing process.

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

[0025]

More specifically, in the case of applying an alkali developing process, the base
15 component containing the component (A1) is hardly soluble in an alkali developing solution prior to exposure, but when acid is generated from the component (B) upon exposure, the action of this acid causes an increase in the polarity of the base component, thereby increasing the solubility of the component (A1) in an alkali developing solution. Therefore, in the formation of a resist pattern, by conducting selective exposure of a resist
20 film formed by applying the resist composition to a substrate, the exposed portions of the resist film change from an insoluble state to a soluble state in an alkali developing solution, whereas the unexposed portions of the resist film remain insoluble in an alkali developing solution, and hence, a positive-tone resist pattern is formed by alkali developing.

[0026]

25 On the other hand, in the case of a solvent developing process, the base component containing the component (A1) exhibits high solubility in an organic developing solution prior to exposure, and when 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.
30 Therefore, in the formation of a resist pattern, by conducting selective exposure of a resist film formed by applying the resist composition to a substrate, the exposed portions of the resist film changes from an soluble state to an insoluble state in an organic developing solution, whereas the unexposed portions of the resist film remain soluble in an organic

developing solution. As a result, by conducting development using an organic developing solution, a contrast can be made between the exposed portions and unexposed portions, thereby forming a negative resist pattern.

[0027]

5 In the resist composition of the present embodiment, as the component (A), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

[0028]

- Component (A1)

10 The component (A1) is a resin component which exhibits changed solubility in a developing solution under action of acid. The component (A1) is preferably a resin component which has a structural unit (a1) containing an acid decomposable group that exhibits increased polarity by the action of acid.

15 If desired, the component (A1) may include, in addition to the structural unit (a1), other structural unit.

[0029]

<<Structural unit (a1)>>

The structural unit (a1) is a structural unit containing an acid decomposable group that exhibits increased polarity by the action of acid.

20 The term "acid decomposable group" refers to a group in which at least a part of the bond within the structure thereof is cleaved by the action of an acid.

Examples of acid decomposable groups which exhibit increased polarity by the action of an acid include groups which are decomposed by the action of an acid to form a polar group.

25 Examples of the polar group include a carboxy group, a hydroxy 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 (hereafter, referred to as "OH-containing polar group") is preferable, a carboxy group or a hydroxy group is more preferable, and a carboxy group is particularly desirable.

30 More specifically, as an example of an acid decomposable group, a group in which the aforementioned polar group has been protected with an acid dissociable group (such as a group in which the hydrogen atom of the OH-containing polar group has been protected with an acid dissociable group) can be given.

[0030]

The "acid dissociable group" refers to both (i) a group in which the bond between the acid dissociable group and the adjacent atom is cleaved by the action of acid; and (ii) a group in which one of the bonds is cleaved by the action of acid, and then a decarboxylation reaction occurs, thereby cleaving the bond between the acid dissociable group and the adjacent atom.

It is necessary that the acid dissociable group that constitutes the acid decomposable group is a group which exhibits a lower polarity than the polar group generated by the dissociation of the acid dissociable group. Thus, when the acid dissociable group is dissociated by the action of acid, a polar group exhibiting a 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 an alkali developing solution changes, and the solubility in an alkali developing solution is relatively increased, whereas the solubility in an organic developing solution is relatively decreased.

[0031]

Examples of the acid dissociable group include groups which have been proposed as acid dissociable groups for the base resin of a conventional chemically amplified resist composition.

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

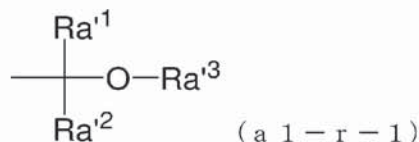
[0032]

- Acetal-type acid dissociable group

Examples of the acid dissociable group for protecting the carboxy group or hydroxy group as a polar group include the acid dissociable group represented by general formula (a1-r-1) shown below (hereafter, referred to as "acetal-type acid dissociable group").

[0033]

[Chemical Formula 1]



In the formula, Ra'¹ and Ra'² each independently represents a hydrogen atom or an alkyl group; Ra'³ represents a hydrocarbon group, provided that Ra'³ may be bonded to Ra'¹ or Ra'² to form a ring.

5 [0034]

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

In the case where Ra'¹ or Ra'² is an alkyl group, as the alkyl group, the same alkyl
 10 groups as those described above for the substituent which may be bonded to the carbon atom on the α -position of the aforementioned α -substituted acrylate ester can be mentioned, and an alkyl group of 1 to 5 carbon atoms is preferable. Specific examples 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. Of these, a methyl
 15 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 for Ra'³ include a linear or branched alkyl group and a cyclic hydrocarbon group.

20 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 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.

25 [0036]

The branched alkyl group preferably has 3 to 10 carbon atoms, and more preferably 3 to 5 carbon atoms. Specific examples 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.

30 [0037]

In the 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 polycyclic or monocyclic.

As the monocyclic aliphatic hydrocarbon group, a group in which 1 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 polycyclic aliphatic hydrocarbon group, a group in which 1 hydrogen atom has been removed from a polycycloalkane is preferable, and the polycyclic group preferably has 7 to 12 carbon atoms. Examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane and tetracyclododecane.

[0038]

When the monovalent hydrocarbon group for 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 compound having $(4n + 2)\pi$ electrons, and may be either monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, and still more preferably 6 to 15 carbon atoms, and most preferably 6 to 12 carbon atoms. Examples of the aromatic ring include aromatic hydrocarbon rings, such as benzene, naphthalene, anthracene and phenanthrene; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic hydrocarbon rings has been substituted with a hetero atom. Examples of the hetero atom within 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 for Ra'^3 include a group in which one hydrogen atom has been removed from the aforementioned aromatic hydrocarbon ring or aromatic hetero ring (aryl group or 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 aforementioned 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 alkylene group bonded to the aforementioned aromatic hydrocarbon ring or the aromatic hetero ring preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and most preferably 1 carbon atom.

[0039]

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

10 Here, R^{P1} is a monovalent chain 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. Further, R^{P2} is a single bond, a divalent chain 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.

15 However, the saturated chain hydrocarbon group, the saturated cyclic aliphatic hydrocarbon group and the aromatic hydrocarbon group for R^{P1} and R^{P2} may have part or all of the hydrogen atoms substituted with fluorine. The aliphatic cyclic hydrocarbon group may have 1 or more substituents of 1 kind, or 1 or more substituents of a plurality of kinds.

20 Examples of the monovalent chain 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.

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

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

[0040]

In the 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 tetrahydropyranyl group and tetrahydrofuranyl group.

[0041]

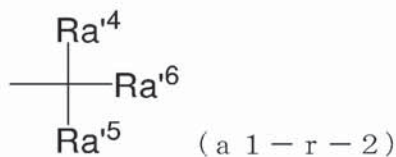
5 - Tertiary alkyl ester-type acid dissociable group

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.

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

[0042]

[Chemical Formula 2]



15 In the formula, Ra'^4 to Ra'^6 each independently represents a hydrocarbon group, provided that Ra'^5 and Ra'^6 may be mutually bonded to form a ring.

[0043]

Examples of the hydrocarbon group for Ra'^4 include a linear or branched alkyl group, a chain or cyclic alkenyl group, and a cyclic hydrocarbon group.

20 The linear or branched alkyl group and the cyclic hydrocarbon group (monocyclic aliphatic hydrocarbon group, polycyclic aliphatic hydrocarbon group or aromatic hydrocarbon group) for Ra'^4 are the same as defined for Ra'^3 .

The chain or cyclic alkenyl group for Ra'^4 is preferably an alkenyl group having 2 to 10 carbon atoms.

25 The hydrocarbon group for Ra'^5 and Ra'^6 is the same as defined for Ra'^3 .

[0044]

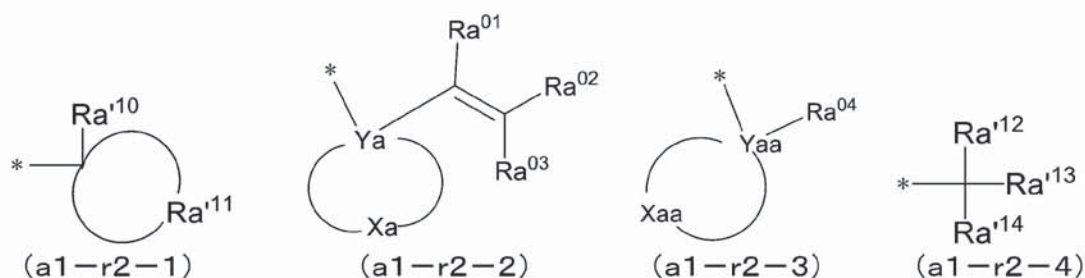
In the case where Ra'^5 and Ra'^6 are mutually bonded to form a ring, a group represented by general formula (a1-r2-1) shown below, a group represented by general formula (a1-r2-2) shown below, and a group represented by general formula (a1-r2-3) shown below may be given as preferable examples.

30

On the other hand, in the case where Ra'^4 to Ra'^6 are not mutually bonded and independently represent a hydrocarbon group, the group represented by general formula (a1-r2-4) shown below may be given as a preferable example.

[0045]

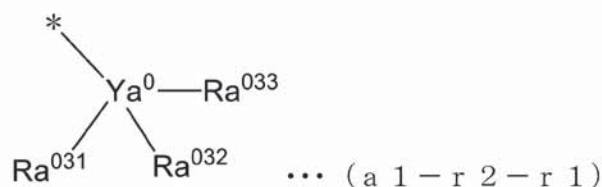
5 [Chemical Formula 3]



In formula (a1-r2-1), Ra'^{10} represents an alkyl group of 1 to 10 carbon atoms, or a group represented by general formula (a1-r2-r1) shown below; Ra'^{11} is a group which forms an aliphatic cyclic group together with a carbon atom having Ra'^{10} bonded thereto. In formula (a1-r2-2), Ya represents a carbon atom; Xa represents a group which forms a cyclic hydrocarbon group together with Ya , provided that part or all of the hydrogen atoms of the cyclic hydrocarbon group may be substituted; Ra'^{01} to Ra'^{03} each independently represents a hydrogen atom, a monovalent saturated chain hydrocarbon group of 1 to 10 carbon atoms or a monovalent saturated aliphatic cyclic hydrocarbon group of 3 to 20 carbon atoms, provided that part or all of the hydrogen atoms of the saturated chain hydrocarbon or the saturated aliphatic cyclic hydrocarbon may be substituted; two or more of Ra'^{01} to Ra'^{03} may be mutually bonded to form a cyclic structure. In formula (a1-r2-3), Yaa represents a carbon atom; Xaa represents a group which 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 hydrogen atom or a monovalent saturated hydrocarbon group of 1 to 10 carbon atoms, provided that part or all of the hydrogen atoms of the saturated hydrocarbon group may be substituted; Ra'^{14} represents a hydrocarbon group which may have a substituent; and $*$ represents a bonding site.

25 [0046]

[Chemical Formula 4]



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; provided that at least one Ra^{031} , Ra^{032} and Ra^{033} is a hydrocarbon group having a polar group.

5 [0047]

In the formula (a1-r2-1), as the alkyl group of 1 to 10 carbon atoms for Ra^{10} , the same groups as described above for the linear or branched alkyl group for Ra^3 in the formula (a1-r-1) are preferable. Ra^{10} is preferably an alkyl group of 1 to 5 carbon atoms.

[0048]

10 In formula (a1-r2-r1), Ya^0 represents a quaternary carbon atom. That is, the number of carbon atoms bonded to Ya^0 (carbon atom) is 4.

[0049]

In formula (a1-r2-r1), Ra^{031} , Ra^{032} and Ra^{033} each independently represents a hydrocarbon group which may have a substituent. Examples of the hydrocarbon group for Ra^{031} , Ra^{032} and Ra^{033} include a linear or branched alkyl group, a chain or cyclic alkenyl group, and a cyclic hydrocarbon group.

15 [0050]

The linear alkyl group for Ra^{031} , Ra^{032} and Ra^{033} preferably has 1 to 5 carbon atoms, more preferably 1 to 4 carbon atoms, and still more preferably 1 or 2 carbon atoms.

20 Specific examples 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.

The branched alkyl group for Ra^{031} , Ra^{032} and Ra^{033} preferably has 3 to 10 carbon atoms, and more preferably 3 to 5 carbon atoms. Specific examples 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.

25 The chain or cyclic alkenyl group for Ra^{031} , Ra^{032} and Ra^{033} is preferably an alkenyl group having 2 to 10 carbon atoms.

[0051]

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

5 As the monocyclic aliphatic hydrocarbon group, a group in which 1 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.

10 As the polycyclic aliphatic hydrocarbon group, a group in which 1 hydrogen atom has been removed from a polycycloalkane is preferable, and the polycyclic group preferably has 7 to 12 carbon atoms. Examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane and tetracyclododecane.

[0052]

15 The aromatic hydrocarbon group for Ra^{031} , Ra^{032} and Ra^{033} 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 compound having $(4n + 2)$ π electrons, and may be either monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20, still more preferably 6 to 15, and most preferably 6 to 12. Examples of the aromatic ring include aromatic hydrocarbon rings, such as benzene, naphthalene, anthracene and phenanthrene; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic hydrocarbon rings has been substituted with a hetero atom. Examples of the hetero atom within 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 aforementioned aromatic hydrocarbon ring or aromatic hetero ring (aryl group or 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 aforementioned 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 alkylene group bonded to the aforementioned aromatic hydrocarbon ring or the aromatic hetero ring preferably

20

25

30

has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and most preferably 1 carbon atom.

[0053]

In the case where the hydrocarbon group for Ra^{031} , Ra^{032} and Ra^{033} is substituted, examples of the substituent include a hydroxy group, a carboxy group, a halogen atom (such as a fluorine atom, a chlorine atom or a chlorine atom), an alkoxy group (such as a methoxy group, an ethoxy group, a propoxy group or a butoxy group), and an alkyloxycarbonyl group.

[0054]

Among these examples, as the hydrocarbon group (which may have a substituent) for Ra^{031} , Ra^{032} and Ra^{033} , a linear or branched alkyl group which may have a substituent is preferable, and a linear alkyl group is more preferable.

[0055]

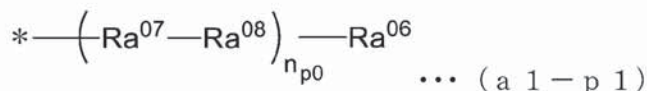
However, at least one of Ra^{031} , Ra^{032} and Ra^{033} is a hydrocarbon group having a polar group.

The "hydrocarbon group having a polar group" includes a group in which a methylene group ($-CH_2-$) constituting the hydrocarbon group is substituted with a polar group, and a group in which at least one hydrogen atom constituting the hydrocarbon group has been substituted with a polar group.

Examples of the "hydrocarbon group having a polar group" include a functional group represented by general formula (a1-p1) shown below.

[0056]

[Chemical Formula 5]



In the formula, Ra^{07} represents a divalent hydrocarbon group having 2 to 12 carbon atoms; Ra^{08} represents a divalent linking group containing a hetero atom; Ra^{06} represents a monovalent hydrocarbon group having 1 to 12 carbon atoms; and 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 2 to 8 carbon atoms, more

preferably 2 to 6 carbon atoms, still more preferably 2 to 4 carbon atoms, and most preferably 2 carbon atoms.

The hydrocarbon group for Ra^{07} is preferably a chain or cyclic aliphatic hydrocarbon group, and more preferably a chain hydrocarbon group.

5 Examples of Ra^{07} include a linear alkanediyl group, such as an ethylene group, a propane-1,3-diyl group, butane-1,4-diyl group, a pentane-1,5-diyl group, a hexane-1,6-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; a
10 branched alkanediyl group, 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; a cycloalkanediyl group, such as a cyclobutane-1,3-diyl group, a cyclopentane-1,3-diyl group, a cyclohexane-1,4-diyl group, and a cyclooctane-1,5-diyl group; and a polycyclic divalent alicyclic hydrocarbon group, such as a norbornane-1,4-diyl group, a norbornane-2,5-diyl group, an adamantane-1,5-diyl group, and an
15 adamantane-2,6-diyl group.

Among these examples, an alkanediyl group is preferable, and a linear alkanediyl group is more preferable.

[0058]

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

Examples of Ra^{08} include $-O-$, $-C(=O)-O-$, $-C(=O)-$, $-O-C(=O)-O-$, $-C(=O)-NH-$, $-NH-$, $-NH-C(=NH)-$ (H may be substituted with a substituent such as an alkyl group or an acyl group), $-S-$, $-S(=O)_2-$, and $-S(=O)_2-O-$.

25 Among these examples, in terms of solubility in a developing solution, $-O-$, $-C(=O)-O-$, $-C(=O)-$, or $-O-C(=O)-O-$ are preferable, and $-O-$ or $-C(=O)-$ is most preferable.

[0059]

30 In formula (a1-p1), Ra^{06} represents a monovalent hydrocarbon group having 1 to 12 carbon atoms. Ra^{06} has 1 to 12 carbon atoms. In terms of solubility in a developing solution, Ra^{06} preferably has 1 to 8 carbon atoms, more preferably 1 to 5 carbon atoms, still more preferably 1 to 3 carbon atoms, still more preferably 1 or 2 carbon atoms, and most preferably 1 carbon atoms.

[0060]

Examples of the hydrocarbon group for Ra^{06} include a chain hydrocarbon group, a cyclic hydrocarbon group, and a combination of a chain hydrocarbon group and a cyclic hydrocarbon group.

Examples of the chain hydrocarbon group include a methyl group, an ethyl group,
 5 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.

[0061]

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

The alicyclic hydrocarbon group may be monocyclic or polycyclic. Examples of monocyclic alicyclic hydrocarbon groups include cycloalkyl groups, such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a dimethylcyclohexyl
 15 group, a cycloheptyl group, a cyclooctyl group, a cyclononyl group, and a cyclodecyl group. Examples of polycyclic alicyclic hydrocarbon groups include a decahydronaphthyl group, an adamantyl group, a 2-alkyladamantan-2-yl group, a 1-(adamantan-1-yl)alkan-1-yl group, a norbornyl group, a methylnorbornyl group, and an isonorbornyl group.

Examples of aromatic hydrocarbon groups include a phenyl group, a naphthyl
 20 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, 2,6-diethylphenyl group, and 2-methyl-6-ethyl phenyl group.

[0062]

25 In terms of solubility in a developing solution, Ra^{06} is preferably a chain hydrocarbon group, more preferably an alkyl group, and still more preferably a linear alkyl group.

[0063]

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

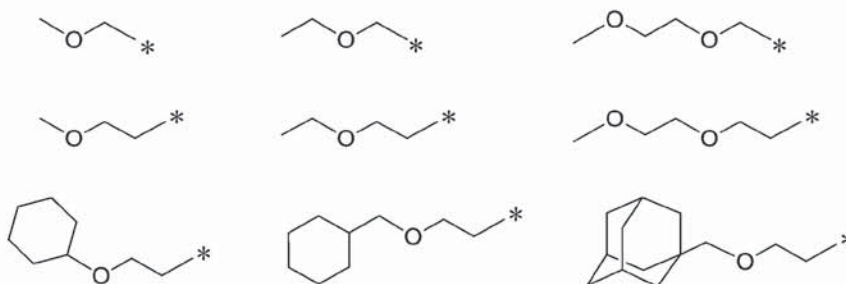
[0064]

Specific examples of the hydrocarbon group having a polar group are shown below.

In the following formulae, * represents a valence bond which is bonded to the quaternary carbon atom (Y_a^0).

[0065]

[Chemical Formula 6]



5

[0066]

In formula (a1-r2-r1), at least one of Ra^{031} , Ra^{032} and Ra^{033} is a hydrocarbon group having a polar group. However, the number of hydrocarbon groups having a polar group may be appropriately selected depending on the solubility in the developing solution used in the formation of a resist pattern. For example, it is preferable that one or two of Ra^{031} , Ra^{032} and Ra^{033} is a hydrocarbon group having a polar group, and it is more preferable that one of Ra^{031} , Ra^{032} and Ra^{033} is hydrocarbon group having a polar group.

10

[0067]

The hydrocarbon group having a polar group may have a substituent other than a polar group. Examples of such substituent include a halogen atom (such as a fluorine atom, a chlorine atom or a bromine atom), and a halogenated alkyl group having 1 to 5 carbon atoms.

15

[0068]

In formula (a1-r2-1), the aliphatic cyclic group which is formed by Ra^{11} together with the carbon atom bonded to Ra^{10} , the same groups as those described above for the monocyclic or polycyclic aliphatic hydrocarbon group for Ra^{13} in formula (a1-r-1) are preferable.

20

[0069]

In formula (a1-r2-2), as the cyclic hydrocarbon group formed by X_a together with Y_a , a group in which 1 or more hydrogen atoms have been removed from the monovalent cyclic hydrocarbon group (aliphatic hydrocarbon group) for Ra^{13} in the aforementioned formula (a1-r-1) may be mentioned.

25

The cyclic hydrocarbon group which Xa forms with Ya may have a substituent. Examples of substituents include the same substituents as those which the cyclic hydrocarbon group for Ra³ may have.

In formula (a1-r2-2), examples of the monovalent saturated chain hydrocarbon group of 1 to 10 carbon atoms for Ra⁰¹ to Ra⁰³ 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 for Ra⁰¹ to Ra⁰³ include a monocyclic aliphatic saturated hydrocarbon group such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclodecyl group, and a cyclododecyl group; and a polycyclic aliphatic saturated hydrocarbon group 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 these examples, as Ra⁰¹ to Ra⁰³, in terms of ease in synthesis of the monomeric compound which derives the structural unit (a1), a hydrogen atom or a saturated chain hydrocarbon group having 1 to 10 carbon atoms is preferable, a hydrogen atom, a methyl group or an ethyl group is more preferable, and a hydrogen atom is most preferable.

[0070]

As the substituent for the saturated chain hydrocarbon group or saturated cyclic aliphatic hydrocarbon group represented by Ra⁰¹ to Ra⁰³, for example, the same substituents as those described above for Ra⁰⁵ may be mentioned.

25 [0071]

Examples of the group containing a carbon-carbon double bond which is generated by forming a cyclic structure in which two or more of Ra⁰¹ to Ra⁰³ are bonded to each other include a cyclopentenyl group, a cyclohexenyl group, a methyl cyclopentenyl group, a methyl cyclohexenyl group, a cyclopentylideneethenyl group, and a cyclohexylidenethenyl group. Among these examples, from the viewpoint of the ease of synthesis of the monomer compound which derives the structural unit (a1), a cyclopentenyl group, a cyclohexenyl group, and a cyclopentylidenethenyl group are preferable.

[0072]

In formula (a1-r2-3), an aliphatic cyclic group which is formed of Xaa together with Yaa is preferably a group exemplified as an aliphatic hydrocarbon group which is a monocyclic group or a polycyclic group of Ra'^3 in general formula (a1-r-1).

In general formula (a1-r2-3), examples of the aromatic hydrocarbon group for Ra^{04} include a group obtained by removing one or more hydrogen atoms from an aromatic hydrocarbon ring having 5 to 30 carbon atoms. Among these examples, Ra^{04} is preferably a group obtained by removing one or more hydrogen atoms from an aromatic hydrocarbon ring having 6 to 15 carbon atoms, a group obtained by removing one or more hydrogen atoms from benzene, naphthalene, anthracene, or phenanthrene is further preferable, a group obtained by removing one or more hydrogen atoms from benzene, naphthalene, or anthracene is still further preferable, a group obtained by removing one or more hydrogen atoms from benzene and naphthalene is particularly preferable, and a group obtained by removing one or more hydrogen atoms from benzene is most preferable.

[0073]

Examples of the substituent that Ra^{04} in general formula (a1-r2-3) may have include a methyl group, an ethyl group, a propyl group, a hydroxyl group, a carboxyl group, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, or the like), an alkoxy group (a methoxy group, an ethoxy group, a propoxy group, a butoxy group, or the like), and an alkylxycarbonyl group.

[0074]

In general formula (a1-r2-4), Ra'^{12} and Ra'^{13} each independently represent a monovalent chain saturated hydrocarbon group having 1 to 10 carbon atoms or a hydrogen atom. With respect to Ra'^{12} and Ra'^{13} , examples of the monovalent chain saturated hydrocarbon group having 1 to 10 carbon atoms include the same monovalent chain saturated hydrocarbon group having 1 to 10 carbon atoms as that for Ra^{01} to Ra^{03} , provided that part or all of the hydrogen atoms of the saturated hydrocarbon group may be substituted;

Among these examples, as Ra'^{12} and Ra'^{13} , a hydrogen atom and an alkyl group having 1 to 5 carbon atoms are preferable, an alkyl group having 1 to 5 carbon atoms is further preferable, a methyl group and an ethyl group are still further preferable, and a methyl group is particularly preferable.

In the case where the chain saturated hydrocarbon group represented by Ra'^{12} and Ra'^{13} is substituted, examples of the substituent include the same group as that of Ra^{05} .

[0075]

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

5 [0076]

The linear alkyl group for 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 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
10 preferable, and a methyl group or an ethyl group is more preferable.

[0077]

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

[0078]

In the 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 polycyclic or monocyclic.

20 As the monocyclic aliphatic hydrocarbon group, a group in which 1 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 polycyclic aliphatic hydrocarbon group, a group in which 1 hydrogen atom
25 has been removed from a polycycloalkane is preferable, and the polycyclic group preferably has 7 to 12 carbon atoms. Examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane and tetracyclododecane.

[0079]

Examples of the aromatic hydrocarbon group for Ra'^{14} include the same aromatic
30 hydrocarbon groups as those described above for Ra^{04} . Among these examples, Ra'^{14} is preferably a group formed by removing one or more hydrogen atoms from an aromatic hydrocarbon ring having 6 to 15 carbon atoms, more preferably a group formed by removing one or more hydrogen atoms from benzene, naphthalene, anthracene, or

phenanthrene, still more preferably a group formed by removing one or more hydrogen atoms from benzene, naphthalene, or anthracene, still more preferably a group formed by removing one or more hydrogen atoms from naphthalene or anthracene, and most preferably a group formed by removing one or more hydrogen atoms from naphthalene.

- 5 Examples of the substituent that Ra'^{14} may have include the same group as the substituent that Ra^{04} may have.

[0080]

- 10 In the case where Ra'^{14} in general formula (a1-r2-4) is a naphthyl group, a position which is bonded to a tertiary carbon atom in general formula (a1-r2-4) may be 1-position and 2-position of the naphthyl group.

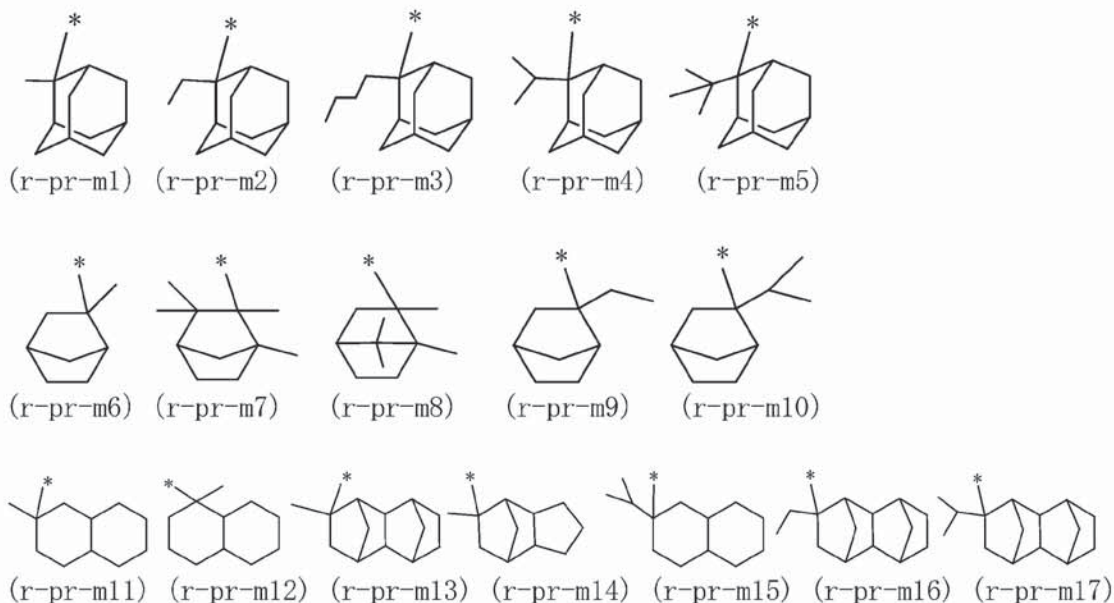
In the case where Ra'^{14} in general formula (a1-r2-4) is an anthryl group, a position which is bonded to a tertiary carbon atom in general formula (a1-r2-4) may be any one of 1-position, 2-position, and 9-position of the anthryl group.

[0081]

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

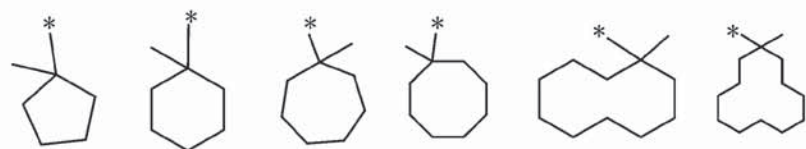
[0082]

[Chemical Formula 7]

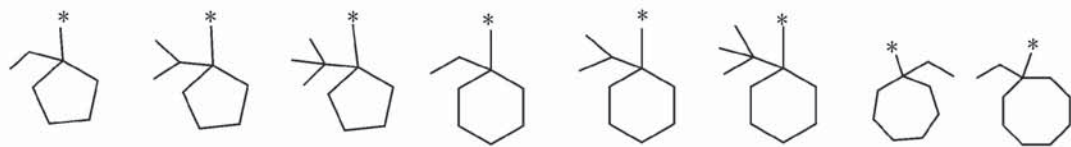


[0083]

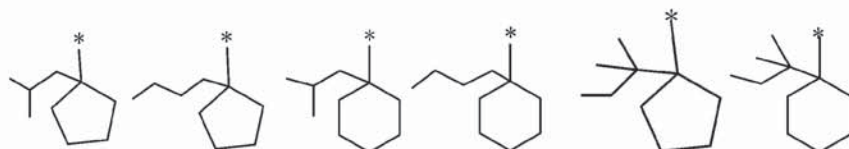
[Chemical Formula 8]



(r-pr-s1) (r-pr-s2) (r-pr-s3) (r-pr-s4) (r-pr-s5) (r-pr-s6)



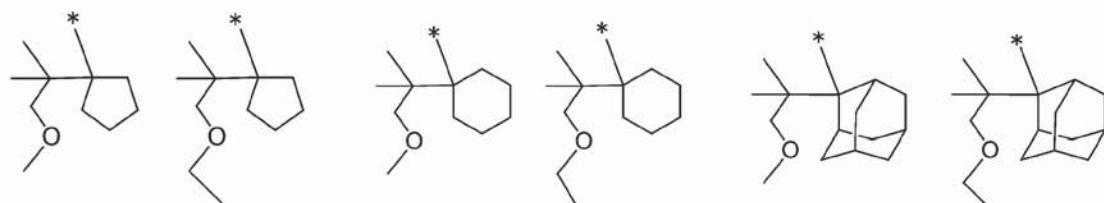
(r-pr-s7) (r-pr-s8) (r-pr-s9) (r-pr-s10) (r-pr-s11) (r-pr-s12) (r-pr-s13) (r-pr-s14)



(r-pr-s15) (r-pr-s16) (r-pr-s17) (r-pr-s18) (r-pr-s19) (r-pr-s20)

[0084]

[Chemical Formula 9]



(r-pr-sp1) (r-pr-sp2) (r-pr-sp3) (r-pr-sp4) (r-pr-mp1) (r-pr-mp2)

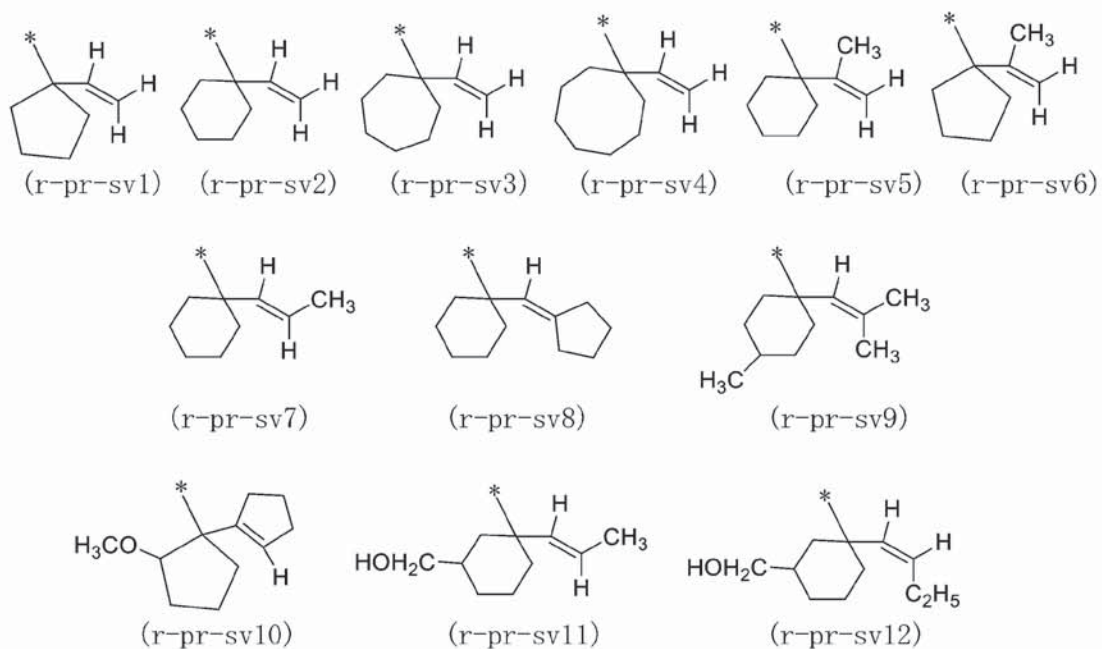
5

[0085]

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

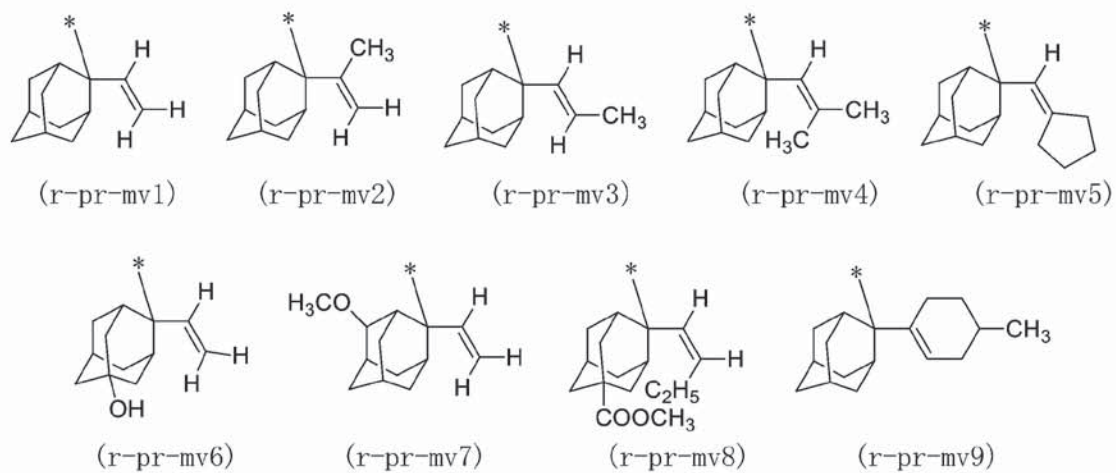
[0086]

[Chemical Formula 10]



[0087]

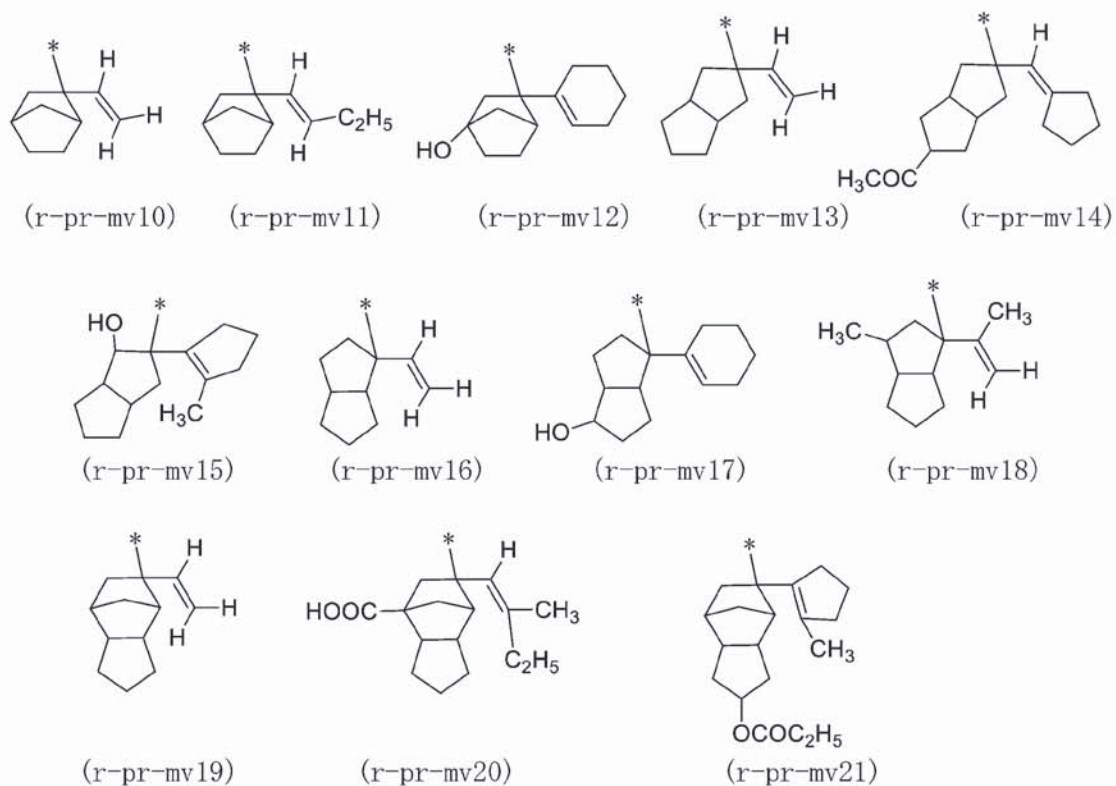
[Chemical Formula 11]



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[0088]

[Chemical Formula 12]



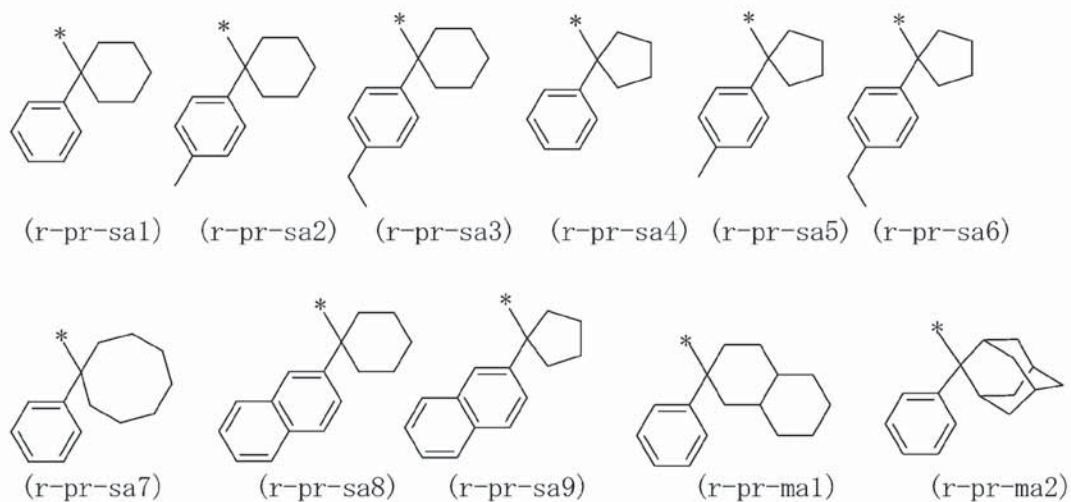
[0089]

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

5

[0090]

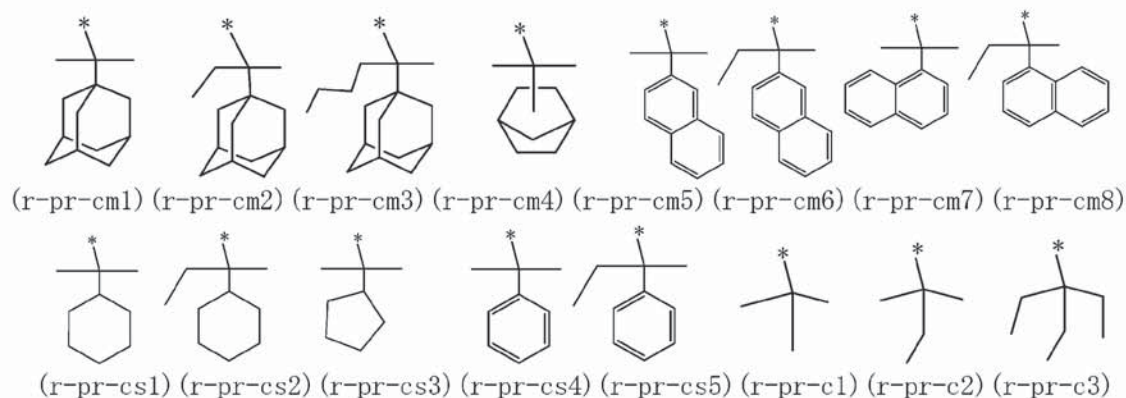
[Chemical Formula 13]



[0091]

[0092]

[Chemical Formula 14]



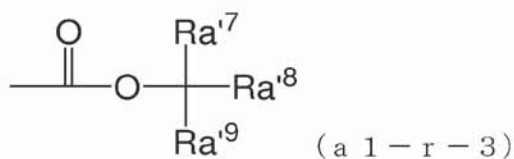
[0093]

- Tertiary alkyloxycarbonyl acid dissociable group

Examples of the acid dissociable group for protecting a hydroxy group as a polar group include the acid dissociable group represented by general formula (a1-r-3) shown below (hereafter, for convenience, referred to as "tertiary alkyloxycarbonyl-type acid dissociable group").

[0094]

[Chemical Formula 15]



15 In the formula, Ra'⁷ to Ra'⁹ each independently represents an alkyl group.

[0095]

In formula (a1-r-3), each of Ra⁷ to Ra⁹ is preferably 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 the alkyl groups is preferably 3 to 7, more preferably 3 to 5, and still more preferably 3 or 4.

[0096]

As the structural unit (a1), in terms of suppressing deterioration of light transmittance of the thick-film resist film, a structural unit containing an acid dissociable

group represented by the aforementioned general formula (a1-r-2) is preferable, and a structural unit containing an acid dissociable group represented by the aforementioned general formula (a1-r2-4) is more preferable. In the aforementioned general formula (a1-r2-4), Ra'¹² and Ra'¹³ each independently represents preferably 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 most preferably a methyl group. In the aforementioned general formula (a1-r2-4), Ra'¹⁴ represents preferably 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 most preferably a methyl group.

10 [0097]

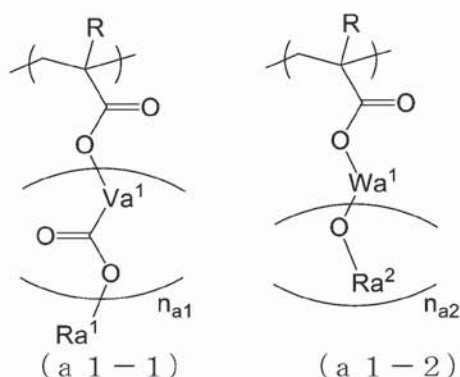
Examples of the structural unit (a1) include a structural unit derived from an acrylate ester which may have the hydrogen atom bonded to the carbon atom on the α -position substituted with a substituent; a structural unit derived from an acrylamide; a structural unit derived from hydroxystyrene or a hydroxystyrene derivative in which at least a part of the hydrogen atom of the hydroxy group is protected with a substituent containing an acid decomposable group; and a structural unit derived from vinylbenzoic acid or a vinylbenzoic acid derivative in which at least a part of the hydrogen atom within -C(=O)-OH is protected with a substituent containing an acid decomposable group.

[0098]

20 As the structural unit (a1), a structural unit derived from an acrylate ester which may have the hydrogen atom bonded to the carbon atom on the α -position substituted with a substituent is preferable. Specific examples of preferable structural units for the structural unit (a1) include structural units represented by general formula (a1-1) or (a1-2) shown below.

25 [0099]

[Chemical Formula 16]



In the formula, R represents a hydrogen atom, an alkyl group of 1 to 5 carbon atoms or a halogenated alkyl group of 1 to 5 carbon atoms; Va¹ represents a divalent hydrocarbon group optionally having an ether bond; n_{a1} represents an integer of 0 to 2; Ra¹ represents an acid dissociable group represented by the aforementioned formula(a1-r-1) or (a1-r-2);

5 Wa¹ represents a hydrocarbon group having a valency of n_{a2} + 1; n_{a2} represents an integer of 1 to 3; and Ra² represents an acid dissociable group represented by the aforementioned general formula (a1-r-1) or (a1-r-3).

[0100]

10 In the aforementioned formula (a1-1), as the alkyl group of 1 to 5 carbon atoms for R, a linear or branched alkyl group of 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 of 1 to 5 carbon atoms

15 represented by R is a group in which part or all of the hydrogen atoms of the aforementioned alkyl group 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 desirable.

As R, a hydrogen atom, an alkyl group of 1 to 5 carbon atoms or a fluorinated

20 alkyl group of 1 to 5 carbon atoms is preferable, and a hydrogen atom or a methyl group is particularly desirable in terms of industrial availability.

[0101]

In formula (a1-1), the divalent hydrocarbon group for V¹ may be either an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

[0102]

The aliphatic hydrocarbon group as the divalent hydrocarbon group for Va¹ may

be either saturated or unsaturated. In general, the aliphatic hydrocarbon group is preferably saturated.

As specific examples of the aliphatic hydrocarbon group, a linear or branched aliphatic hydrocarbon group, and an aliphatic hydrocarbon group containing a ring in the structure thereof can be given.

[0103]

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. As the linear aliphatic hydrocarbon group, a linear alkylene group is preferable. 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 preferably has 2 to 10 carbon atoms, more preferably 3 to 6, still more preferably 3 or 4, and most preferably 3. As the branched aliphatic hydrocarbon group, branched alkylene groups are preferred, and specific examples include various alkylalkylene groups, including 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 within the alkylalkylene group, a linear alkyl group of 1 to 5 carbon atoms is preferable.

[0104]

As examples of the hydrocarbon group containing a ring in the structure thereof, 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 hydrocarbon group is bonded to the terminal of the aforementioned chain-like aliphatic hydrocarbon group, and a group in which the alicyclic group is interposed within the aforementioned linear or branched aliphatic hydrocarbon group, can be given. The linear or branched aliphatic hydrocarbon group is the same as defined for the aforementioned linear aliphatic hydrocarbon group or the aforementioned 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 either a monocyclic group or a polycyclic group. As the monocyclic aliphatic hydrocarbon group, a group in which 2 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 group, a group in which two hydrogen atoms have been removed from a polycycloalkane is preferable, and the polycyclic group preferably has 7 to 12 carbon atoms. Examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane and tetracyclododecane.

[0105]

The aromatic hydrocarbon group as the divalent hydrocarbon group for Va^1 is a hydrocarbon group having an aromatic ring.

The aromatic hydrocarbon group preferably has 3 to 30 carbon atoms, more preferably 5 to 30, still more preferably 5 to 20, still more preferably 6 to 15, and most preferably 6 to 12. Here, the number of carbon atoms within a substituent(s) is not included in the number of carbon atoms of the aromatic hydrocarbon group. Examples of the aromatic ring contained in the aromatic hydrocarbon group include aromatic hydrocarbon rings, such as benzene, biphenyl, fluorene, naphthalene, anthracene and phenanthrene; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic hydrocarbon rings has been substituted with a hetero atom. Examples of the hetero atom within the aromatic hetero rings include an oxygen atom, a sulfur atom and a nitrogen atom.

Specific examples of the aromatic hydrocarbon group include a group in which two hydrogen atoms have been removed from the aforementioned aromatic hydrocarbon ring (arylene group); and a group in which one hydrogen atom has been removed from the aforementioned aromatic hydrocarbon ring (aryl group) and one hydrogen atom has been substituted with an alkylene 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 (alkyl chain within the arylalkyl group) preferably has 1 to 4 carbon atom, more preferably 1 or 2, and most preferably 1.

[0106]

In formula (a1-1), Ra^1 represents an acid dissociable group represented by the aforementioned formula (a1-r-1) or (a1-r-2).

[0107]

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

[0108]

In the aforementioned formula (a1-2), the hydrocarbon group for Wa^1 having a
 5 valency of $n_{a2}+1$ may be either an aliphatic hydrocarbon group or an aromatic hydrocarbon group. The aliphatic cyclic group refers to a hydrocarbon group that has no aromaticity, and may be either saturated or unsaturated, but is preferably 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
 10 of the linear or branched aliphatic hydrocarbon group and the aliphatic hydrocarbon group containing a ring in the structure thereof. The valency of $n_{a2}+1$ is preferably divalent, trivalent or tetravalent, and divalent or trivalent is more preferable.

[0109]

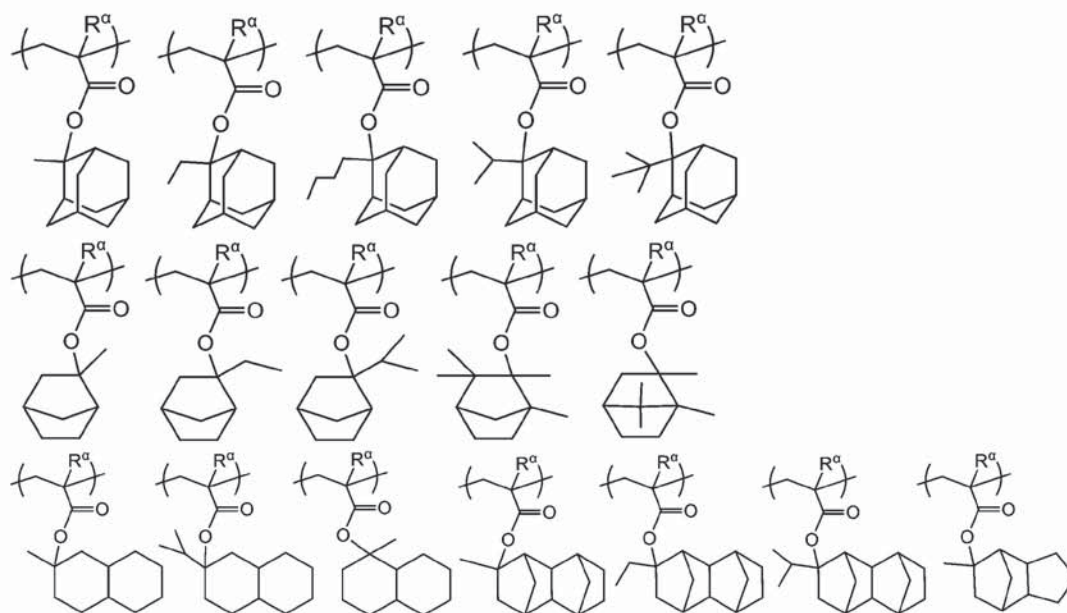
In formula (a1-2), Ra^2 represents an acid dissociable group represented by the
 15 aforementioned formula (a1-r-1) or (a1-r-3).

[0110]

Specific examples of structural 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.

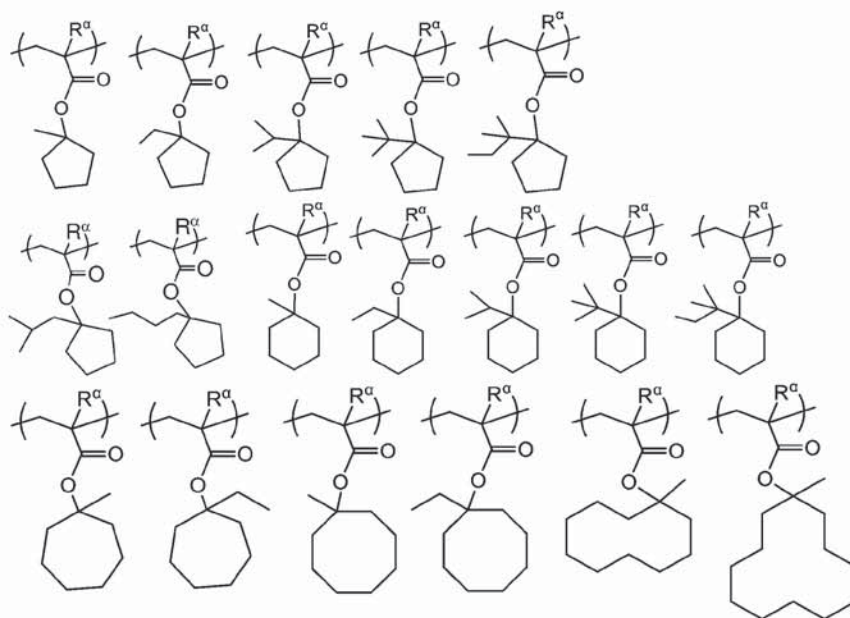
20 [0111]

[Chemical Formula 17]



[0112]

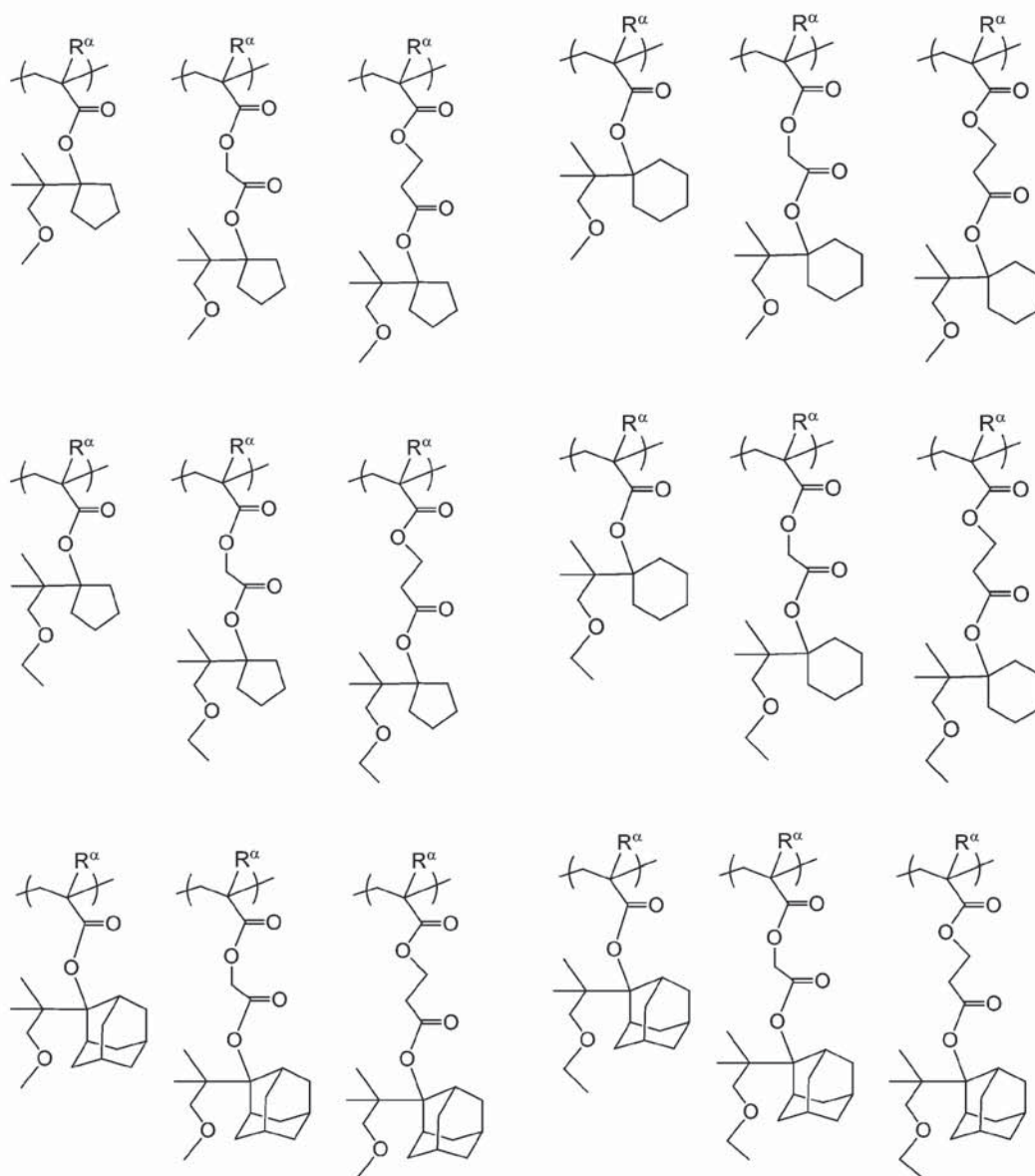
[Chemical Formula 18]



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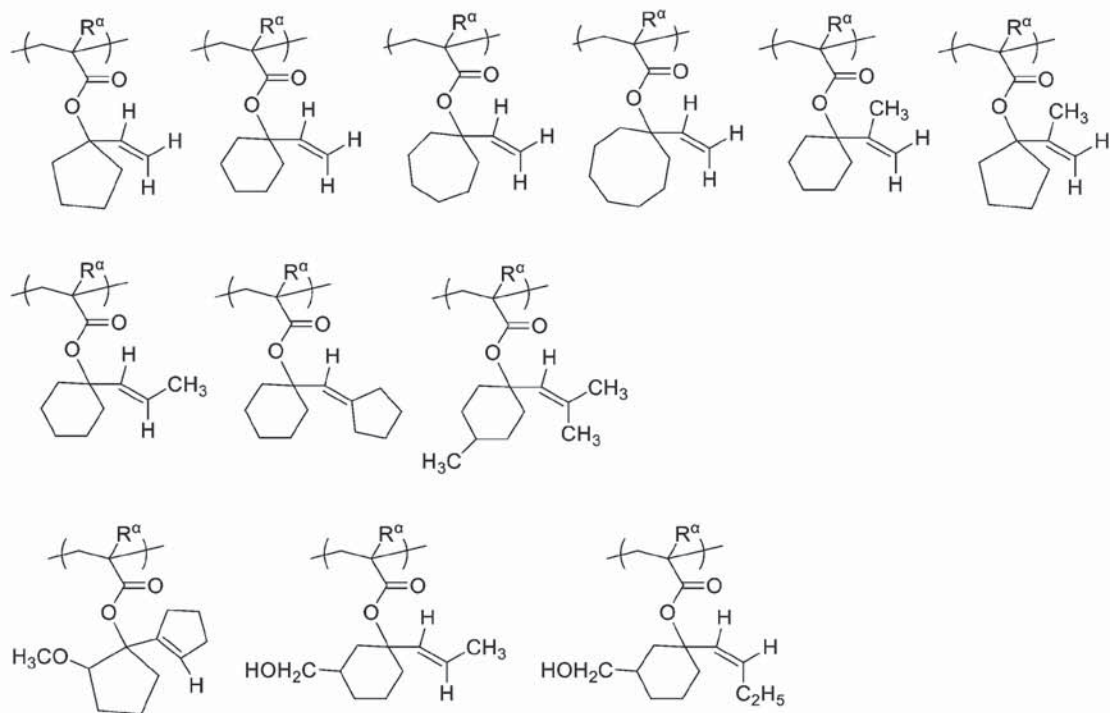
[0113]

[Chemical Formula 19]



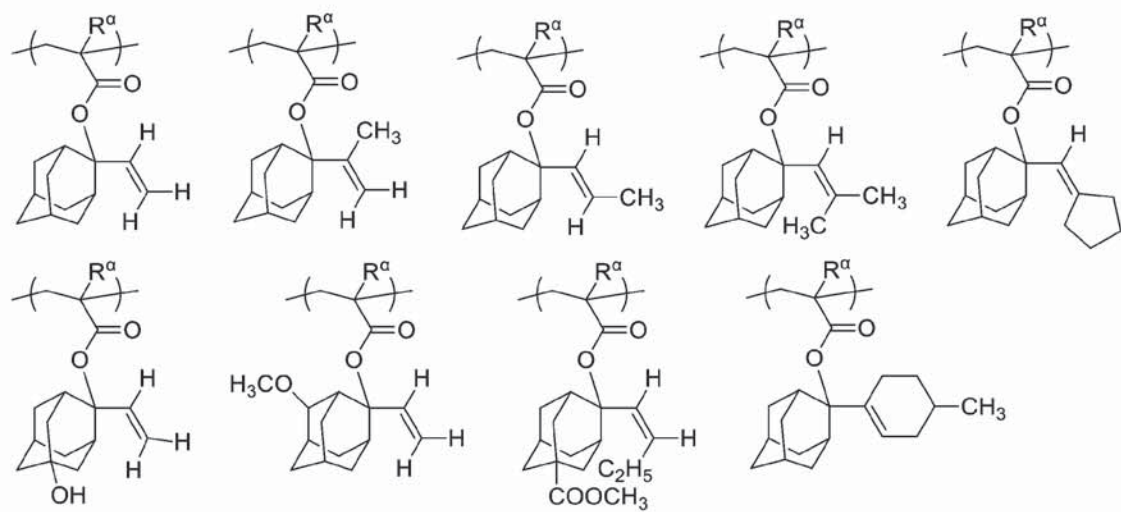
[0114]

[Chemical Formula 20]



[0115]

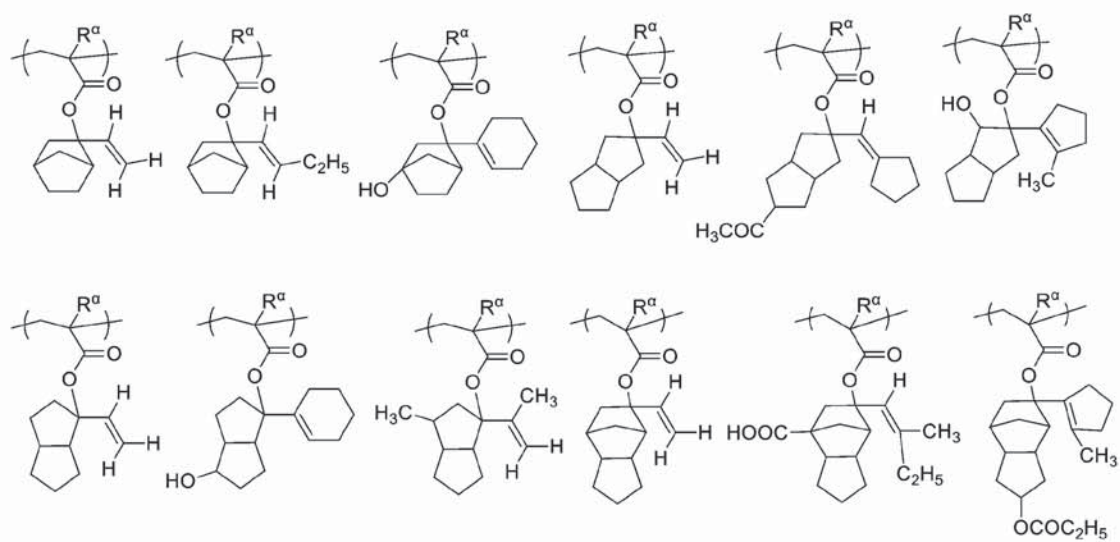
[Chemical Formula 21]



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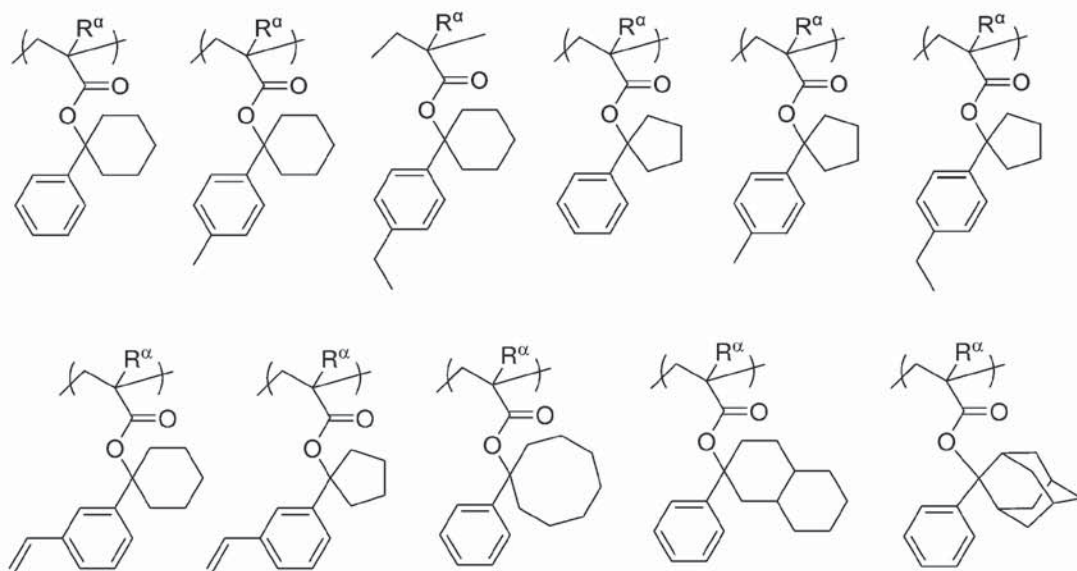
[0116]

[Chemical Formula 22]



[0117]

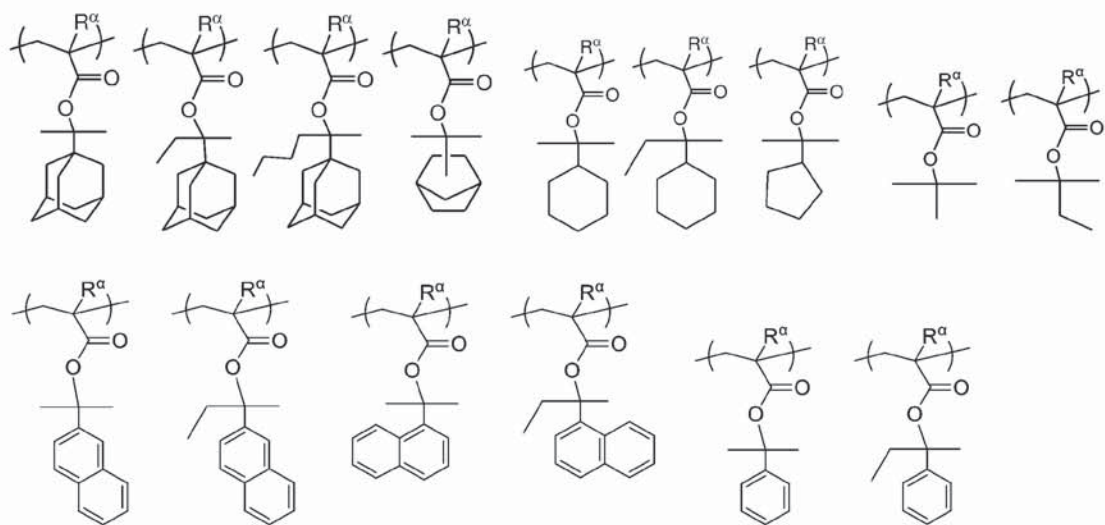
[Chemical Formula 23]



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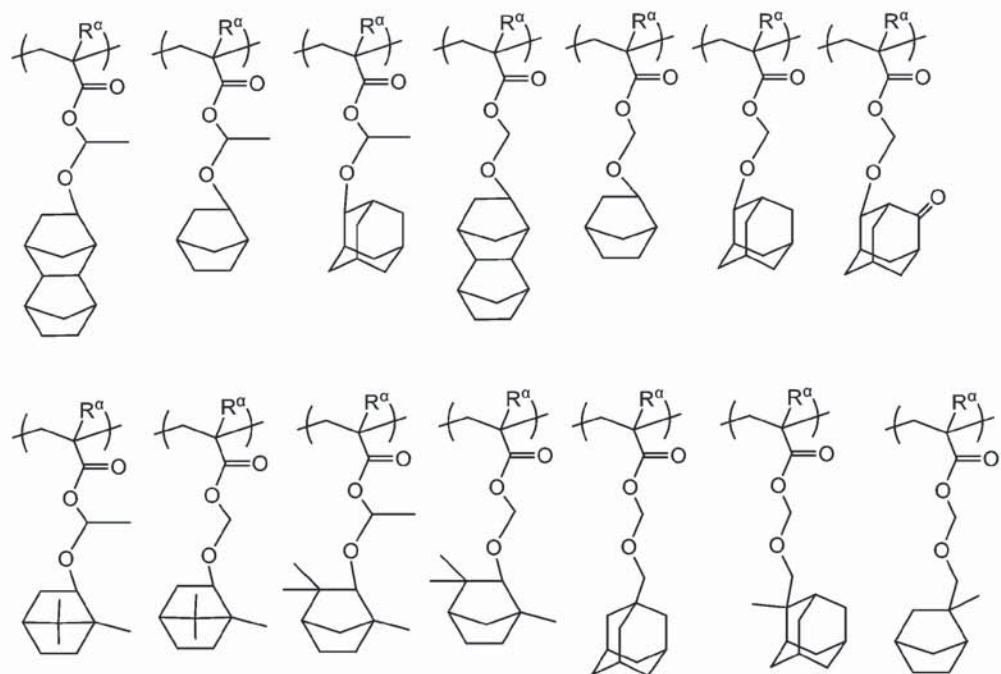
[0118]

[Chemical Formula 24]



[0119]

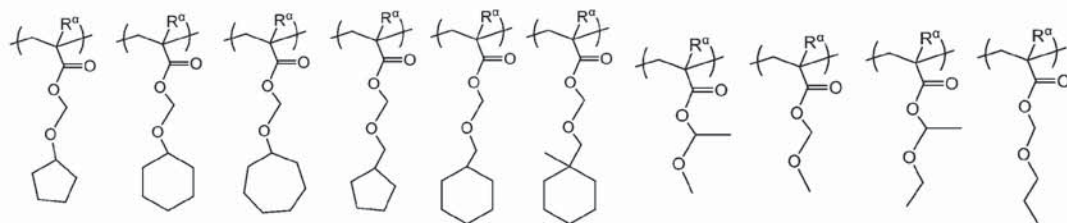
[Chemical Formula 25]



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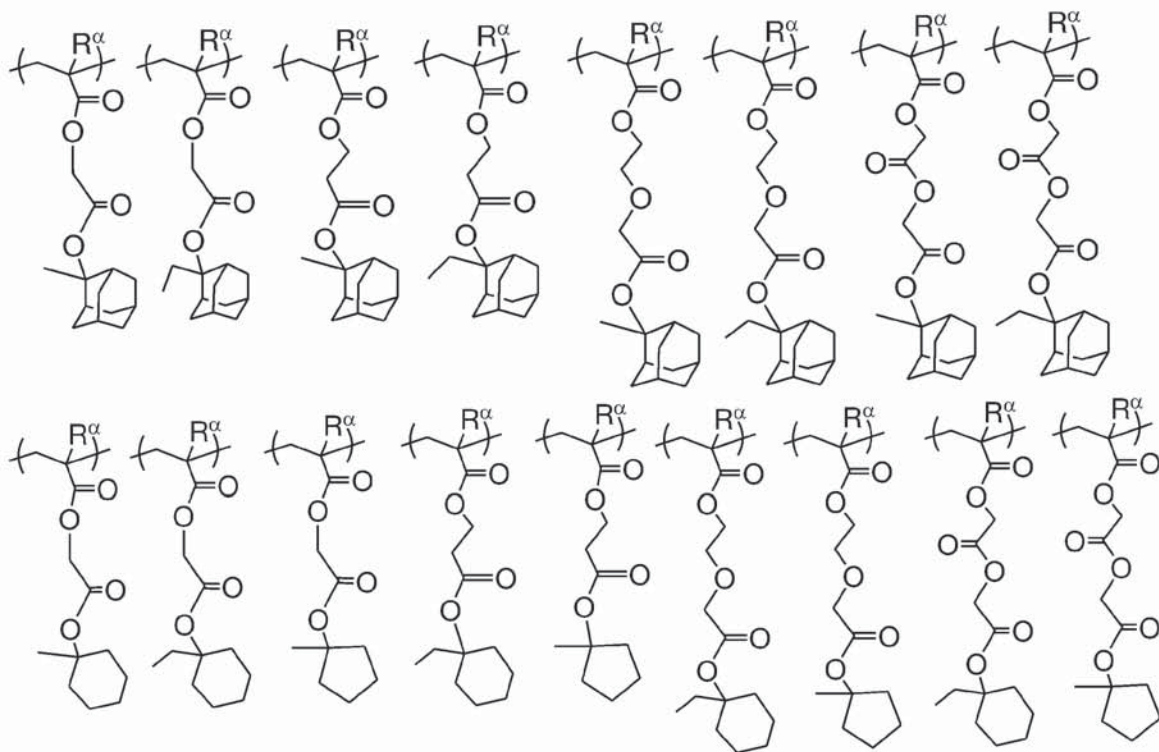
[0120]

[Chemical Formula 26]



[0121]

[Chemical Formula 27]



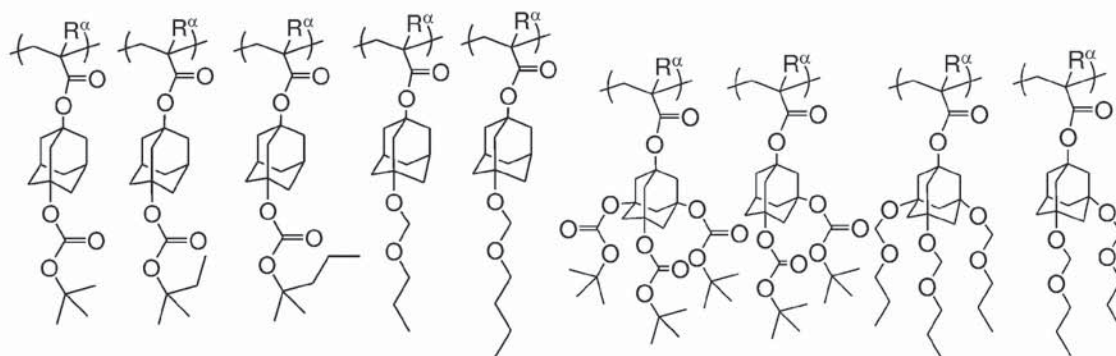
5

[0122]

Specific examples of structural unit represented by formula (a1-2) are shown below.

[0123]

[Chemical Formula 28]



[0124]

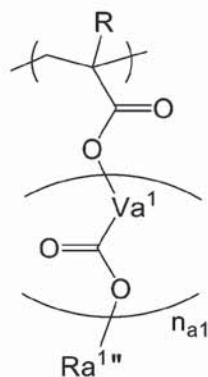
As the structural unit (a1) contained in the component (A1), 1 type of structural unit may be used, or 2 or more types may be used.

- 5 From the viewpoint that the properties of the lithography (sensitivity, shape, and the like) by electron beam and EUV are more likely to be enhanced, the structural unit (a1) is further preferably a structural unit represented by general formula (a1-1).

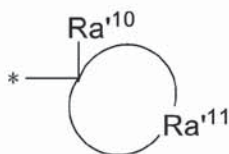
Among these examples, as the structural unit (a1), a structural unit represented by general formula (a1-1-1) is particularly preferable.

10 [0125]

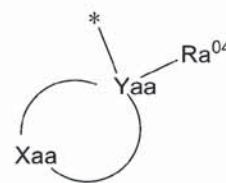
[Chemical Formula 29]



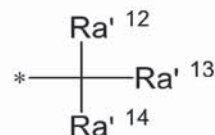
(a1-1-1)



(a1-r2-1)



(a1-r2-3)



(a1-r2-4)

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

15 [0126]

In general formula (a1-1-1), R , Va^1 and n_{a1} are the same as defined for R , Va^1 and n_{a1} in general formula (a1-1).

The description of the acid dissociable group represented by general formula (a1-r2-1), (a1-r2-3), or (a1-r2-4) is the same as described above. In terms of maintaining the transparency of the thick-film resist film, Ra^{1'} is preferably an acid dissociable group represented by the aforementioned general formula (a1-r2-4). In general formula
 5 (a1-r2-4), preferable examples of Ra^{'12}, Ra^{'13} and Ra^{'14} are the same as described above.

[0127]

In the component (A1), the amount of the structural unit (a1) based on the combined total (100 mol%) of all structural units constituting the component (A1) is preferably 5 to 80 mol%, more preferably 10 to 75 mol%, still more preferably 15 to 70
 10 mol%, and most preferably 20 to 60 mol%.

When the amount of the structural unit (a1) is at least as large as the lower limit of the above-mentioned preferable range, various lithography properties such as sensitivity, resolution and roughness may be improved. On the other hand, when the amount of the structural unit (a1) is no more than the upper limit of the above-mentioned preferable range,
 15 a good balance may be achieved with the other structural units, and the lithography properties may be improved.

[0128]

<<Other structural units>>

If desired, the component (A1) may include, in addition to the structural unit (a1),
 20 any other structural unit.

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

[0129]

Structural unit (a2):

The component (A1) may have, in addition to the structural unit (a1), a structural
 30 unit (a2) containing a lactone-containing cyclic group, an -SO₂- containing cyclic group or a carbonate-containing cyclic group (provided that structural units which fall under the definition of the structural unit (a1) are excluded).

When the component (A1) is used for forming a resist film, the lactone-containing

cyclic group, the $-\text{SO}_2-$ containing cyclic group or the carbonate-containing cyclic group within the structural unit (a2) is effective in improving the adhesion between the resist film and the substrate. In addition, by virtue of containing the structural unit (a2), for example, the acid diffusion length is appropriately adjusted, the adhesion of the resist film to the substrate is enhanced, or the solubility during development is appropriately adjusted. As a result, the lithography properties are enhanced.

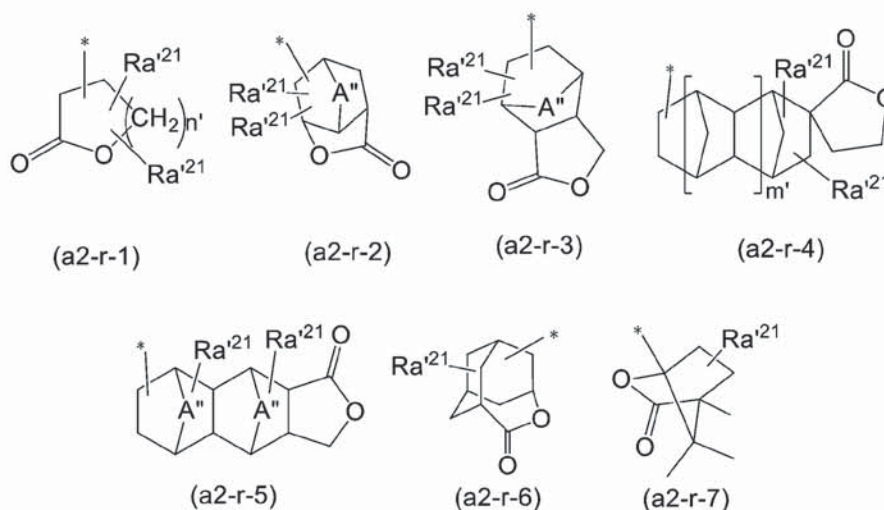
[0130]

The term “lactone-containing cyclic group” refers to a cyclic group including a ring containing a $-\text{O}-\text{C}(=\text{O})-$ structure (lactone ring). The term “lactone ring” refers to a single ring containing a $-\text{O}-\text{C}(=\text{O})-$ structure, and this ring is counted as the first ring. A lactone-containing cyclic group in which the only ring structure is the lactone ring is referred to as a monocyclic group, and groups containing other ring structures are described as polycyclic groups regardless of the structure of the other rings. The lactone-containing cyclic group may be either a monocyclic group or a polycyclic group.

The lactone-containing cyclic group for the structural unit (a2) is not particularly limited, and an arbitrary structural unit may be used. Specific examples include groups represented by general formulae (a2-r-1) to (a2-r-7) shown below.

[0131]

[Chemical Formula 30]



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 hydroxy group, $-\text{COOR}''$, $-\text{OC}(=\text{O})\text{R}''$, 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 an $-\text{SO}_2-$ containing cyclic group; A'' represents an oxygen atom ($-\text{O}-$), a sulfur atom ($-\text{S}-$) or an alkylene group of 1 to 5 carbon atoms which may contain an oxygen atom or a sulfur atom; n' represents an integer of 0 to 2; and m' represents 0 or 1.

5 [0132]

In formulae (a2-r-1) to (a2-r-7), the alkyl group for Ra'^{21} is preferably an alkyl group of 1 to 6 carbon atoms. Further, the alkyl group is preferably a linear alkyl group or a branched alkyl group. Specific examples 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 desirable.

The alkoxy group for Ra'^{21} is preferably an alkoxy group of 1 to 6 carbon atoms. Further, the alkoxy group is preferably a linear or branched alkoxy group. Specific examples of the alkoxy groups include the aforementioned alkyl groups for Ra'^{21} having an oxygen atom ($-\text{O}-$) bonded thereto.

As examples of the halogen atom for Ra'^{21} , a fluorine atom, chlorine atom, bromine atom and iodine atom can be given. Among these, a fluorine atom is preferable.

Examples of the halogenated alkyl group for Ra'^{21} include groups in which part or all of the hydrogen atoms within the aforementioned alkyl group for Ra'^{21} has been substituted with the aforementioned halogen atoms. As the halogenated alkyl group, a fluorinated alkyl group is preferable, and a perfluoroalkyl group is particularly desirable.

[0133]

With respect to $-\text{COOR}''$ and $-\text{OC}(=\text{O})\text{R}''$ for Ra'^{21} , R'' represents a hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group or an $-\text{SO}_2-$ containing cyclic group.

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

When R'' represents a linear or branched alkyl group, it is preferably an alkyl group of 1 to 10 carbon atoms, more preferably an alkyl group of 1 to 5 carbon atoms, and most preferably a methyl group or an ethyl group.

When R'' is a cyclic alkyl group (cycloalkyl group), it preferably has 3 to 15 carbon atoms, more preferably 4 to 12 carbon atoms, and most preferably 5 to 10 carbon atoms. Specific examples include groups in which one or more hydrogen atoms have been

removed from a monocycloalkane or a polycycloalkane such as a bicycloalkane, tricycloalkane or tetracycloalkane which may or may not be substituted with a fluorine atom or a fluorinated alkyl group. Specific examples 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.

Examples of the lactone-containing cyclic group for R'' include groups represented by the aforementioned general formulae (a2-r-1) to (a2-r-7).

The carbonate-containing cyclic group for R'' is the same as defined for the carbonate-containing cyclic group described later. Specific examples of the carbonate-containing cyclic group include groups represented by general formulae (ax3-r-1) to (ax3-r-3).

The -SO₂- containing cyclic group for R'' is the same as defined for the -SO₂- containing cyclic group described later. Specific examples of the -SO₂- containing cyclic group include groups represented by general formulae (a5-r-1) to (a5-r-4).

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

[0134]

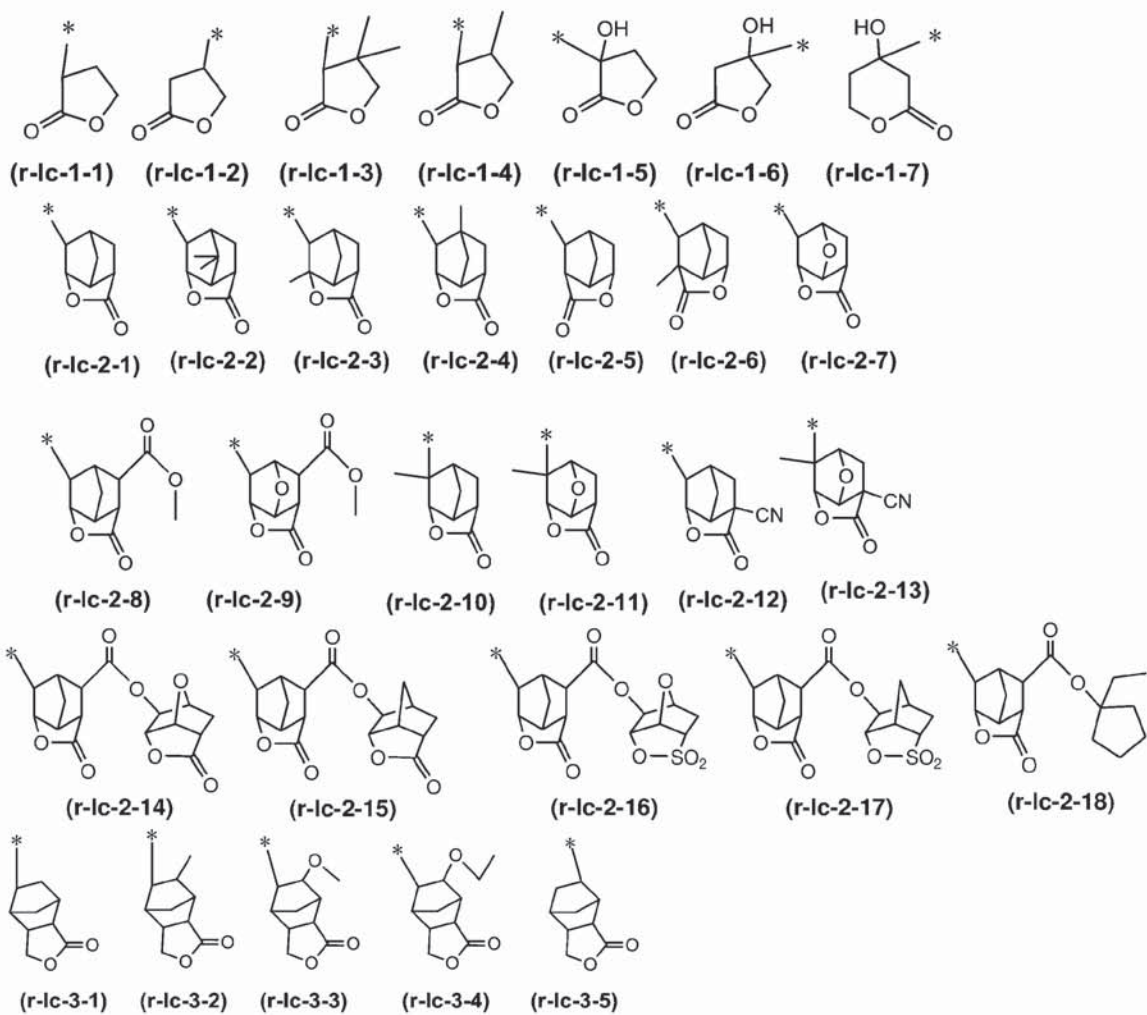
In formulae (a2-r-2), (a2-r-3) and (a2-r-5), as the alkylene group of 1 to 5 carbon atoms represented by A'', a linear or branched alkylene group is preferable, and examples thereof include a methylene group, an ethylene group, an n-propylene group and an isopropylene group. Examples of alkylene groups that contain an oxygen atom or a sulfur atom include the aforementioned alkylene groups in which -O- or -S- is bonded to the terminal of the alkylene group or present between the carbon atoms of the alkylene group. Specific examples of such alkylene groups include O-CH₂-, -CH₂-O-CH₂-, -S-CH₂-, and -CH₂-S-CH₂-. As A'', an alkylene group of 1 to 5 carbon atoms or -O- is preferable, more preferably an alkylene group of 1 to 5 carbon atoms, and most preferably a methylene group.

[0135]

Specific examples of the groups represented by the aforementioned general formulae (a2-r-1) to (a2-r-7) are shown below.

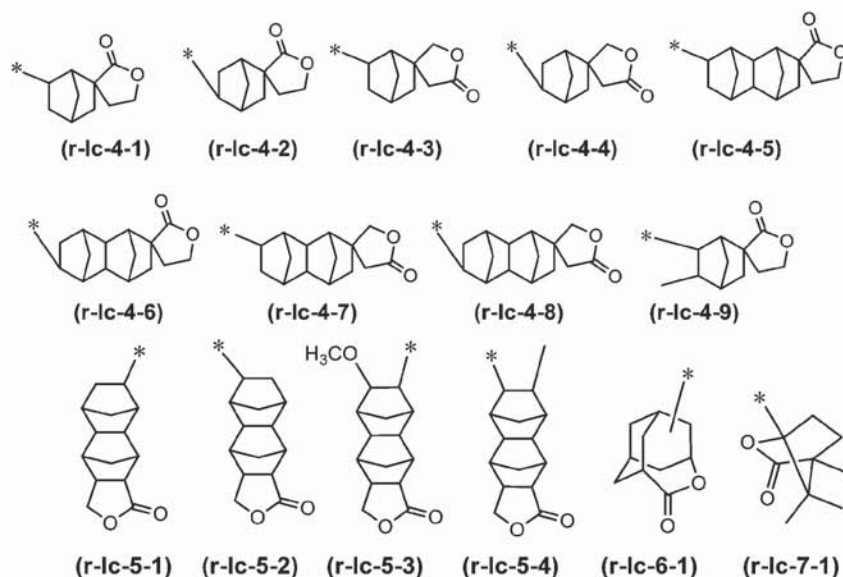
[0136]

[Chemical Formula 31]



[0137]

[Chemical Formula 32]



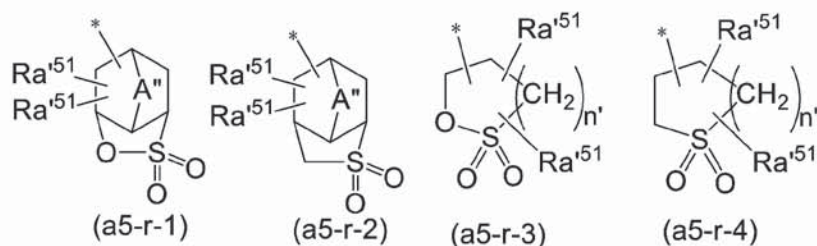
[0138]

An "-SO₂- containing cyclic group" refers to a cyclic group having a ring containing -SO₂- within the ring structure thereof, i.e., a cyclic group in which the sulfur atom (S) within -SO₂- forms part of the ring skeleton of the cyclic group. The ring containing -SO₂- within the ring skeleton thereof is counted as the first ring. A cyclic group in which the only ring structure is the ring that contains -SO₂- in the ring skeleton thereof is referred to as a monocyclic group, and a group containing other ring structures is described as a polycyclic group regardless of the structure of the other rings. The -SO₂- containing cyclic group may be either a monocyclic group or a polycyclic group. As the -SO₂- containing cyclic group, a cyclic group containing -O-SO₂- within the ring skeleton thereof, i.e., a cyclic group containing a sultone ring in which -O-S- within the -O-SO₂- group forms part of the ring skeleton thereof is particularly desirable.

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

[0139]

[Chemical Formula 33]



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 hydroxy 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 an $-SO_2-$ containing cyclic group; A'' represents an oxygen atom, a sulfur atom or an alkylene group of 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]

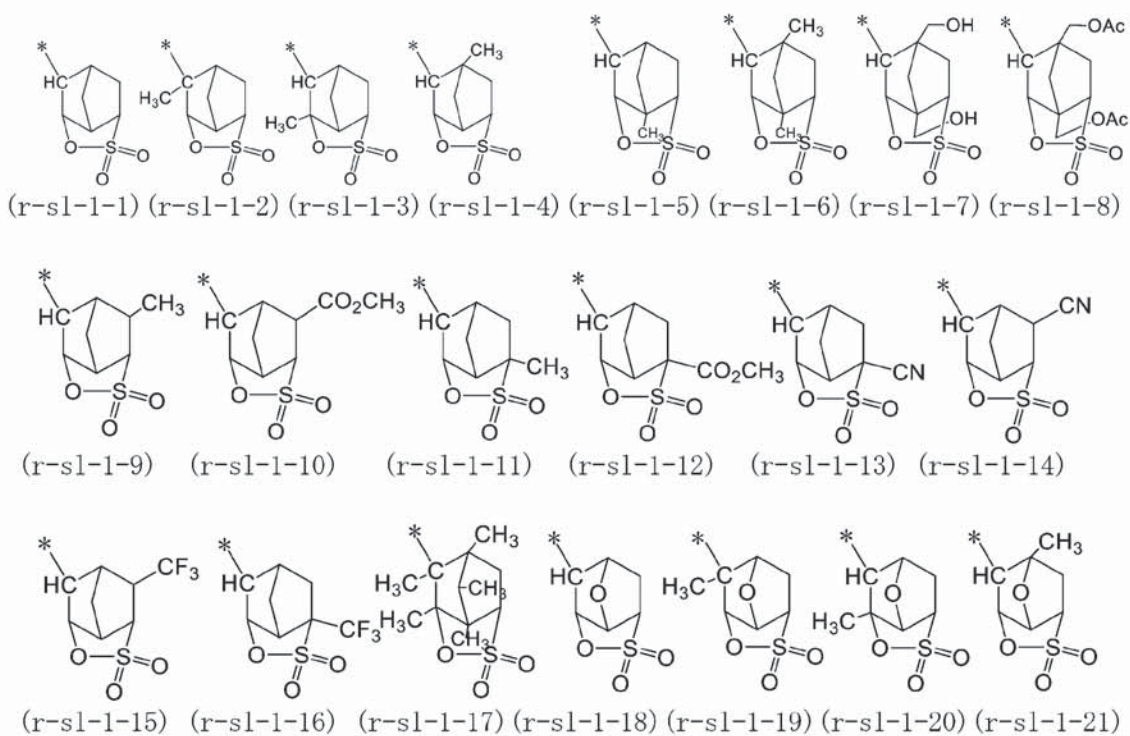
In general formulae (a5-r-1) and (a5-r-2), A'' is the same as defined for A'' in general formulae (a2-r-2), (a2-r-3) and (a2-r-5).

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

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

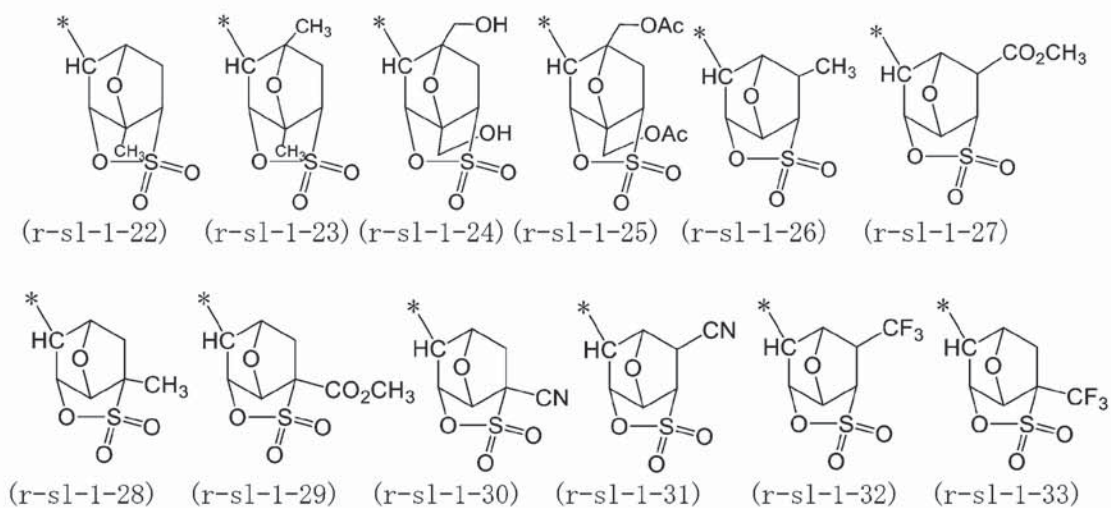
[0141]

[Chemical Formula 34]



[0142]

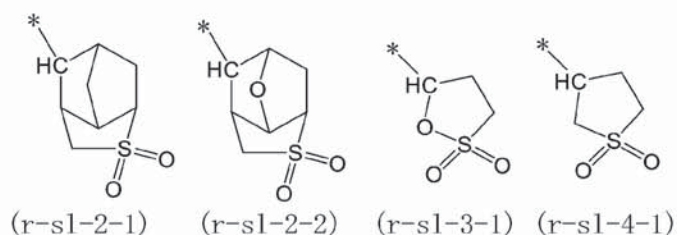
[Chemical Formula 35]



5

[0143]

[Chemical Formula 36]



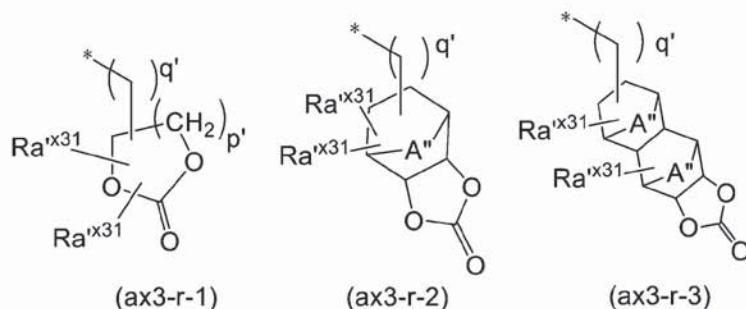
[0144]

The term “carbonate-containing cyclic group” refers to a cyclic group including a ring containing a $-\text{O}-\text{C}(=\text{O})-\text{O}-$ structure (carbonate ring). The term “carbonate ring” refers to a single ring containing a $-\text{O}-\text{C}(=\text{O})-\text{O}-$ structure, and this ring is counted as the first ring. A carbonate-containing cyclic group in which the only ring structure is the carbonate ring is referred to as a monocyclic group, and groups containing other ring structures are described as polycyclic groups regardless of the structure of the other rings. The carbonate-containing cyclic group may be either a monocyclic group or a polycyclic group.

The carbonate-containing cyclic group is not particularly limited, and an arbitrary group may be used. Specific examples include groups represented by general formulae (ax3-r-1) to (ax3-r-3) shown below.

[0145]

[Chemical Formula 37]



In the formulae, each Ra^{x31} independently represents a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxy group, $-\text{COOR}''$, $-\text{OC}(=\text{O})\text{R}''$, 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 an $-\text{SO}_2-$ containing cyclic group; A'' represents an oxygen atom, a sulfur atom or an alkylene group of 1 to 5 carbon atoms which may contain an oxygen atom or a sulfur atom; p' represents an integer of 0 to 3; and q' represents 0 or 1.

[0146]

In general formulae (ax3-r-2) and (ax3-r-3), A'' is the same as defined for A'' in general formulae (a2-r-2), (a2-r-3) and (a2-r-5).

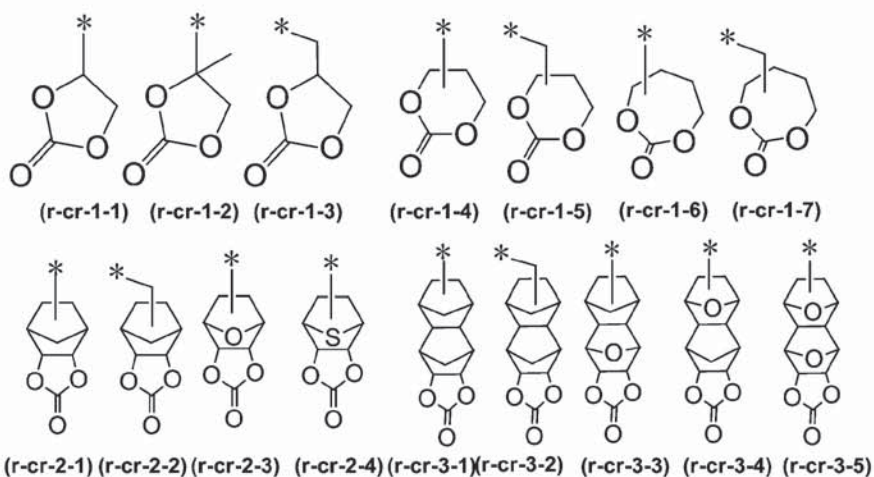
Examples of the alkyl group, alkoxy group, halogen atom, halogenated alkyl group, -COOR'', -OC(=O)R'' and hydroxyalkyl group for Ra'³¹ include the same groups as those described above in the explanation of Ra'²¹ in the general formulas (a2-r-1) to (a2-r-7).

Specific examples of the groups represented by the aforementioned general formulae (ax3-r-1) to (ax3-r-3) are shown below.

10

[0147]

[Chemical Formula 38]



[0148]

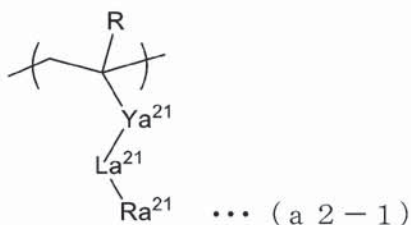
As the structural unit (a2), a structural unit derived from an acrylate ester which may have the hydrogen atom bonded to the carbon atom on the α -position substituted with a substituent is preferable.

The structural unit (a2) is preferably a structural unit represented by general formula (a2-1) shown below.

[0149]

20

[Chemical Formula 39]



In the formula, R represents a hydrogen atom, an alkyl group of 1 to 5 carbon atoms or a halogenated alkyl group of 1 to 5 carbon atoms; Ya²¹ represents a single bond or a divalent linking group; La²¹ represents -O-, -COO-, -CON(R')-, -OCO-, -CONHCO- or
 5 -CONHCS-; and R' represents a hydrogen atom or a methyl group; provided that, when La²¹ represents -O-, Ya²¹ does not represent -CO-; and Ra²¹ represents a lactone-containing cyclic group, a carbonate-containing cyclic group or an -SO₂- containing cyclic group.

[0150]

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

[0151]

15 In the formula (a2-1), the divalent linking group for Ya²¹ is not particularly limited, and preferable examples thereof include a divalent hydrocarbon group which may have a substituent and a divalent linking group containing a hetero atom.

[0152]

- Divalent hydrocarbon group which may have a substituent:

20 In the case where Ya²¹ is a divalent linking group which may have a substituent, the hydrocarbon group may be either an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

[0153]

- Aliphatic hydrocarbon group for Ya²¹

25 An "aliphatic hydrocarbon group" refers to a hydrocarbon group that has no aromaticity. The aliphatic hydrocarbon group may be saturated or unsaturated. In general, the aliphatic hydrocarbon group 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 can be given.

[0154]

- Linear or branched aliphatic hydrocarbon group

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

5 As the linear aliphatic hydrocarbon group, a linear alkylene group is preferable. 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, still more preferably 3 or 4, and most preferably 3.

As the branched aliphatic hydrocarbon group, branched alkylene groups are preferred, and specific examples include various alkylalkylene groups, including 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 15 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 within the alkylalkylene group, a linear alkyl group of 1 to 5 carbon atoms is preferable.

20 [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 of 1 to 5 carbon atoms, and a carbonyl group.

[0156]

25 - Aliphatic hydrocarbon group containing a ring in the structure thereof

As examples of the hydrocarbon group containing a ring in the structure thereof, a cyclic aliphatic hydrocarbon group containing a hetero atom in the ring structure thereof and may have a substituent (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 the aforementioned chain-like aliphatic hydrocarbon 30 group, and a group in which the cyclic aliphatic group is interposed within the aforementioned linear or branched aliphatic hydrocarbon group, can be given. As the linear or branched aliphatic hydrocarbon group, the same groups as those described above can be

used.

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 either a polycyclic group or a monocyclic group. As the monocyclic aliphatic hydrocarbon group, a group in which 2 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 group, a group in which 2 hydrogen atoms have been removed from a polycycloalkane is preferable, and the polycyclic group preferably has 7 to 12 carbon atoms. Examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane and tetracyclododecane.

[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 of 1 to 5 carbon atoms, and more preferably a methyl group, an ethyl group, a propyl group, an n-butyl group or a tert-butyl group.

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

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.

Examples of the halogenated alkyl group for the substituent include groups in which part or all of the hydrogen atoms within the aforementioned alkyl groups has been substituted with the aforementioned halogen atoms.

The cyclic aliphatic hydrocarbon group may have part of the carbon atoms constituting the ring structure thereof 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.

[0158]

- Aromatic hydrocarbon group for 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 compound having $(4n + 2)\pi$ electrons, and may be either monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, and still more preferably 6 to 15 carbon atoms, and most preferably 6 to 12 carbon atoms. Here, the number of carbon atoms within a substituent(s) is not included in the number of carbon atoms of the aromatic hydrocarbon group.

Examples of the aromatic ring include aromatic hydrocarbon rings, such as benzene, naphthalene, anthracene and phenanthrene; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic hydrocarbon rings has been substituted with a hetero atom. Examples of the hetero atom within 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 aforementioned aromatic hydrocarbon ring or aromatic hetero ring (arylene group or heteroarylene group); a group in which two hydrogen atoms have 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 aforementioned aromatic hydrocarbon ring or aromatic hetero ring has been substituted with an alkylene group (a group in which one hydrogen atom has been removed from the aryl group within the aforementioned 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, or a heteroarylalkyl group). The alkylene group which is bonded to the aforementioned aryl group or heteroaryl group preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and most preferably 1 carbon atom.

[0159]

With respect to the aromatic hydrocarbon group, the hydrogen atom within the aromatic hydrocarbon group may be substituted with a substituent. For example, the hydrogen atom bonded to the aromatic ring within 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 of 1 to 5 carbon

atoms, and more preferably a methyl group, an ethyl group, a propyl group, an n-butyl group or a tert-butyl group.

As the alkoxy group, the halogen atom and the halogenated alkyl group for the substituent, the same groups as the aforementioned substituent groups for substituting a hydrogen atom within the cyclic aliphatic hydrocarbon group can be used.

[0160]

- Divalent linking group containing a hetero atom

In the case where Y^{21} represents a divalent linking group containing a hetero atom, preferable examples of the linking group include $-O-$, $-C(=O)-O-$, $-O-C(=O)-$, $-C(=O)-$, $-O-C(=O)-O-$, $-C(=O)-NH-$, $-NH-$, $-NH-C(=NH)-$ (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 the 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, and most preferably 1 to 5.

In general formulae $-Y^{21}-O-Y^{22}-$, $-Y^{21}-O-$, $-Y^{21}-C(=O)-O-$, $-C(=O)-O-Y^{21}-$, $-[Y^{21}-C(=O)-O]_{m'}-Y^{22}-$, $-Y^{21}-O-C(=O)-Y^{22}-$ or $-Y^{21}-S(=O)_2-O-Y^{22}-$, Y^{21} and Y^{22} each independently represents a divalent hydrocarbon group which may have a substituent. Examples of the divalent hydrocarbon group include the same groups as those described above as the "divalent hydrocarbon group which may have a substituent" in the explanation of the aforementioned divalent linking group for Y^{21} .

As Y^{21} , a linear aliphatic hydrocarbon group is preferable, more preferably a linear alkylene group, still more preferably a linear alkylene group of 1 to 5 carbon atoms, and a methylene group or an ethylene group is particularly desirable.

As Y^{22} , 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 within the alkylmethylene group is preferably a linear alkyl group of 1 to 5 carbon atoms, more preferably a linear alkyl group of 1 to 3 carbon atoms, and most preferably a methyl group.

In the group represented by the formula $-\text{[Y}^{21}\text{-C(=O)-O]}_m\text{-Y}^{22}\text{-}$, m represents an integer of 0 to 3, preferably an integer of 0 to 2, more preferably 0 or 1, and most preferably 1. Namely, it is particularly desirable that the group represented by the formula $-\text{[Y}^{21}\text{-C(=O)-O]}_m\text{-Y}^{22}\text{-}$ is a group represented by the formula $-\text{Y}^{21}\text{-C(=O)-O-Y}^{22}\text{-}$. Among these, a group represented by the formula $-(\text{CH}_2)_{a'}\text{-C(=O)-O-(CH}_2)_{b'}\text{-}$ is preferable. In the formula, a' is 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' is 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.

[0161]

Among these examples, as Y^{21} , a single bond, an ester bond $[-\text{C(=O)-O-}]$, an ether bond $(-\text{O-})$, a linear or branched alkylene group, or a combination thereof is preferable.

[0162]

In the formula (a2-1), Ra^{21} represents a lactone-containing cyclic group, an $-\text{SO}_2\text{-}$ containing cyclic group or a carbonate-containing cyclic group.

Preferable examples of the lactone-containing cyclic group, the $-\text{SO}_2\text{-}$ containing cyclic group and the carbonate-containing cyclic group for Ra^{21} include groups represented by general formulae (a2-r-1) to (a2-r-7), groups represented by general formulae (a5-r-1) to (a5-r-4) and groups represented by general formulae (ax3-r-1) to (ax3-r-3).

Among the above examples, a lactone-containing cyclic group or a $-\text{SO}_2\text{-}$ containing cyclic group is preferable, and a group represented by general formula (a2-r-1), (a2-r-2), (a2-r-6) or (a5-r-1) is more preferable. Specifically, a group 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) is still more preferable.

[0163]

As the structural unit (a2) contained in the component (A1), 1 kind of structural unit may be used, or 2 or more kinds may be used.

When the component (A1) contains the structural unit (a2), the amount of the structural unit (a2) based on the combined total (100 mol%) of all structural units

constituting the component (A1) is preferably 5 to 60 mol%, more preferably 10 to 60 mol%, still more preferably 20 to 55 mol%, and most preferably 30 to 50 mol%.

When the amount of the structural unit (a2) is at least as large as the lower limit of the above preferable range, the effect of using the structural unit (a2) may be satisfactorily achieved due to the aforementioned effects. On the other hand, when the amount of the structural unit (a2) is no more than the upper limit of the above preferable range, a good balance may be achieved with the other structural units, and various lithography properties may be improved.

[0164]

10 Structural unit (a3):

The component (A1) may have, in addition to the structural unit (a1), a structural unit (a3) containing a polar group-containing aliphatic hydrocarbon group (provided that the structural units that fall under the definition of structural units (a1) and (a2) are excluded). When the component (A1) includes the structural unit (a3), the hydrophilicity of the component (A1) is enhanced, thereby contributing to improvement in resolution. Further, the acid diffusion length may be appropriately adjusted.

[0165]

Examples of the polar group include a hydroxyl group, cyano group, carboxyl group, or hydroxyalkyl group in which part of the hydrogen atoms of the alkyl group have been substituted with fluorine atoms, although a hydroxyl group is particularly desirable.

Examples of the aliphatic hydrocarbon group include linear or branched hydrocarbon groups (preferably alkylene groups) of 1 to 10 carbon atoms, and cyclic aliphatic hydrocarbon groups (cyclic groups). These cyclic groups can be selected appropriately from the multitude of groups that have been proposed for the resins of resist compositions designed for use with ArF excimer lasers.

[0166]

In the case where the cyclic group is a monocyclic group, the monocyclic group preferably has 3 to 10 carbon atoms. Of the various possibilities, structural units derived from an acrylate ester that include an aliphatic monocyclic group that contains a hydroxyl group, cyano group, carboxyl group or a hydroxyalkyl group in which part of the hydrogen atoms of the alkyl group have been substituted with fluorine atoms are particularly desirable. Examples of the monocyclic groups include groups in which two or more hydrogen atoms have been removed from a monocycloalkane. Specific examples include

groups in which two or more hydrogen atoms have been removed from a monocycloalkane such as cyclopentane, cyclohexane or cyclooctane. Of these polycyclic groups, groups in which two or more hydrogen atoms have been removed from cyclopentane or cyclohexane are preferred industrially.

5 [0167]

In the case where the cyclic group is a polycyclic group, the polycyclic group preferably has 7 to 30 carbon atoms. Of the various possibilities, structural units derived from an acrylate ester that include an aliphatic polycyclic group that contains a hydroxyl group, cyano group, carboxyl group or a hydroxyalkyl group in which part of the hydrogen
10 atoms of the alkyl group have been substituted with fluorine atoms are particularly desirable. 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 include groups in which two or more hydrogen atoms have been removed from a polycycloalkane such as adamantane, norbornane, isobornane,
15 tricyclodecane or tetracyclododecane. Of these polycyclic groups, groups in which two or more hydrogen atoms have been removed from adamantane, norbornane or tetracyclododecane are preferred industrially.

[0168]

As the structural unit (a3), there is no particular limitation as long as it is a
20 structural unit containing a polar group-containing aliphatic hydrocarbon group, and an arbitrary structural unit may be used.

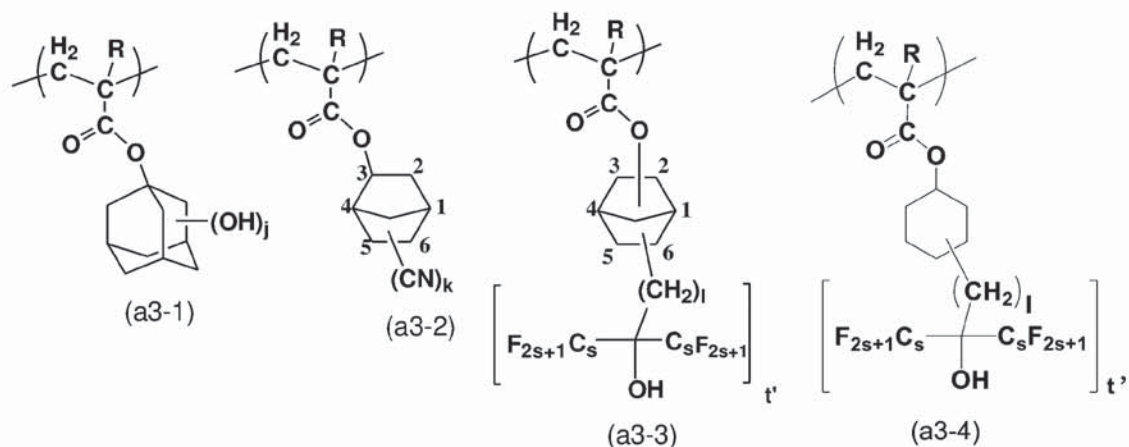
The structural unit (a3) is preferably a structural unit derived from an acrylate ester which may have the hydrogen atom bonded to the carbon atom on the α -position substituted with a substituent and contains a polar group-containing aliphatic hydrocarbon
25 group.

When the aliphatic hydrocarbon group within the polar group-containing aliphatic hydrocarbon group is a linear or branched hydrocarbon group of 1 to 10 carbon atoms, the structural unit (a3) is preferably a structural unit derived from a hydroxyethyl ester of acrylic acid.

30 On the other hand, in the structural unit (a3), when the hydrocarbon group within the polar group-containing aliphatic hydrocarbon group is a polycyclic group, structural units represented by formulas (a3-1), (a3-2), (a3-3) and (a3-4) shown below are preferable.

[0169]

[Chemical Formula 40]



In the formulae, R is the same as defined above; j is an integer of 1 to 3; k is an integer of 1 to 3; t' is an integer of 1 to 3; l is an integer of 0 to 5; and s is an integer of 1 to 3.

5 [0170]

In formula (a3-1), j is preferably 1 or 2, and more preferably 1. When j is 2, it is preferable that the hydroxyl groups be bonded to the 3rd and 5th positions of the adamantyl group. When j is 1, it is preferable that the hydroxyl group be bonded to the 3rd position of the adamantyl group. j is preferably 1, and it is particularly desirable that the hydroxyl group be bonded to the 3rd position of the adamantyl group.

[0171]

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

[0172]

15 In formula (a3-3), t' is preferably 1. l is preferably 1. s is preferably 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. The fluorinated alkyl alcohol is preferably bonded to the 5th or 6th position of the norbornyl group.

[0173]

20 In formula (a3-4), t' is preferably 1 or 2. l is preferably 0 or 1. s is preferably 1. The fluorinated alkyl alcohol is preferably bonded to the 3rd or 5th position of the cyclohexyl group.

[0174]

As the structural unit (a3) contained in the component (A1), 1 type of structural

unit may be used, or 2 or more types may be used.

When the component (A1) includes the structural unit (a3), the amount of the structural unit (a3) based on the combined total (100 mol%) of all structural units constituting the component (A1) is preferably 1 to 30 mol%, more preferably 2 to 25 mol%, and still more preferably 5 to 20 mol%.

When the amount of the structural unit (a3) is at least as large as the lower limit of the above preferable range, the effect of using the structural unit (a3) may be satisfactorily achieved due to the aforementioned effects. On the other hand, when the amount of the structural unit (a3) is no more than the upper limit of the above preferable range, a good balance may be achieved with the other structural units, and various lithography properties may be improved.

[0175]

Structural unit (a4):

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

When the component (A1) includes the structural unit (a4), dry etching resistance of the resist pattern to be formed is improved. Further, the hydrophobicity of the component (A) is further improved. Increase in the hydrophobicity contributes to improvement in terms of resolution, shape of the resist pattern and the like, particularly in a solvent developing process. An "acid non-dissociable, aliphatic cyclic group" in the structural unit (a4) refers to a cyclic group which is not dissociated by the action of the acid (e.g., acid generated from a structural unit which generates acid upon exposure or acid generated from the component (B)) upon exposure, and remains in the structural unit.

[0176]

As the structural unit (a4), a structural unit which contains a non-acid-dissociable aliphatic cyclic group, and is also derived from an acrylate ester is preferable. As the cyclic group, any of the multitude of conventional polycyclic groups used within the resin component of resist compositions for ArF excimer lasers or KrF excimer lasers (preferably for KrF excimer lasers) may be used.

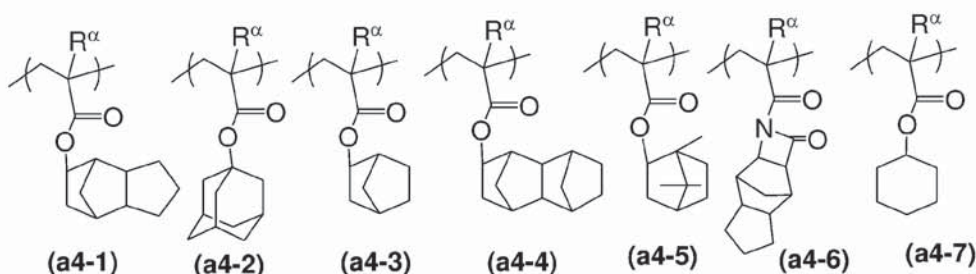
As the aliphatic polycyclic group, at least one polycyclic group selected from amongst a tricyclodecyl group, adamantyl group, tetracyclododecyl group, isobornyl group, and norbornyl group is particularly desirable in consideration of industrial availability and the like. These polycyclic groups may be substituted with a linear or branched alkyl group

of 1 to 5 carbon atoms.

Specific examples of the structural unit (a4) include structural units represented by general formulae (a4-1) to (a4-7) shown below.

[0177]

5 [Chemical Formula 41]



In the formulae, R^α is the same as defined above.

[0178]

10 As the structural unit (a4) contained in the component (A1), 1 type of structural unit may be used, or 2 or more types may be used.

When the component (A1) contains the structural unit (a4), the amount of the structural unit (a4) based on the combined total (100 mol%) of all structural units constituting the component (A1) is preferably 1 to 40 mol%, and more preferably 5 to 20 mol%.

15 When the amount of the structural unit (a4) is at least as large as the lower limit of the above-mentioned preferable range, the effect of using the structural unit (a4) can be satisfactorily achieved. On the other hand, when the amount of the structural unit (a4) is no more than the upper limit of the above-mentioned preferable range, a good balance can be achieved with the other structural units.

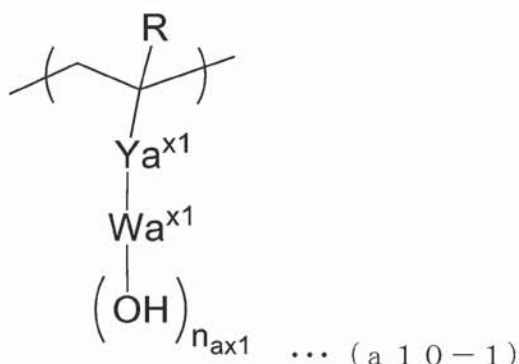
20 [0179]

Structural unit (a10):

The structural unit (a10) is a structural unit represented by general formula (a10-1) shown below.

[0180]

25 [Chemical Formula 42]



In the formula, R represents a hydrogen atom, an alkyl group of 1 to 5 carbon atoms or a halogenated alkyl group of 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 aromatic hydrocarbon group having a valency of $(\text{n}_{\text{ax}1}+1)$; and $\text{n}_{\text{ax}1}$ represents an integer of 1 or more.

[0181]

In general formula (a10-1), R represents a hydrogen atom, an alkyl group of 1 to 5 carbon atoms or a halogenated alkyl group of 1 to 5 carbon atoms.

As the alkyl group having 1 to 5 carbon atoms for R, a linear or branched alkyl group of 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 of 1 to 5 carbon atoms represented by R is a group in which part or all of the hydrogen atoms of the aforementioned alkyl group 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 desirable.

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

[0182]

In formula (a10-1), $\text{Y}^{\text{a}^{\text{x}1}}$ represents a single bond or a divalent linking group.

In the aforementioned chemical formula, the divalent linking group for $\text{Y}^{\text{a}^{\text{x}1}}$ is not particularly limited, and preferable examples thereof include a divalent hydrocarbon group which may have a substituent and a divalent linking group containing a hetero atom.

[0183]

- Divalent hydrocarbon group which may have a substituent:

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

[0184]

- Aliphatic hydrocarbon group for Y^{x1}

An "aliphatic hydrocarbon group" refers to a hydrocarbon group that has no aromaticity. The aliphatic hydrocarbon group may be saturated or unsaturated. In general, the aliphatic hydrocarbon group 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 can be given.

[0185]

- Linear or branched aliphatic hydrocarbon group

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

As the linear aliphatic hydrocarbon group, a linear alkylene group is preferable. 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 preferably has 2 to 10 carbon atoms, more preferably 3 to 6, still more preferably 3 or 4, and most preferably 3.

As the branched aliphatic hydrocarbon group, branched alkylene groups are preferred, and specific examples include various alkylalkylene groups, including 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 within the alkylalkylene group, a linear alkyl group of 1 to 5 carbon atoms is preferable.

[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 of 1 to 5 carbon atoms, and a carbonyl group.

[0187]

- Aliphatic hydrocarbon group containing a ring in the structure thereof

5 As examples of the hydrocarbon group containing a ring in the structure thereof, a cyclic aliphatic hydrocarbon group containing a hetero atom in the ring structure thereof and may have a substituent (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 the aforementioned chain-like aliphatic hydrocarbon group, and a group in which the cyclic aliphatic group is interposed within the
10 aforementioned linear or branched aliphatic hydrocarbon group, can be given. As the linear or branched aliphatic hydrocarbon group, the same groups as those described above can be used.

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

The cyclic aliphatic hydrocarbon group may be either a polycyclic group or a monocyclic group. As the monocyclic aliphatic hydrocarbon group, a group in which 2 hydrogen atoms have been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof
20 include cyclopentane and cyclohexane. As the polycyclic group, a group in which 2 hydrogen atoms have been removed from a polycycloalkane is preferable, and the polycyclic group preferably has 7 to 12 carbon atoms. Examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane and tetracyclododecane.

[0188]

25 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 of 1 to 5 carbon atoms, and more preferably a methyl group, an ethyl group, a propyl group, an n-butyl group or a tert-butyl group.
30

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

group or an ethoxy group.

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.

Examples of the halogenated alkyl group for the substituent include groups in
 5 which part or all of the hydrogen atoms within the aforementioned alkyl groups has been substituted with the aforementioned halogen atoms.

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

[0189]

- Aromatic hydrocarbon group for Ya^{x1}

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

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

Examples of the aromatic ring include aromatic hydrocarbon rings, such as benzene, naphthalene, anthracene and phenanthrene; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic hydrocarbon rings has been substituted with a hetero atom. Examples of the hetero atom within the aromatic
 25 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 aforementioned aromatic hydrocarbon ring or aromatic hetero ring (arylene group or heteroarylene group); a group in which two
 30 hydrogen atoms have 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 aforementioned aromatic hydrocarbon ring or aromatic hetero ring has been substituted with an alkylene group (a group in which one hydrogen atom has been removed

from the aryl group within the aforementioned 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, or a heteroarylalkyl group). The alkylene group which is bonded to the aforementioned aryl group or heteroaryl group preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and most preferably 1 carbon atom.

[0190]

With respect to the aromatic hydrocarbon group, the hydrogen atom within the aromatic hydrocarbon group may be substituted with a substituent. For example, the hydrogen atom bonded to the aromatic ring within 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 of 1 to 5 carbon atoms, and more preferably a methyl group, an ethyl group, a propyl group, an n-butyl group or a tert-butyl group.

As the alkoxy group, the halogen atom and the halogenated alkyl group for the substituent, the same groups as the aforementioned substituent groups for substituting a hydrogen atom within the cyclic aliphatic hydrocarbon group can be used.

[0191]

- Divalent linking group containing a hetero atom

In the case where Y^{a1} represents a divalent linking group containing a hetero atom, preferable examples of the linking group include $-O-$, $-C(=O)-O-$, $-O-C(=O)-$, $-C(=O)-$, $-O-C(=O)-O-$, $-C(=O)-NH-$, $-NH-$, $-NH-C(=NH)-$ (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 the 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, and most preferably 1 to 5.

In general formulae $-Y^{21}-O-Y^{22}-$, $-Y^{21}-O-$, $-Y^{21}-C(=O)-O-$, $-C(=O)-O-Y^{21}-$, $-[Y^{21}-C(=O)-O]_m-Y^{22}-$, $-Y^{21}-O-C(=O)-Y^{22}-$ or $-Y^{21}-S(=O)_2-O-Y^{22}-$, Y^{21} and Y^{22} each independently represents a divalent hydrocarbon group which may have a substituent. Examples of the divalent hydrocarbon group include the same groups as those described above as the "divalent hydrocarbon group which may have a substituent" in the explanation of the aforementioned divalent linking group for Y^{a1} .

As Y^{21} , a linear aliphatic hydrocarbon group is preferable, more preferably a linear alkylene group, still more preferably a linear alkylene group of 1 to 5 carbon atoms, and a methylene group or an ethylene group is particularly desirable.

As Y^{22} , 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 within the alkylmethylene group is preferably a linear alkyl group of 1 to 5 carbon atoms, more preferably a linear alkyl group of 1 to 3 carbon atoms, and most preferably a methyl group.

In the group represented by the 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 most preferably 1. Namely, it is particularly desirable that the group represented by the formula $-[Y^{21}-C(=O)-O]_m-Y^{22}-$ is a group represented by the formula $-Y^{21}-C(=O)-O-Y^{22}-$. Among these, a group represented by the formula $-(CH_2)_{a'}-C(=O)-O-(CH_2)_{b'}-$ is preferable. In the formula, a' is 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' is 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 example, as Y^{a1} , a single bond, an ester bond $[-C(=O)-O-$, $-O-C(=O)-]$, an ether bond $(-O-)$, a linear or branched alkylene group, or a combination of these is preferable, and a single bond or 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), W^{a1} represents an aromatic hydrocarbon group having a valency of $(n_{ax1}+1)$.

Examples of the aromatic hydrocarbon group for W^{a1} 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 compound having $(4n + 2)\pi$ electrons, and may be either monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, and still more preferably 6 to 15 carbon atoms, and most preferably 6 to 12 carbon atoms. Specific examples of the aromatic ring include an aromatic hydrocarbon ring, such as benzene, naphthalene, anthracene or phenanthrene; and an aromatic heterocyclic ring in which part of the carbon atoms constituting the aromatic hydrocarbon ring has been substituted with a heteroatom. Examples of the hetero atom within 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.

Further examples of the aromatic hydrocarbon group for Wa^{x1} include a group in which ($n_{ax1}+1$) hydrogen atom(s) has been removed from an aromatic group containing 2 or more aromatic rings (e.g., biphenyl, fluorene, or the like).

Among the above examples, as Wa^{x1} , a group in which ($n_{ax1}+1$) hydrogen atoms have been removed from benzene, naphthalene, anthracene or biphenyl is preferable, a group in which ($n_{ax1}+1$) hydrogen atoms have been removed from benzene or naphthalene is more preferable, and a group in which ($n_{ax1}+1$) hydrogen atoms have been removed from benzene is still more preferable.

[0194]

The aromatic hydrocarbon group for Wa^{x1} may or may not have a substituent, but preferably has no substituent. Examples of the substituent include an alkyl group, an alkoxy group, a halogen atom, and a halogenated alkyl group. The alkyl group, the alkoxy group and the halogen atom and the halogenated alkyl group as the substituent are the same as defined for the substituent for the cyclic aliphatic hydrocarbon group represented by Ya^{x1} . In the case where Wa^{x1} is a group in which ($n_{ax1}+1$) hydrogen atoms have been removed from an aromatic ring, the substituent(s) substitutes hydrogen atom(s) of the aromatic ring having ($n_{ax1}+1$) hydrogen atoms removed therefrom. 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 most preferably a methyl group.

[0195]

In formula (a10-1), n_{ax1} is 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 most preferably 1 or 2. Among the above examples, n_{ax1} is preferably 1.

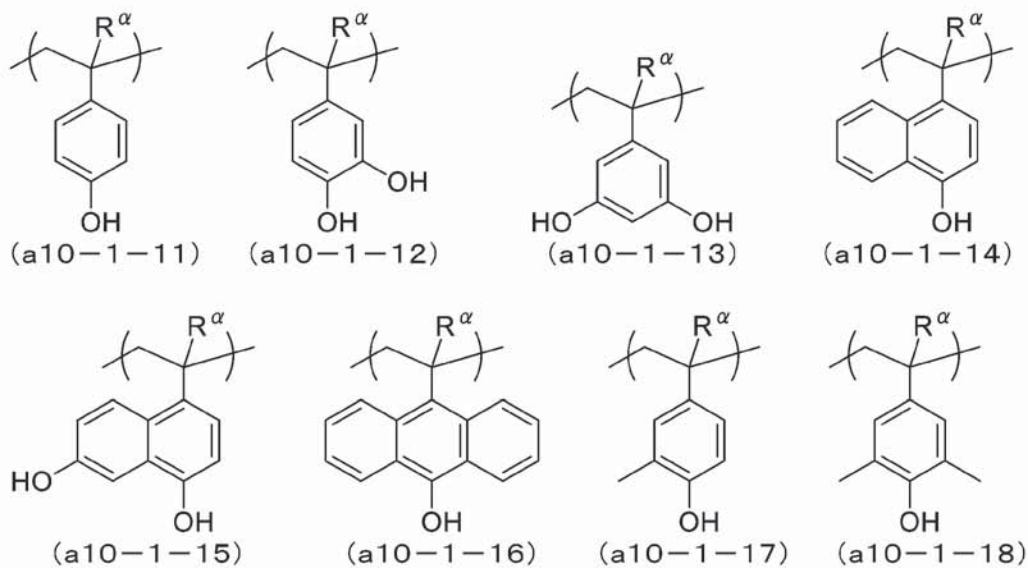
[0196]

Specific examples of the structural unit (a10) represented by formula (a10-1) are
5 shown below.

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

[0197]

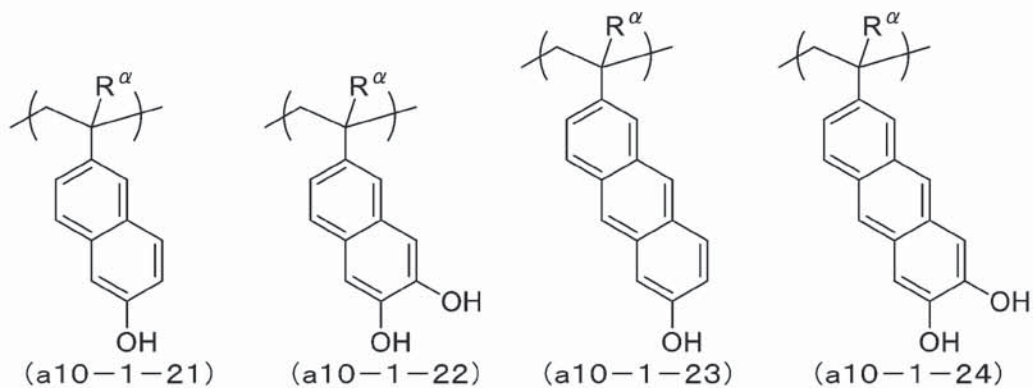
[Chemical Formula 43]



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[0198]

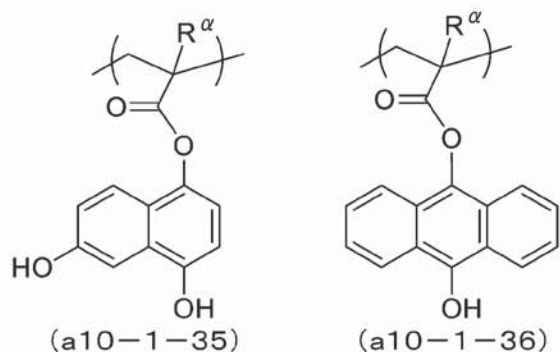
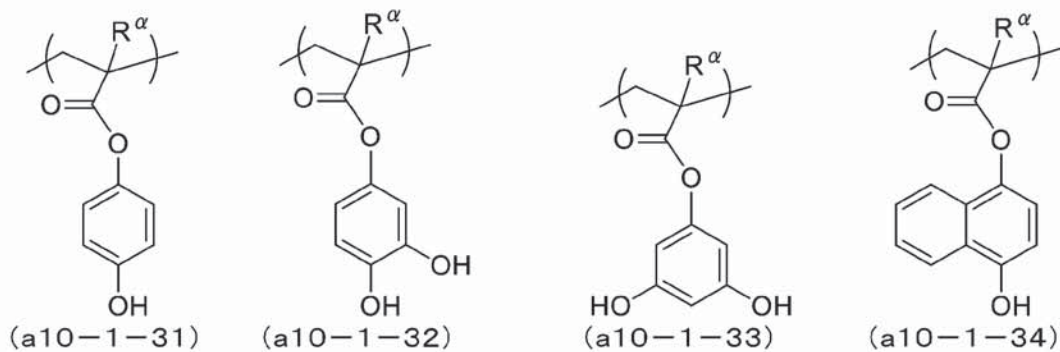
[Chemical Formula 44]



[0199]

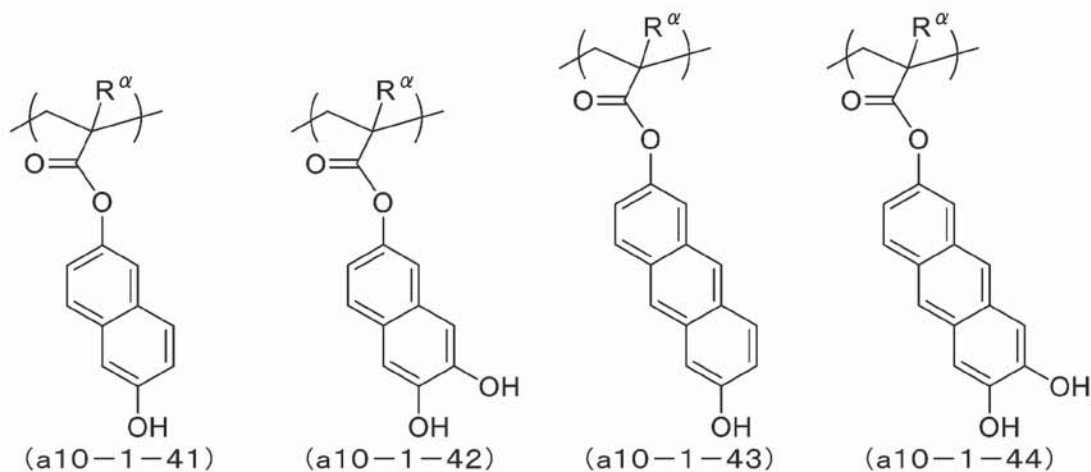
[Chemical Formula 45]

15



[0200]

[Chemical Formula 46]



5

[0201]

As the structural unit (a10) contained in the component (A1), 1 kind of structural unit may be used, or 2 or more kinds of structural units may be used.

When the component (A1) includes the structural unit (a10), the amount of the structural unit (a10) based on the combined total of all structural units constituting the component (A1) (100 mol%) is preferably 5 to 80 mol%, more preferably 5 to 75 mol%,

10

and still more preferably 10 to 70 mol%.

When the amount of the structural unit (a10) is at least as large as the lower limit of the above preferable range, the sensitivity may be more reliably enhanced. On the other hand, when the amount of the structural unit (a10) is no more than the upper limit of the above-mentioned range, a good balance may be reliably achieved with the other structural units.

[0202]

- Structural unit (st)

The structural unit (st) is a structural unit derived from styrene or a styrene derivative. A "structural unit derived from styrene" refers to a structural unit that is formed by the cleavage of the ethylenic double bond of styrene. A "structural unit derived from styrene" refers to a structural unit that is formed by the cleavage of the ethylenic double bond of a styrene derivative.

[0203]

A "styrene derivative" refers to a compound in which at least part of the hydrogen atoms of styrene has been substituted with a substituent. Examples of the styrene derivative include a compound in which the hydrogen at the α -position of styrene has been substituted with a substituent, a compound in which at least one hydrogen atom on the benzene ring of styrene has been substituted with a substituent, and a compound in which the hydrogen at the α -position of styrene and at least one hydrogen atom on the benzene ring of styrene has been substituted with a substituent.

[0204]

Examples of the substituent which substitutes the hydrogen atom at the α -position of styrene include an alkyl group having 1 to 5 carbon atoms, and a halogenated alkyl group having 1 to 5 carbon atoms.

The alkyl group of 1 to 5 carbon atoms is preferably a linear or branched alkyl group of 1 to 5 carbon atoms, and specific examples 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 of 1 to 5 carbon atoms represented by R is a group in which part or all of the hydrogen atoms of the aforementioned alkyl group of 1 to 5 carbon atoms have been substituted with halogen atom(s). 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 desirable. As the substituent which substitutes the hydrogen atom at the α -position of styrene, an alkyl group having 1 to 5 carbon atoms or a fluorinated alkyl group having 1 to 5 carbon atoms is preferable, an alkyl group having 1 to 3 carbon atoms or a fluorinated alkyl group having 1 to 3 carbon atoms is more preferable, and in terms of industrial availability, a methyl group is more preferable.

[0205]

Examples of the substituent which substitutes a hydrogen atom on 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 of 1 to 5 carbon atoms, and more preferably a methyl group, an ethyl group, a propyl group, an n-butyl group or a tert-butyl group.

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

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.

Examples of the halogenated alkyl group for the substituent include groups in which part or all of the hydrogen atoms within the aforementioned alkyl groups has been substituted with the aforementioned halogen atoms.

As the substituent which substitutes a hydrogen atom on 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]

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

[0207]

As the structural unit (st) contained in the component (A1), 1 kind of structural unit may be used, or 2 or more kinds of structural units may be used.

When the component (A1) includes the structural unit (st), the amount of the structural unit (st) based on the combined total of all structural units constituting the component (A1) (100 mol%) is preferably 1 to 30 mol%, and more preferably 3 to 20 mol%.

[0208]

In the resist composition, as the component (A1), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

10 In the resist composition of the present embodiment, examples of the component (A1) include a polymeric compound having a repeating structure of the structural unit (a1).

Preferable examples of the component (A1) include a polymeric compound having a repeating structure of at least the structural unit (a1) and any other structural unit(s). Examples of the other structural unit(s) include the structural unit (a10) and the structural unit (st).

15 In addition to the combination of the two structural units described above, the structural unit described above may be combined appropriately in order to obtain desired effects as a third structural unit, or alternatively, three or more of such structural units may be combined. Examples of the combination of 3 or more structural units include a combination of a structural unit (a1), a structural unit (a10) and a structural unit (st).

20 Specific examples of the component (A1) include a polymeric compound having a repeating structure of the structural unit (a1) and the structural unit (a10); a polymeric compound having a repeating structure of the structural unit (a1) and the structural unit (st); and a polymeric compound having a repeating structure of the structural unit (a1), the structural unit (a10) and the structural unit (st).

[0209]

The component (A1) may be produced, for example, by dissolving the monomers corresponding with each of the structural units in a polymerization solvent, followed by addition of a radical polymerization initiator such as azobisisobutyronitrile (AIBN) or dimethyl-2,2'-azobisisoutrate (e.g., V-601).

30 Alternatively, the component (A1) may be prepared by dissolving a monomer from which the structural unit (a1) is derived, and a monomer from which the structural unit other than the structural unit (a1) is derived in a polymerization solvent, polymerizing

the dissolved monomers using the radical polymerization initiator described above, followed by performing a deprotection reaction.

In the polymerization, a chain transfer agent such as $\text{HS-CH}_2\text{-CH}_2\text{-CH}_2\text{-C}(\text{CF}_3)_2\text{-OH}$ may be used to introduce a $\text{-C}(\text{CF}_3)_2\text{-OH}$ group at the terminal(s) of the polymer. Such a copolymer having introduced a hydroxyalkyl group in which some of the hydrogen atoms of the alkyl group are substituted with fluorine atoms is effective in reducing developing defects and LER (line edge roughness: unevenness of the side walls of a line pattern).

[0210]

The weight average molecular weight (Mw) (the polystyrene equivalent value determined by gel permeation chromatography (GPC)) of the component (A1) is not particularly limited, but is preferably 1,000 to 50,000, more preferably 2,000 to 30,000, and still more preferably 3,000 to 20,000.

When the Mw of the component (A1) is no more than the upper limit of the above-mentioned preferable range, the resist composition exhibits a satisfactory solubility in a resist solvent. On the other hand, when the Mw of the component (A1) is at least as large as the lower limit of the above-mentioned preferable range, dry etching resistance and the cross-sectional shape of the resist pattern becomes satisfactory.

The dispersity (Mw/Mn) of the component (A1) is not particularly limited, but is preferably 1.0 to 4.0, more preferably 1.0 to 3.0, and most preferably 1.0 to 2.0. Here, Mn is the number average molecular weight.

[0211]

• Base component other than (A1)

In the resist composition of the present embodiment, as the component (A), “a base component which exhibits changed solubility in a developing solution under action of acid” other than the component (A1) may be used in combination. Such base component other than the component (A1) is not particularly limited, and any of the multitude of conventional base components used within chemically amplified resist compositions may be appropriately selected for use. As such base component other than the component (A1), one kind of a polymer or a low molecular weight compound may be used, or a combination of two or more kinds may be used.

[0212]

In the component (A), the amount of the component (A1) based on the total weight

of the component (A) is preferably 25% by weight or more, more preferably 50% by weight or more, still more preferably 75% by weight or more, and may be even 100% by weight. When the amount of the component (A1) is 25% by weight or more, a resist pattern with improved lithography properties may be reliably formed.

5 [0213]

In the resist composition according to the present embodiment, the amount of the component (A) based on the total weight (100% by weight) of the resist composition is preferably 20% by weight or more. When the amount of the component (A) is 20% by weight or more, a resist film having a large film thickness (e.g., a film thickness of 5 μ m or more) may be more reliably formed. The upper limit of the amount of the component (A) is not particularly limited as long as a resist film may be formed, and for example, may be 50% by weight or less. The amount of the component (A) is preferably 20 to 50% by weight, more preferably 22 to 50% by weight, and still more preferably 25 to 50% by weight.

[0214]

15 <Component (Z)>

The component (Z) is an ion liquid.

An ion liquid refers to a salt which is present in the form of a liquid. An ion liquid is constituted of a cation moiety and an anion moiety. The electrostatic interaction between the cation moiety and the anion moiety is weak, and the salt is unlikely to be crystallized.

20 The ion liquid has a boiling point of 100°C or lower, and has the following characteristics 1) to 5).

Characteristic 1) The vapor pressure is extremely low. Characteristic 2) Non-flammable over a wide temperature range. Characteristic 3) Maintains a liquid state over a wide temperature range Characteristic 4) The density can be largely changed.

25 Characteristic 5) The polarity can be controlled.

In the present embodiment, the ion liquid may be non-polymeric.

The weight average molecular weight (Mw) of the ion liquid is preferably 1,000 or less, more preferably 750 or less, and still more preferably 500 or less.

[0215]

30 - Cation moiety of component (Z)

The cation moiety of the component (Z) is not particularly limited. However, in terms of improvement in the phase-separation performance, the cation moiety preferably has a dipole moment of 3 debye or more, more preferably 3.2 to 15 debye, and still more

preferably 3.4 to 12 debye.

The "dipole moment of the cation moiety" is a parameter quantitatively indicating the polarity (deviation of charge) of the cation moiety. 1 debye is defined as $1 \times 10^{-18} \text{esu} \cdot \text{cm}$. In the present specification, the dipole moment of the cation moiety refers to a simulation value by CAChe. For example, the dipole moment of the cation moiety can be determined by optimization of the structure by CAChe Work System Pro Version 6.1.12.33, using MM geometry (MM2) and PM3 geometry.

[0216]

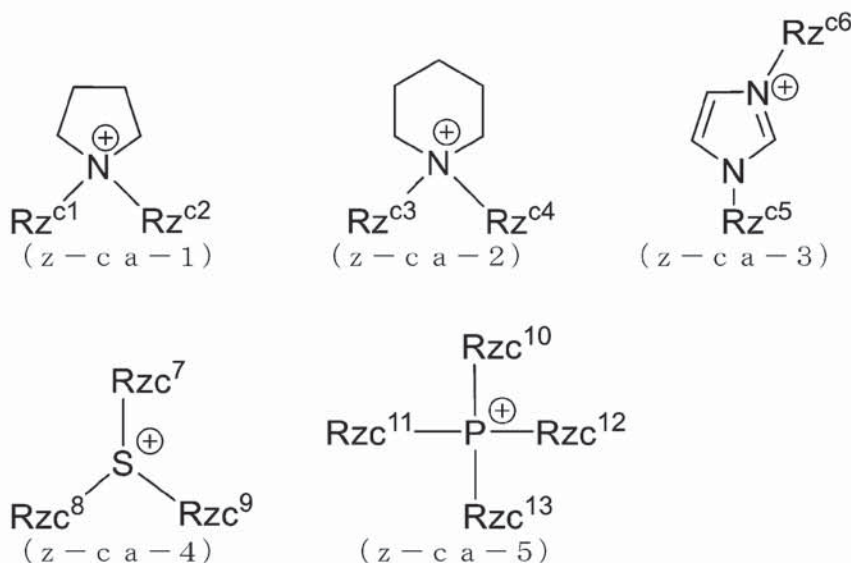
Preferable examples of cation moiety having a dipole moment of 3 debye or more include an imidazolium ion, a pyrrolidinium ion, a piperidinium ion, an ammonium ion, a sulfonium ion and a phosphonium.

That is, preferable examples of the component (Z) include an imidazolium salt, a pyrrolidinium salt, a piperidinium salt, an ammonium salt, a sulfonium salt and a phosphonium salt. Among these salts, in terms of improving the phase-separation performance, the cation moiety preferably has a substituent. Among these, a cation containing an alkyl group of 1 or more carbon atoms optionally having a substituent, or a cation containing a polar group. The alkyl group of 1 or more carbon atoms contained in the cation preferably has 1 to 12 carbon atoms, more preferably 1 to 6 carbon atoms. The alkyl group may be a linear alkyl group or a branched alkyl group, but is preferably a linear alkyl group. Examples of the substituent for the alkyl group of 2 or more carbon atoms include a hydroxy group, a vinyl group and an allyl group. The alkyl group of 1 or more carbon atoms preferably has no substituent. Examples of the polar group contained in the cation include a carboxy group, a hydroxy group, an amino group and a sulfo group.

More preferable examples of the cation moiety of the component (Z) include a cation represented by any one of general formulae (z-ca-1) to (z-ca-5) shown below.

[0217]

[Chemical Formula 47]



In the formulae, Rz^{c1} to Rz^{c6} each independently represents an alkyl group having 1 to 12 carbon atoms; Rz^{c7} to Rz^{c9} each independently represents an aryl group which may have a substituent; Rz^{c10} to Rz^{c13} each independently represents a linear alkyl group having 1 to 20 carbon atoms.

[0218]

In formula (z-ca-1), Rz^{c1} and Rz^{c2} each independently represents an alkyl group having 1 to 12 carbon atoms, preferably a linear or branched alkyl group having 1 to 12 carbon atoms, more preferably a linear alkyl group having 1 to 12 carbon atoms, and still more preferably a linear alkyl group having 1 to 6 carbon atoms. Among these examples, it is most preferable that Rz^{c1} represents a methyl group or an ethyl group, and Rz^{c2} represents a linear alkyl group having 1 to 4 carbon atoms.

[0219]

In formula (z-ca-2), Rz^{c3} and Rz^{c4} each independently represents an alkyl group having 1 to 12 carbon atoms, preferably a linear or branched alkyl group having 1 to 12 carbon atoms, more preferably a linear alkyl group having 1 to 12 carbon atoms, and still more preferably a linear alkyl group having 1 to 6 carbon atoms. Among these examples, it is most preferable that Rz^{c3} represents a methyl group or an ethyl group, and Rz^{c4} represents a linear alkyl group having 1 to 4 carbon atoms.

[0220]

In formula (z-ca-3), Rz^{c5} and Rz^{c6} each independently represents an alkyl group having 1 to 12 carbon atoms, preferably a linear or branched alkyl group having 1 to 12

carbon atoms, more preferably a linear alkyl group having 1 to 12 carbon atoms, and still more preferably a linear alkyl group having 1 to 6 carbon atoms. Among these examples, it is most preferable that Rz^{c5} represents a linear alkyl group having 1 to 6 carbon atoms, and Rz^{c6} represents a linear alkyl group having 1 to 4 carbon atoms.

5 [0221]

In formula (z-ca-4), Rz^{c7} to Rz^{c9} each independently represents an aryl group which may have a substituent, preferably a phenyl group or a naphthyl group, and more preferably a phenyl group.

10 Examples of the substituent which Rz^{c7} to Rz^{c9} may have 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 represented by general formulae (ca-r-1) to (ca-r-7) described later.

[0222]

15 In formula (z-ca-5), Rz^{c10} to Rz^{c13} each independently represents a linear alkyl group having 1 to 20 carbon atoms, preferably a linear alkyl group having 3 to 18 carbon atoms, more preferably a linear alkyl group having 4 to 16 carbon atoms, and still more preferably a linear alkyl group having 5 to 15 carbon atoms.

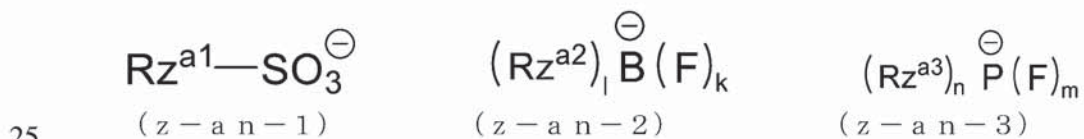
[0223]

- Anion moiety of component (Z)

20 The anion moiety of the compound (IL) is not particularly limited, and examples thereof include anions represented by any one of general formulae (z-an-1) to (z-an-5) shown below.

[0224]

[Chemical Formula 48]



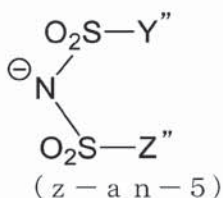
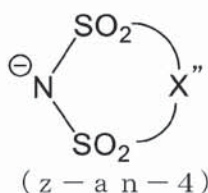
In formula (z-an-1), Rz^{a1} represents an aromatic hydrocarbon group which may have a substituent, an aliphatic cyclic group which may have a substituent, or a chain hydrocarbon group which may have a substituent. In formula (z-an-2), Rz^{a2} represents an alkyl group having 1 to 5 carbon atoms optionally substituted with a fluorine atom. k represents an integer of 1 to 4, and l represents an integer of 0 to 3, provided that $k+l=4$. In formula

30

(z-an-3), Rz^{a3} represents an alkyl group having 1 to 5 carbon atoms optionally substituted with a fluorine atom. m represents an integer of 1 to 6, and n represents an integer of 0 to 5, provided that $m+n = 6$.

[0225]

5 [Chemical Formula 49]



In formula (z-an-4), X'' represents an alkylene group of 2 to 6 carbon atoms in which at least one hydrogen atom has been substituted with a fluorine atom; in formula (z-an-5), Y'' and Z'' each independently represents an alkyl group of 1 to 10 carbon atoms in which at least one hydrogen atom has been substituted with a fluorine atom.

[0226]

In formula (z-an-1), Rz^{a1} represents an aromatic hydrocarbon group which may have a substituent, an aliphatic cyclic group which may have a substituent, or a chain hydrocarbon group which may have a substituent.

15 [0227]

In formula (z-an-1), in the case where Rz^{a1} represents an aromatic hydrocarbon group which may have a substituent, examples of the aromatic ring contained in the aromatic hydrocarbon group include aromatic hydrocarbon rings, such as benzene, biphenyl, fluorene, naphthalene, anthracene and phenanthrene; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic hydrocarbon rings has been substituted with a hetero atom. Examples of the hetero atom within the aromatic hetero rings include an oxygen atom, a sulfur atom and a nitrogen atom.

Specific examples of the aromatic hydrocarbon group include a group in which 1 hydrogen atom has been removed from the aforementioned aromatic hydrocarbon ring (aryl group); and a group in which 1 hydrogen atom of the aforementioned aryl group 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 alkylene group (alkyl chain within the arylalkyl group) preferably has 1 to 4 carbon atom, more preferably 1 or 2, and most preferably 1.

As the aromatic hydrocarbon group for R, a phenyl group or a naphthyl group is preferable, and a phenyl group is more preferable.

[0228]

In formula (z-an-1), in the case where Rz^{a1} represents an aliphatic cyclic group which may have a substituent, the cyclic group may be polycyclic or monocyclic. As the monocyclic aliphatic hydrocarbon group, a group in which one hydrogen atoms have been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 8 carbon atoms, and specific examples thereof include cyclopentane, cyclohexane and cyclooctane. As the polycyclic aliphatic cyclic group, a group in which one hydrogen atoms have been removed from a polycycloalkane is preferable, and the polycyclic group preferably has 7 to 12 carbon atoms. Examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane and tetracyclododecane.

Among these examples, as the aliphatic cyclic group, groups in which one or more hydrogen atoms have been removed from a polycycloalkane such as adamantane, norbornane, isobornane, tricyclodecane or tetracyclododecane are more preferable.

[0229]

In formula (z-an-1), as the chain hydrocarbon group for Rz^{a1} , a chain alkyl group is 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 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. The chain-like alkyl group preferably has 1 to 6 carbon atoms, and more preferably 1 to 3 carbon atoms. Further, a linear alkyl group is preferable.

[0230]

In formula (z-an-1), examples of the substituent for the aromatic hydrocarbon group, the aliphatic cyclic group or the chain hydrocarbon group for Rz^{a1} include a hydroxy group, an alkyl group, a fluorine atom, a fluorinated alkyl group, and a triphenylsulfonium group.

[0231]

In formula (z-an-1), as Rz^{a1} , a methyl group, a trifluoromethyl group, a p-tolyl

group or a propyltriphenylsulfonium group is preferable.

[0232]

In formula (z-an-2), Rz^{a2} represents an alkyl group having 1 to 5 carbon atoms optionally substituted with a fluorine atom.

5 k represents an integer of 1 to 4, preferably an integer of 3 to 4, and most preferably 4.

l represents an integer of 0 to 3, preferably 0 to 2, most preferably 0. When l is 2 or more, the plurality of Rz^{a2} may be the same or different from each other, but are preferably the same.

10 [0233]

In formula (z-an-3), Rz^{a3} represents an alkyl group having 1 to 5 carbon atoms optionally substituted with a fluorine atom.

m represents an integer of 1 to 6, preferably an integer of 3 to 6, and most preferably 6.

15 n represents an integer of 0 to 5, preferably 0 to 3, most preferably 0. When n is 2 or more, the plurality of Rz^{a3} may be the same or different from each other, but are preferably the same.

[0234]

In formula (z-an-4), X'' represents an alkylene group of 2 to 6 carbon atoms in which at least one hydrogen atom has been substituted with a fluorine atom. The alkylene group may be linear or branched, and has 2 to 6 carbon atoms, preferably 3 to 5 carbon atoms, and most preferably 3 carbon atoms.

[0235]

in formula (z-an-5), Y'' and Z'' each independently represents an alkyl group of 1 to 10 carbon atoms in which at least one hydrogen atom has been substituted with a fluorine atom. The alkyl group may be linear or branched, and has 1 to 10 carbon atoms, preferably 1 to 7 carbon atoms, and more preferably 1 to 3 carbon atoms. Among these examples, in formula (z-an-5), it is most preferable that both Y'' and Z'' represents a trifluoromethyl group.

30 The smaller the number of carbon atoms of the alkylene group for X'' or those of the alkyl group for Y'' and Z'' within the above-mentioned range of the number of carbon atoms, the more the solubility in an organic solvent component is improved.

[0236]

In the alkylene group for X'' and the alkyl group for Y'' and Z'', it is preferable that the number of hydrogen atoms substituted with fluorine atoms is as large as possible because the acid strength increases. The amount of fluorine atoms within the alkylene group or alkyl group, i.e., fluorination ratio, is preferably from 70 to 100%, more preferably from 90 to 100%, and it is particularly desirable that the alkylene group or alkyl group be a perfluoroalkylene or perfluoroalkyl group in which all hydrogen atoms are substituted with fluorine atoms.

[0237]

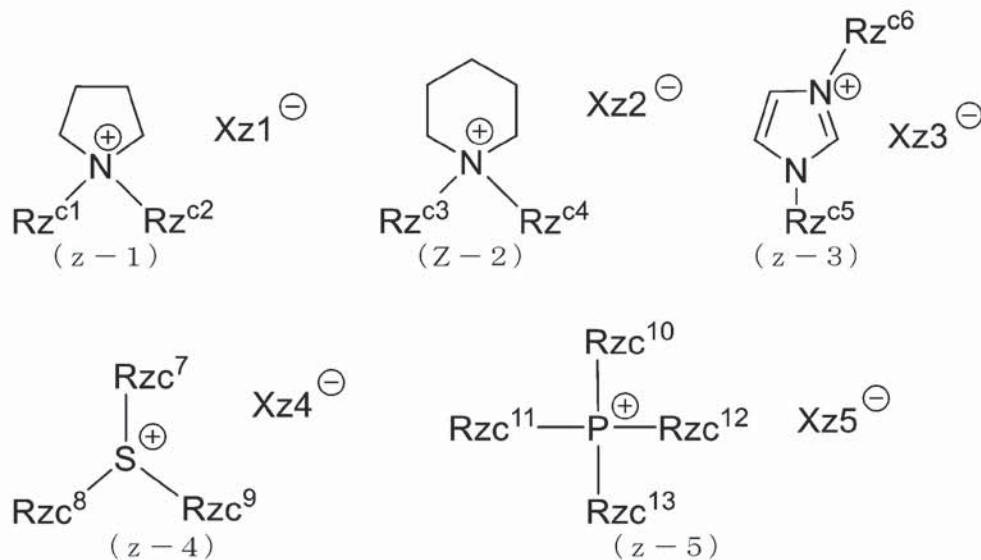
As the anion moiety of the component (Z), among the anion moieties represented by the aforementioned formulae (z-an-1) to (z-an-5), an anion moiety represented by general formula (z-an-1), (z-an-2), (z-an-3) or (z-an-5) is preferable.

[0238]

Among the above example, as the component (Z), a compound represented by any one of general formulae (z-1) to (z-5) shown below is preferable.

[0239]

[Chemical Formula 50]



In the formulae, Rz^{c1} to Rz^{c6} each independently represents an alkyl group having 1 to 12 carbon atoms; and $Xz1^{\ominus}$ to $Xz5^{\ominus}$ each independently represents an anion represented by the aforementioned general formula (z-an-1) to (z-an-5).

[0240]

In formulae (z-1) to (z-3), Rz^{c1} to Rz^{c6} are the same as defined for Rz^{c1} to Rz^{c6}

in the aforementioned formulae (z-ca-1) to (z-ca-3).

In formula (z-1), $Xz1^-$ is preferably an anion represented by the aforementioned formula (z-an-5).

In formula (z-2), $Xz2^-$ is preferably an anion represented by the aforementioned
5 formula (z-an-5).

In formula (z-3), $Xz3^-$ is preferably an anion represented by the aforementioned formula (z-an-2).

In formula (z-4), $Xz4^-$ is preferably an anion represented by the aforementioned formula (z-an-5).

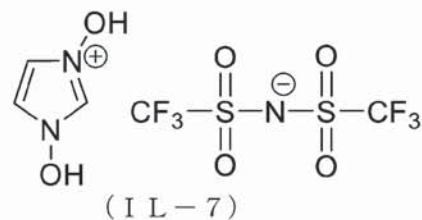
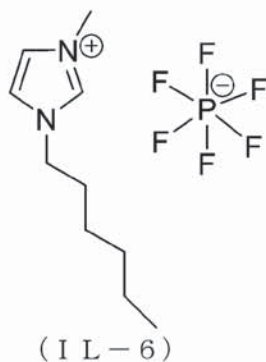
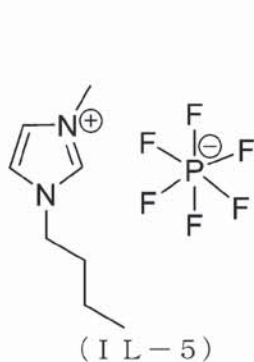
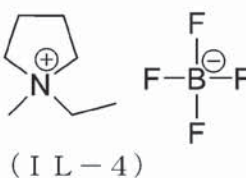
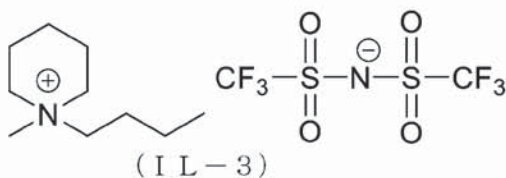
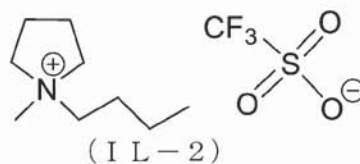
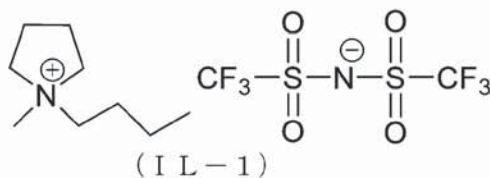
10 In formula (z-5), $Xz5^-$ is preferably an anion represented by the aforementioned formula (z-an-5).

[0241]

Specific examples of the compound (IL) are shown below, but the compound (IL) is by no means limited by these examples.

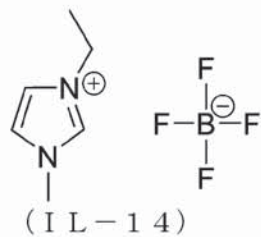
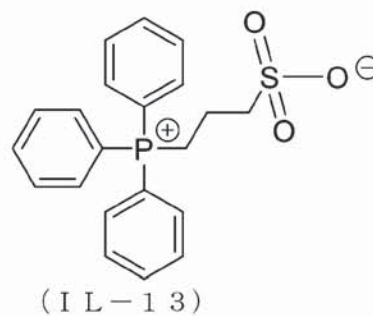
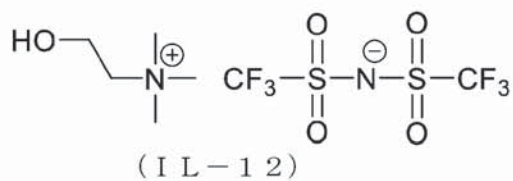
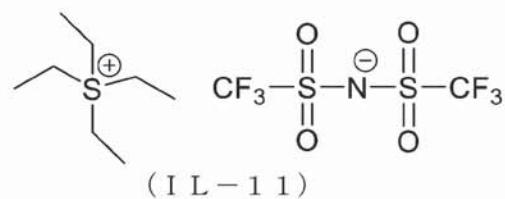
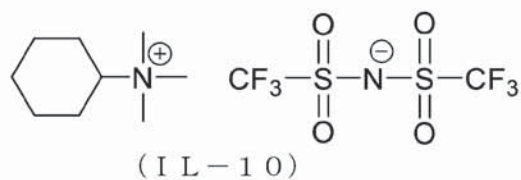
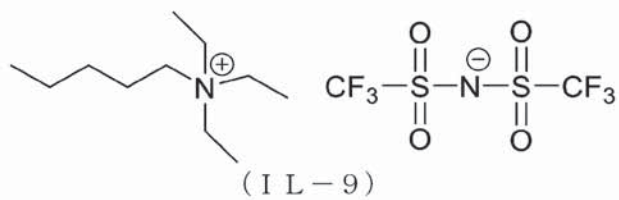
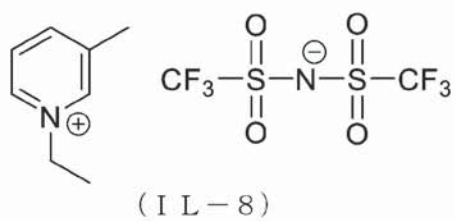
15 [0242]

[Chemical Formula 51]



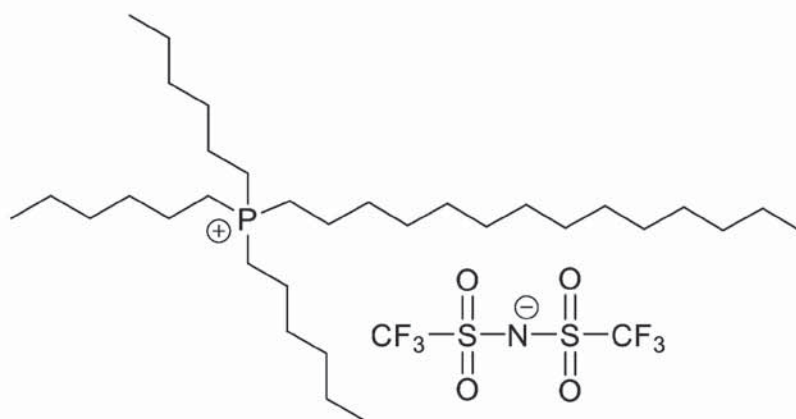
[0243]

[Chemical Formula 52]

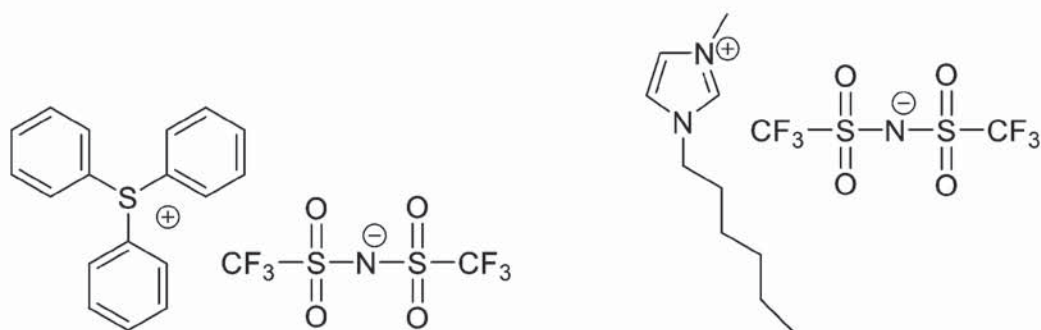


[0244]

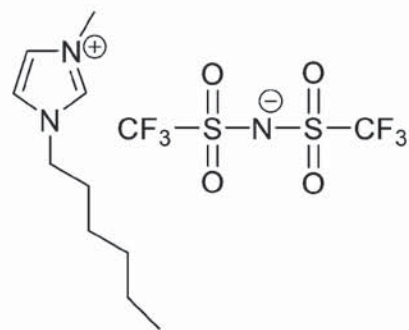
[Chemical Formula 53]



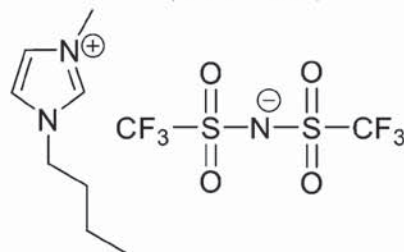
(I L - 1 5)



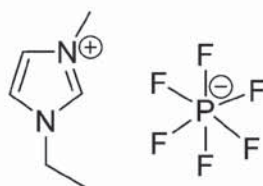
(I L - 1 6)



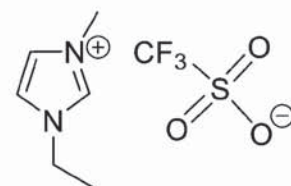
(I L - 1 7)



(I L - 1 8)



(I L - 1 9)



(I L - 2 0)

[0245]

In the resist composition of the present embodiment, as the component (Z), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

In the resist composition of the present embodiment, the amount of the component (Z) relative to 100 parts by weight of the component (A) is preferably within a range from more than 0% by weight to less than 25 parts by weight, more preferably from 0.1 to 20 parts by weight, still more preferably from 0.5 to 15 parts by weight, and most preferably 3 to 12 parts by weight.

When the amount of the component (Z) is at least as large as the lower limit of

the above-mentioned range, sensitivity may be further enhanced, and occurrence of cracks in the formation of a resist pattern may be more reliably suppressed. On the other hand, when the amount of the component (Z) is no more than the upper limit of the above-mentioned range, a resist pattern having a good shape may be more reliably obtained.

5 [0246]

<Other components>

The resist composition of the present embodiment may contain, in addition to the aforementioned components (A) and (Z), any other optional components. Examples of the other components include the component (B), the component (D), the component (E), the
10 component (F) and the component (S) described below.

[0247]

<<Acid-generator component (B)>>

The resist composition of the present embodiment may include, in addition to the components (A) and (Z), an acid-generator component (hereafter, sometimes referred to as
15 "component (B)").

As the component (B), there is no particular limitation, and any of the known acid generators used in conventional chemically amplified resist compositions may be used.

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

The component (B) preferably contains a compound (B1) (hereafter, sometimes referred to as "component (B1)") which is an onium salt.

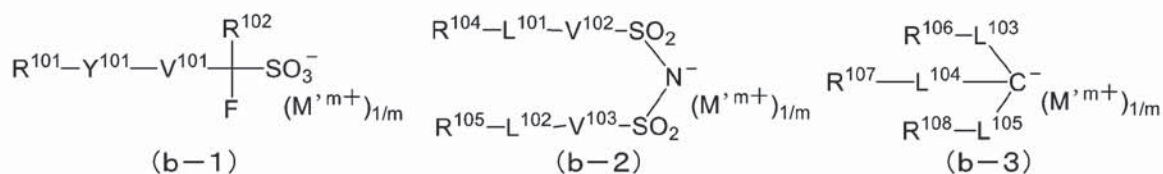
25 [0248]

- Component (B1)

Examples of the component (B1) include a compound represented by general formula (b-1) shown below (hereafter, sometimes referred to as "component (b-1)"), a compound represented by general formula (b-2) shown below (hereafter, sometimes referred to as "component (b-2)"), and a compound represented by general formula (b-3)
30 shown below (hereafter, sometimes referred to as "component (b-3)").

[0249]

[Chemical Formula 54]



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, provided that R^{104} and R^{105} may be mutually bonded to form a ring structure; R^{102} represents a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms; Y^{101} represents a single bond or a divalent group containing an oxygen atom; 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; L^{103} to L^{105} each independently represents a single bond, $-\text{CO}-$ or $-\text{SO}_2-$; m represents an integer of 1 or more; and $\text{M}'^{\text{m}+}$ represents an m -valent onium cation.

[0250]

{ Anion moiety }

- Anion moiety of component (b-1)

In the 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 may have a substituent.

[0251]

Cyclic group which may have a substituent:

The cyclic group is preferably a cyclic hydrocarbon group, and the cyclic hydrocarbon group may be either an aromatic hydrocarbon group or an aliphatic hydrocarbon group. An "aliphatic hydrocarbon group" refers to a hydrocarbon group that has no aromaticity. The aliphatic hydrocarbon group may be either saturated or unsaturated, but in general, the aliphatic hydrocarbon group is preferably saturated.

[0252]

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

Examples of the aromatic ring contained in the aromatic hydrocarbon group represented by R¹⁰¹ include benzene, fluorene, naphthalene, anthracene, phenanthrene and biphenyl; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic rings has been substituted with a hetero atom. Examples of the

5 hetero atom within the aromatic hetero rings include an oxygen atom, a sulfur atom and a nitrogen atom.

Specific examples of the aromatic hydrocarbon group represented by R¹⁰¹ include a group in which one hydrogen atom has been removed from the aforementioned aromatic ring (i.e., an aryl group, such as a phenyl group or a naphthyl group), and a group in which

10 one hydrogen of the aforementioned aromatic ring has been substituted with an alkylene group (e.g., 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 (alkyl chain within the arylalkyl group) preferably has 1 to 4 carbon atom, more preferably 1 or 2, and most preferably 1.

15 [0253]

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

As examples of the hydrocarbon group containing a ring in the structure thereof, 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

20 bonded to the terminal of the aforementioned chain-like aliphatic hydrocarbon group, and a group in which the alicyclic group is interposed within the aforementioned linear or branched aliphatic hydrocarbon group, can be given.

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

25 preferably 3 to 12 carbon atoms.

The alicyclic hydrocarbon group may be either 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 monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof

30 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 polycyclic group preferably has 7 to 30 carbon atoms. Among polycycloalkanes, a polycycloalkane having a bridged ring polycyclic skeleton, such as

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

[0254]

5 Among these examples, as the cyclic aliphatic hydrocarbon group for 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 or more hydrogen atoms have been removed from a polycycloalkane is more preferable, an adamantyl group or a norbornyl group is still more preferable, and an adamantyl group is most preferable.

10 [0255]

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 atoms. As the linear aliphatic hydrocarbon group, a linear alkylene group is preferable. Specific
15 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 hydrocarbon group preferably has 2 to 10 carbon atoms, more preferably 3 to 6 carbon
20 atoms, still more preferably 3 or 4 carbon atoms, and most preferably 3 carbon atoms. As the branched aliphatic hydrocarbon group, branched alkylene groups are preferred, and specific examples include various alkylalkylene groups, including 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 $-CH(CH_3)CH_2-$,
25 $-CH(CH_3)CH(CH_3)-$, $-C(CH_3)_2CH_2-$, $-CH(CH_2CH_3)CH_2-$, 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 within the alkylalkylene group, a linear alkyl group of 1 to 5 carbon atoms is preferable.

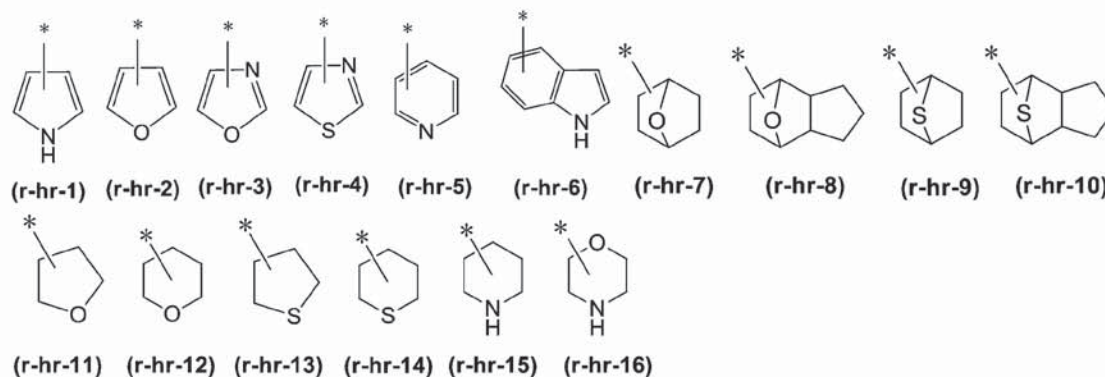
30 [0256]

The cyclic hydrocarbon group for R^{101} may contain a hetero atom such as a heterocycle. Specific examples include lactone-containing cyclic groups represented by the aforementioned general formulae (a2-r-1) to (a2-r-7), the $-SO_2-$ containing cyclic

group represented by the aforementioned formulae (a5-r-1) to (a5-r-4), and other heterocyclic groups represented by chemical formulae (r-hr-1) to (r-hr-16) shown below.

[0257]

[Chemical Formula 55]



5

[0258]

As the substituent for the cyclic group for R^{101} , an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, a carbonyl group, a nitro group or the like can be used. The alkyl group as the substituent is preferably an alkyl group of 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 particularly desirable.

10

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

15

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 aforementioned halogenated alkyl group includes a group in which a part or all of the hydrogen atoms within an alkyl group of 1 to 5 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, an n-butyl group or a tert-butyl group) have been substituted with the aforementioned halogen atoms.

20

The carbonyl group as the substituent is a group that substitutes a methylene group ($-\text{CH}_2-$) constituting the cyclic hydrocarbon group.

[0259]

25

Chain alkyl group which may have a substituent:

The chain-like alkyl group for R^{101} may be linear or branched.

The linear alkyl group preferably has 1 to 20 carbon atoms, more preferably 1 to 15, and most preferably 1 to 10. Specific examples 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 decyl group, an undecyl 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 heniceryl group and a docosyl group.

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

[0260]

Chain alkenyl group which may have a substituent:

The chain-like alkenyl group for R^{101} may be linear or branched, and preferably has 2 to 10 carbon atoms, more preferably 2 to 5 carbon atoms, still more preferably 2 to 4 carbon atoms, and most preferably 3 carbon atoms. Examples of linear alkenyl groups include a vinyl group, a propenyl group (an allyl group) and a butynyl group. Examples of branched alkenyl groups include a 1-methylvinyl group, a 2-methylvinyl group, a 1-methylpropenyl group and a 2-methylpropenyl group.

Among these 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 most preferable.

[0261]

As the substituent for the chain-like alkyl group or alkenyl group for 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 for R^{101} or the like can be used.

[0262]

Among the above examples, as R^{101} , a cyclic group which may have a substituent is preferable, and a cyclic hydrocarbon group which may have a substituent is more preferable. Specifically, a phenyl group, a naphthyl group, a group in which one or more hydrogen atoms have been removed from a polycycloalkane, a lactone-containing cyclic group represented by any one of the aforementioned formula (a2-r-1) to (a2-r-7), and an

—SO₂— containing cyclic group represented by any one of the aforementioned formula (a5-r-1) to (a5-r-4).

[0263]

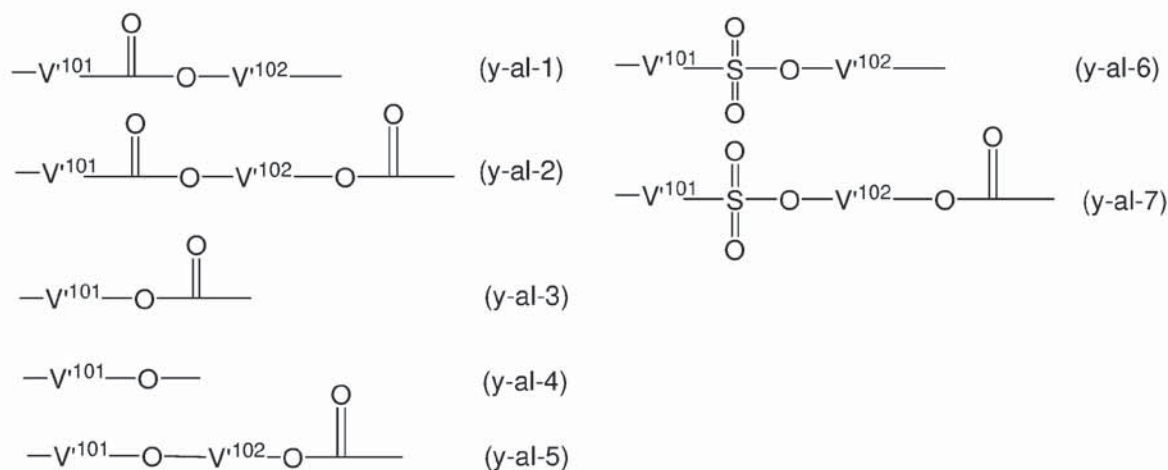
In formula (b-1), Y¹⁰¹ represents a single bond or a divalent linking group containing an oxygen atom.

In the case where Y¹⁰¹ is 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.

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 amido bond (—C(=O)—NH—), a carbonyl group (—C(=O)—) and a carbonate bond (—O—C(=O)—O—); and combinations of the aforementioned non-hydrocarbon, hetero atom-containing linking groups with an alkylene group. Furthermore, the combinations may have a sulfonyl group (—SO₂—) bonded thereto. Examples of the divalent linking group containing an oxygen atom include divalent linking groups represented by general formula (y-al-1) to (y-al-7) shown below.

[0264]

[Chemical Formula 56]



In the formulae, V¹⁰¹ represents a single bond or an alkylene group of 1 to 5 carbon atoms; V¹⁰² represents a divalent saturated hydrocarbon group of 1 to 30 carbon atoms.

[0265]

The divalent saturated hydrocarbon group for V¹⁰² is preferably an alkylene

group of 1 to 30 carbon atoms, more preferably an alkylene group of 1 to 10 carbon atoms, and still more preferably an alkylene group of 1 to 5 carbon atoms.

[0266]

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

Specific examples of the alkylene group for V^{101} and V^{102} include a methylene group $[-CH_2-]$; an alkylmethylene group, 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 $-C(CH_2CH_3)_2-$; an ethylene group $[-CH_2CH_2-]$; an alkylethylene group, such as $-CH(CH_3)CH_2-$,
10 $-CH(CH_3)CH(CH_3)-$, $-C(CH_3)_2CH_2-$ and $-CH(CH_2CH_3)CH_2-$; a trimethylene group (n-propylene group) $[-CH_2CH_2CH_2-]$; an alkyltrimethylene group, such as $-CH(CH_3)CH_2CH_2-$ and $-CH_2CH(CH_3)CH_2-$; a tetramethylene group $[-CH_2CH_2CH_2CH_2-]$; an alkyltetramethylene group, such as $-CH(CH_3)CH_2CH_2CH_2-$,
15 $-CH_2CH(CH_3)CH_2CH_2-$; and a pentamethylene group $[-CH_2CH_2CH_2CH_2CH_2-]$.

Further, part of methylene group within the alkylene group for V^{101} and V^{102}
may be substituted with a divalent aliphatic cyclic group of 5 to 10 carbon atoms. The aliphatic cyclic group is preferably a divalent group in which one hydrogen atom has been removed from the cyclic aliphatic hydrocarbon group (monocyclic aliphatic hydrocarbon group or polycyclic aliphatic hydrocarbon group) for Ra'^3 in the aforementioned formula
20 (a1-r-1), and a cyclohexylene group, 1,5-adamantylene group or 2,6-adamantylene group is preferable.

[0267]

Y^{101} is preferably a divalent linking group containing an ether bond or a divalent linking group containing an ester bond, and groups represented by the aforementioned
25 formulas (y-al-1) to (y-al-5) are preferable.

[0268]

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 for V^{101} preferably has 1 to 4 carbon atoms. Examples of the fluorinated alkylene group for V^{101} include a
30 group in which part or all of the hydrogen atoms within the alkylene group for V^{101} have been substituted with fluorine. Among these examples, as V^{101} , a single bond or a fluorinated alkylene group of 1 to 4 carbon atoms is preferable.

[0269]

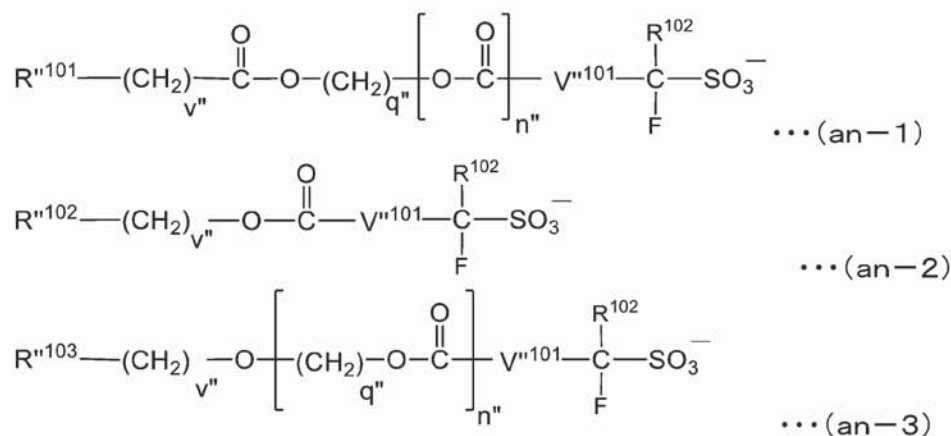
In formula (b-1), R^{102} represents a fluorine atom or a fluorinated alkyl group of 1 to 5 carbon atoms. R^{102} is preferably a fluorine atom or a perfluoroalkyl group of 1 to 5 carbon atoms, and more preferably a fluorine atom.

[0270]

- 5 Specific examples of the anion moiety represented by formula (b-1) include a fluorinated alkylsulfonate anion such as a trifluoromethanesulfonate anion or a perfluorobutanesulfonate anion in the case where Y^{101} is a single bond; and an anion represented by any one of formulae (an-1) to (an-3) in the case where Y^{101} represents a divalent linking group containing an oxygen atom.

10 [0271]

[Chemical Formula 57]



- In the formulae, $R^{''101}$ represents an aliphatic cyclic group which may have a substituent, a monovalent heterocyclic group represented by any of Formulae (r-hr-1) to (r-hr-6), or a chain-like alkyl group which may have a substituent; $R^{''102}$ represents an aliphatic cyclic group which may have a substituent, a lactone-containing cyclic group represented by any of Formulae (a2-r-1) and (a2-r-3) to (a2-r-7), or a $-SO_2-$ -containing cyclic group represented by any of 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; R^{102} represents a fluorine atom or a fluorinated alkyl group of 1 to 5 carbon atoms; each v'' independently represents an integer of 0 to 3; each q'' independently represents an integer of 0 to 20; and n'' represents 0 or 1.

25 [0272]

As the aliphatic cyclic group for R'^{101} , R'^{102} and R'^{103} which may have a substituent, the same groups as the cyclic aliphatic hydrocarbon group for R^{101} in the aforementioned formula (b-1) are preferable. Examples of the substituent include the same substituents as those described above for the cyclic aliphatic hydrocarbon group for R^{101} in the aforementioned formula (b-1).

[0273]

As the aromatic cyclic group for R'^{103} which may have a substituent, the same groups as the aromatic hydrocarbon group for the cyclic hydrocarbon group represented by R^{101} in the aforementioned formula (b-1) is preferable. Examples of the substituent include the same substituents as those described above for the aromatic hydrocarbon group for R^{101} in the aforementioned formula (b-1).

[0274]

As the chain alkyl group for R'^{101} which may have a substituent, the same chain alkyl groups as those described above for R^{101} in the aforementioned formula (b-1) are preferable.

As the chain alkenyl group for R'^{103} which may have a substituent, the same chain alkenyl groups as those described above for R^{101} in the aforementioned formula (b-1) are preferable.

[0275]

- Anion moiety of component (b-2)

In formula (b-2), R^{104} and R^{105} 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, and is the same as defined for R^{101} in formula (b-1). R^{104} and R^{105} may be mutually bonded 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. The smaller the number of carbon atoms of the chain-like alkyl group for R^{104} and R^{105} , the more the solubility in a resist solvent is improved. Further, in the chain alkyl group for R^{104} and R^{105} , the larger the number of hydrogen atoms being substituted with fluorine atom(s), the acid strength becomes stronger, and the transparency to a high energy beam having a wavelength of no

more than 250 nm or electron beam may be improved. The fluorination ratio of the chain-like alkyl group is preferably from 70 to 100%, more preferably from 90 to 100%, and it is particularly desirable that the chain-like alkyl group be a perfluoroalkyl group in which all hydrogen atoms are substituted with fluorine atoms.

5 In formula (b-2), V^{102} and V^{103} each independently represents a single bond, an alkylene group or a fluorinated alkylene group, and is the same as defined 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.

10 [0276]

- Anion moiety of component (b-3)

 In formula (b-3), R^{106} 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, and is the same as defined for R^{101} in
15 formula (b-1).

 In formula (b-3), L^{103} to L^{105} each independently represents a single bond, $-\text{CO}-$ or $-\text{SO}_2-$.

 [0277]

 Among these examples, as the anion moiety of the component (B), an anion for
20 the component (b-1) is preferable. Among these, a fluorinated alkylsulfonate anion or an anion represented by any one of the aforementioned general formulae (an-1) to (an-3) is more preferable, and a fluorinated alkylsulfonate anion or an anion represented by the aforementioned general formula (an-1) or (an-2) is still more preferable.

 [0278]

25 { Cation moiety }

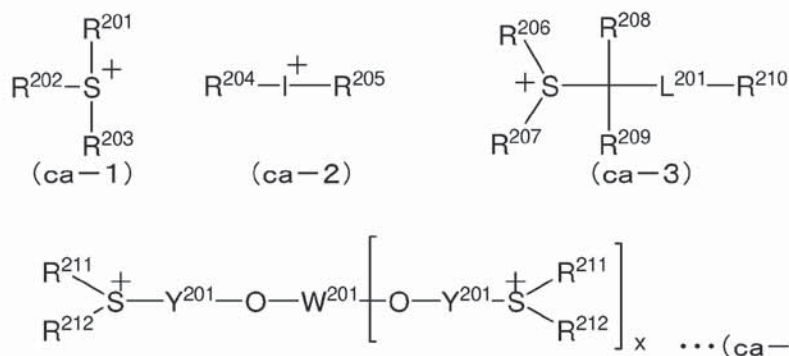
 In formulae (b-1), (b-2) and (b-3), M'^{m+} represents an m-valent onium cation. Among these, a sulfonium cation or an iodonium cation is preferable. m represents an integer of 1 or more.

 [0279]

30 Preferable examples of the cation moiety $((M'^{m+})_{1/m})$ include an organic cation represented by any of general formulae (ca-1) to (ca-4) shown below.

 [0280]

 [Chemical Formula 58]



In the formulae, R^{201} to R^{207} , R^{211} and R^{212} each independently represents an aryl group which may have a substituent, an alkyl group which may have a substituent, or an alkenyl group which may have a substituent. R^{201} to R^{203} , R^{206} and R^{207} , and R^{211} and R^{212} may be mutually bonded to form a ring with the sulfur atom. R^{208} and R^{209} each independently represents a hydrogen atom or an alkyl group of 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 an $-\text{SO}_2-$ containing cyclic group which may have a substituent. L^{201} represents $-\text{C}(=\text{O})-$ or $-\text{C}(=\text{O})-\text{O}-$. Each Y^{201} 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.

[0281]

In formulae (ca-1) to (ca-4), as the aryl group for R^{201} to R^{207} , R^{211} and R^{212} , an unsubstituted aryl group of 6 to 20 carbon atoms can be mentioned, and a phenyl group or a naphthyl group is preferable.

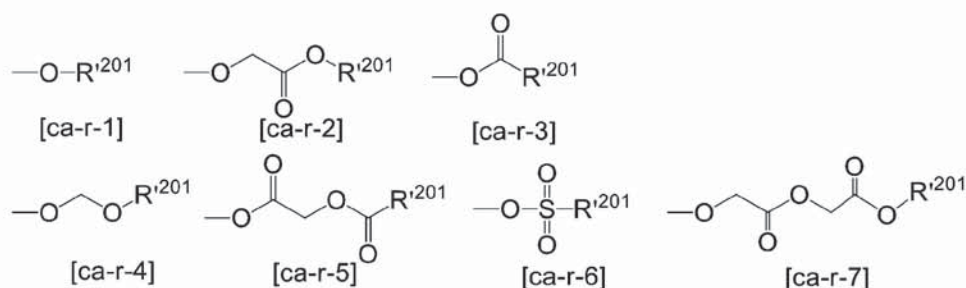
The alkyl group for R^{201} to R^{207} , R^{211} and R^{212} is preferably a chain-like or cyclic alkyl group having 1 to 30 carbon atoms.

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

Specific examples of the substituent which R^{201} to R^{207} and R^{210} to R^{212} may have 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 represented by general formulae (ca-r-1) to (ca-r-7) shown below.

[0282]

[Chemical Formula 59]



In the formulae, each R'^{201} 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.

5 [0283]

Cyclic group which may have a substituent:

The cyclic group is preferably a cyclic hydrocarbon group, and the cyclic hydrocarbon group may be either an aromatic hydrocarbon group or an aliphatic hydrocarbon group. An “aliphatic hydrocarbon group” refers to a hydrocarbon group that has no aromaticity. The aliphatic hydrocarbon group may be either saturated or unsaturated, but in general, the aliphatic hydrocarbon group is preferably saturated.

[0284]

The aromatic hydrocarbon group for R'^{201} 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, still more preferably 6 to 15 carbon atoms, and most preferably 6 to 10 carbon atoms. Here, the number of carbon atoms within a substituent(s) is not included in the number of carbon atoms of the aromatic hydrocarbon group.

Examples of the aromatic ring contained in the aromatic hydrocarbon group for R'^{201} include benzene, fluorene, naphthalene, anthracene, phenanthrene, biphenyl, or an aromatic hetero ring in which part of the carbon atoms constituting the aromatic ring has been substituted with a hetero atom. Examples of the hetero atom within the aromatic hetero rings include an oxygen atom, a sulfur atom and a nitrogen atom.

Specific examples of the aromatic hydrocarbon group for R'^{201} include a group in which 1 hydrogen atom has been removed from the aforementioned aromatic ring (an aryl group, such as a phenyl group or a naphthyl group), and a group in which 1 hydrogen atom of the aforementioned 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, a 1-naphthylethyl group, or a 2-naphthylethyl group). The alkylene group (alkyl chain within the arylalkyl group) preferably has 1 to 4 carbon atom, more preferably 1 or 2, and most preferably 1.

5 [0285]

Examples of the cyclic aliphatic hydrocarbon group for R^{'201} include aliphatic hydrocarbon groups containing a ring in the structure thereof.

As examples of the hydrocarbon group containing a ring in the structure thereof, 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
10 bonded to the terminal of the aforementioned chain-like aliphatic hydrocarbon group, and a group in which the alicyclic group is interposed within the aforementioned linear or branched aliphatic hydrocarbon group, can be given.

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

The alicyclic hydrocarbon group may be either 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 monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof
20 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 polycyclic group preferably has 7 to 30 carbon atoms. Among polycycloalkanes, a polycycloalkane having a bridged ring polycyclic skeleton, such as adamantane, norbornane, isobornane, tricyclodecane or tetracyclodecane, and a
25 polycycloalkane having a condensed ring polycyclic skeleton, such as a cyclic group having a steroid skeleton are preferable.

[0286]

Among these examples, as the cyclic aliphatic hydrocarbon group for R^{'201}, 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 or more hydrogen atoms have
30 been removed from a polycycloalkane is more preferable, an adamantyl group or a norbornyl group is still more preferable, and an adamantyl group is most preferable.

[0287]

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 most preferably 1 to 3 carbon atoms.

5 As the linear aliphatic hydrocarbon group, a linear alkylene group is preferable. 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 As the branched aliphatic hydrocarbon group, branched alkylene groups are preferred, and specific examples include various alkylalkylene groups, including 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 within the alkylalkylene group, a linear alkyl group of 1 to 5 carbon atoms is preferable.

[0288]

20 The cyclic hydrocarbon group for R^{201} may contain a hetero atom such as a heterocycle. Specific examples include lactone-containing cyclic groups represented by the aforementioned general formulae (a2-r-1) to (a2-r-7), the $-SO_2-$ containing cyclic group represented by the aforementioned formulae (a5-r-1) to (a5-r-4), and other heterocyclic groups represented by the aforementioned chemical formulae (r-hr-1) to (r-hr-16).

25 [0289]

As the substituent for the cyclic group for R^{201} , an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, a carbonyl group, a nitro group or the like can be used.

30 The alkyl group as the substituent is preferably an alkyl group of 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 particularly desirable.

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

propoxy group, n-butoxy group or tert-butoxy group, and most preferably a methoxy group or an ethoxy group.

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.

- 5 Example of the aforementioned halogenated alkyl group includes a group in which a part or all of the hydrogen atoms within an alkyl group of 1 to 5 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, an n-butyl group or a tert-butyl group) have been substituted with the aforementioned halogen atoms.

10 The carbonyl group as the substituent is a group that substitutes a methylene group ($-\text{CH}_2-$) constituting the cyclic hydrocarbon group.

[0290]

Chain alkyl group which may have a substituent:

The chain alkyl group for R^{201} may be linear or branched.

- 15 The linear alkyl group preferably has 1 to 20 carbon atoms, more preferably 1 to 15 carbon atoms, and still more preferably 1 to 10 carbon atoms. Specific examples 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 decyl group, an undecyl 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, 20 a nonadecyl group, an icosyl group, a heneicosyl group and a docosyl group.

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

[0291]

Chain alkenyl group which may have a substituent:

- 30 The chain alkenyl group for R^{201} may be linear or branched, and preferably has 2 to 10 carbon atoms, more preferably 2 to 5 carbon atoms, still more preferably 2 to 4 carbon atoms, and most preferably 3 carbon atoms. Examples of linear alkenyl groups include a vinyl group, a propenyl group (an allyl group) and a butynyl group. Examples of branched alkenyl groups include a 1-methylvinyl group, a 2-methylvinyl group, a 1-methylpropenyl

group and a 2-methylpropenyl group.

Among these 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 most preferable.

5 [0292]

As the substituent for the chain-like alkyl group or alkenyl group for 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 for R^{201} or the like may be used.

[0293]

10 As the cyclic group which may have a substituent, the chain alkyl group which may have a substituent and the chain alkenyl group which may have a substituent for R^{201} , the same groups as those described above may be mentioned. As the cyclic group which may have a substituent and chain alkyl group which may have a substituent, the same groups as those described above for the acid dissociable group represented by the
15 aforementioned formula (a1-r-2) may be also mentioned.

[0294]

Among these 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. Specifically, for example, a phenyl group, a naphthyl group, a group in which
20 one or more hydrogen atoms have been removed from a polycycloalkane, a lactone-containing cyclic group represented by any one of the aforementioned formula (a2-r-1) to (a2-r-7), and an $-SO_2-$ containing cyclic group represented by any one of the aforementioned formula (a5-r-1) to (a5-r-4) are preferable.

[0295]

25 In general formulae (ca-1) to (ca-4), in the case where R^{201} to R^{203} , R^{206} , R^{207} , R^{211} and R^{212} are mutually bonded to form a ring with the sulfur atom, these groups may be mutually bonded 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 $-N(R_N)-$ (wherein R_N represents an alkyl group of 1 to 5 carbon atoms). The
30 ring containing the sulfur atom in the skeleton thereof is preferably a 3 to 10-membered ring, and most preferably a 5 to 7-membered ring. Specific examples of the ring 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 phenoxathiin ring, a tetrahydrothiophenium ring, and a tetrahydrothiopyranium ring.

[0296]

R^{208} and R^{209} each independently represents a hydrogen atom or an alkyl group of 1 to 5 carbon atoms, preferably a hydrogen atom or an alkyl group of 1 to 3 carbon atoms, and when R^{208} and R^{209} each represents an alkyl group, R^{208} and R^{209} may be mutually bonded to form a ring.

[0297]

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 an $-SO_2-$ containing cyclic group which may have a substituent.

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

As the alkyl group for R^{210} , a chain-like or cyclic alkyl group having 1 to 30 carbon atoms is preferable.

The alkenyl group for R^{210} preferably has 2 to 10 carbon atoms. As the $-SO_2-$ -containing cyclic group for R^{210} which may have a substituent, an " $-SO_2-$ -containing polycyclic group" is preferable, and a group represented by the aforementioned general formula (a5-r-1) is more preferable.

[0298]

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

Examples of the arylene group for Y^{201} include groups in which one hydrogen atom has been removed from an aryl group given as an example of the aromatic hydrocarbon group for R^{101} in the aforementioned formula (b-1).

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

[0299]

In the formula (ca-4), x represents 1 or 2.

W^{201} represents a linking group having a valency of $(x + 1)$, i.e., a divalent or trivalent linking group.

As the divalent linking group for W^{201} , a divalent hydrocarbon group which may have a substituent is preferable, and as examples thereof, the same hydrocarbon groups

(which may have a substituent) as those described above for Y^{21} in the general formula (a2-1) can be mentioned. The divalent linking group for 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
 5 include a phenylene group and a naphthylene group, and a phenylene group is particularly desirable.

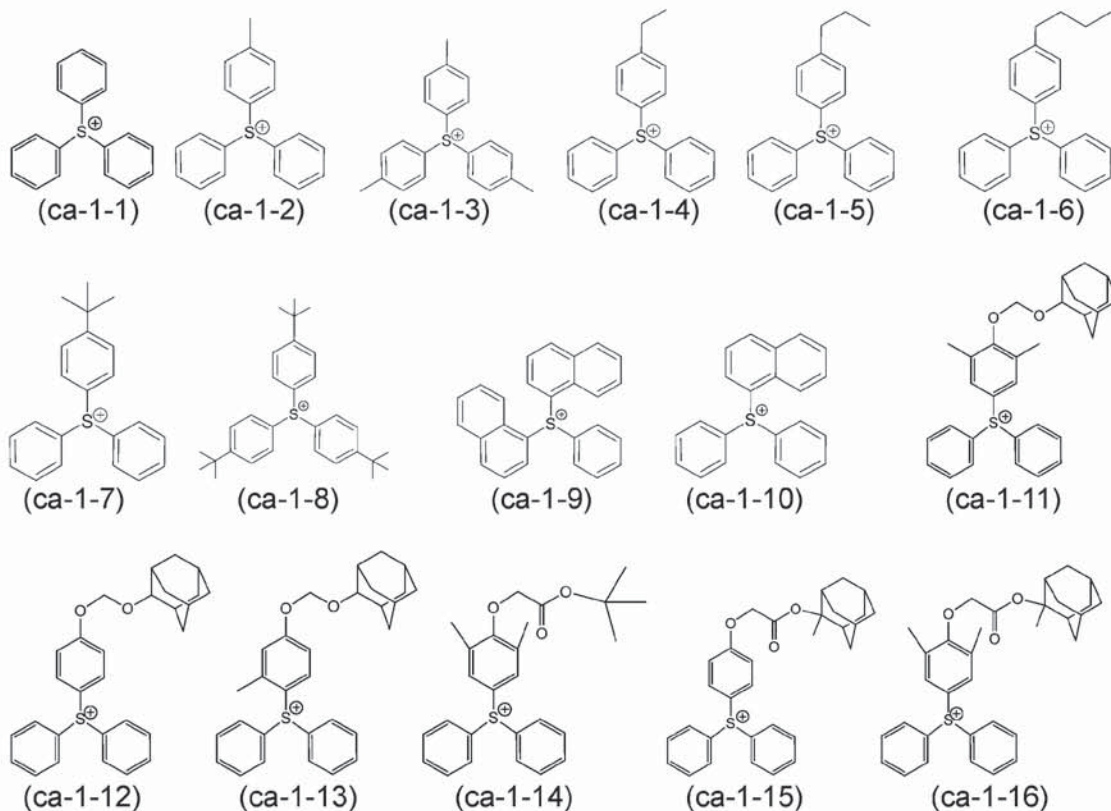
As the trivalent linking group for W^{201} , a group in which one hydrogen atom has been removed from the aforementioned divalent linking group for W^{201} and a group in which the divalent linking group has been bonded to another divalent linking group can be
 10 mentioned. The trivalent linking group for W^{201} is preferably a group in which 2 carbonyl groups are bonded to an arylene group.

[0300]

Specific examples of preferable cations represented by formula (ca-1) include cations represented by chemical formulae (ca-1-1) to (ca-1-70) shown below.

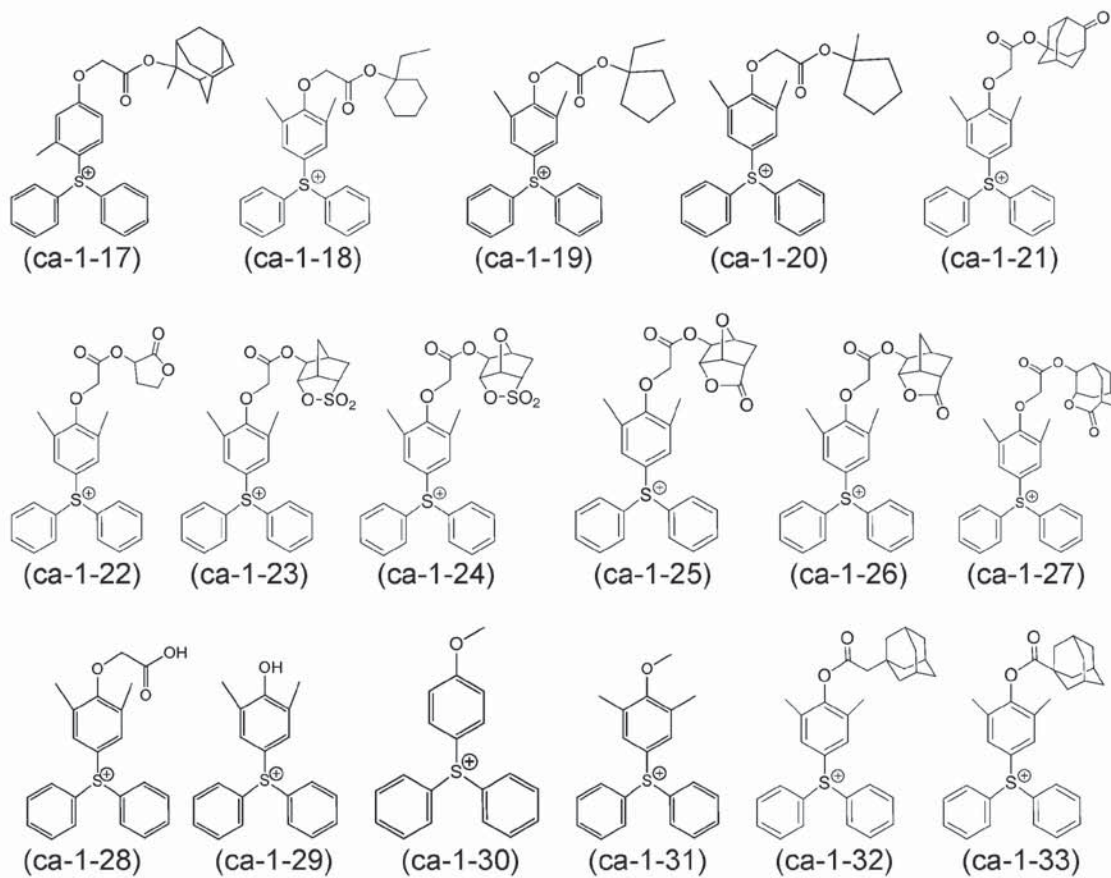
15 [0301]

[Chemical Formula 60]



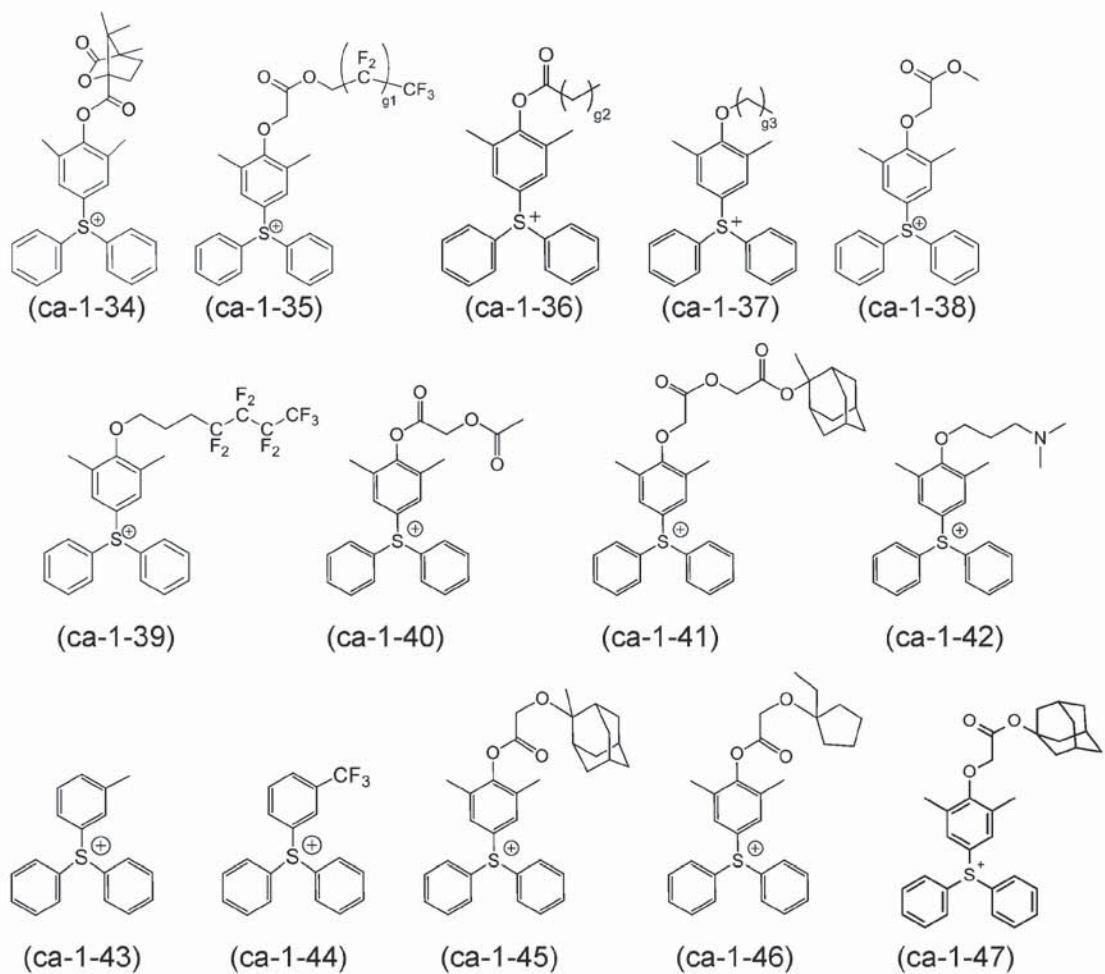
[0302]

[Chemical Formula 61]



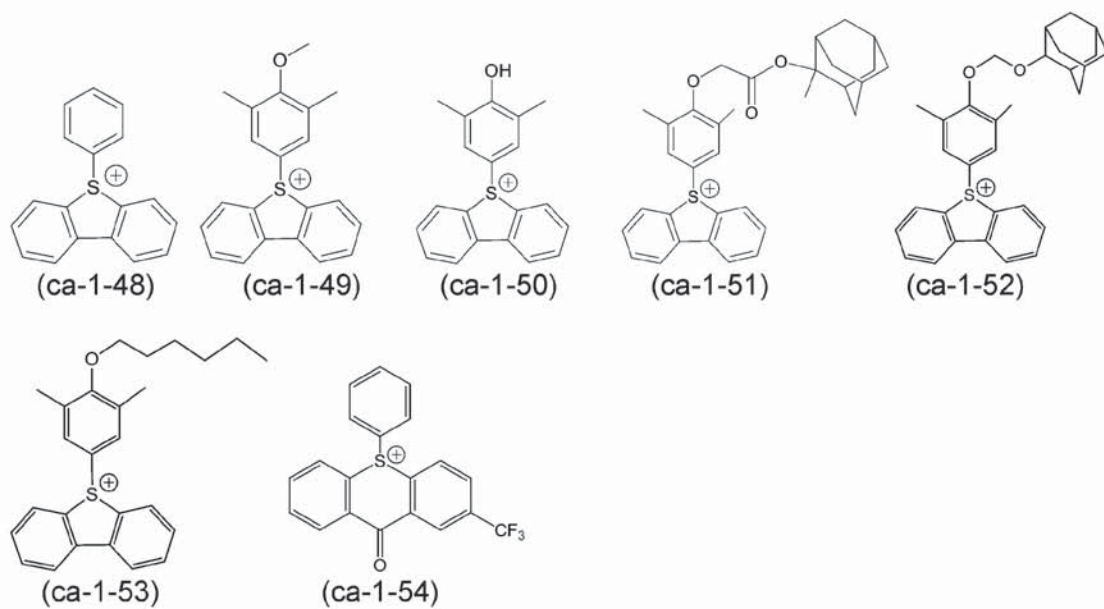
[0303]

[Chemical Formula 62]



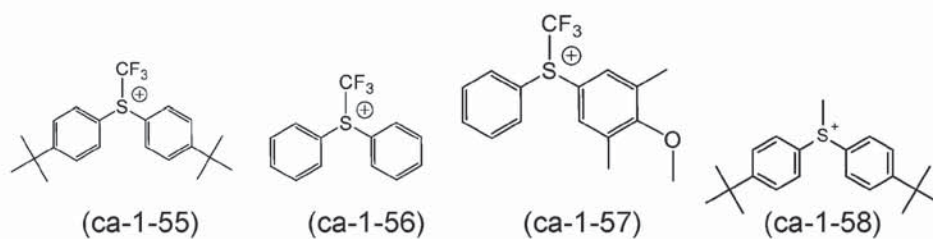
In the formulae, g1, g2 and g3 represent recurring numbers, wherein g1 is an integer of 1 to 5, g2 is an integer of 0 to 20, and g3 is an integer of 0 to 20.

[0304]



[0305]

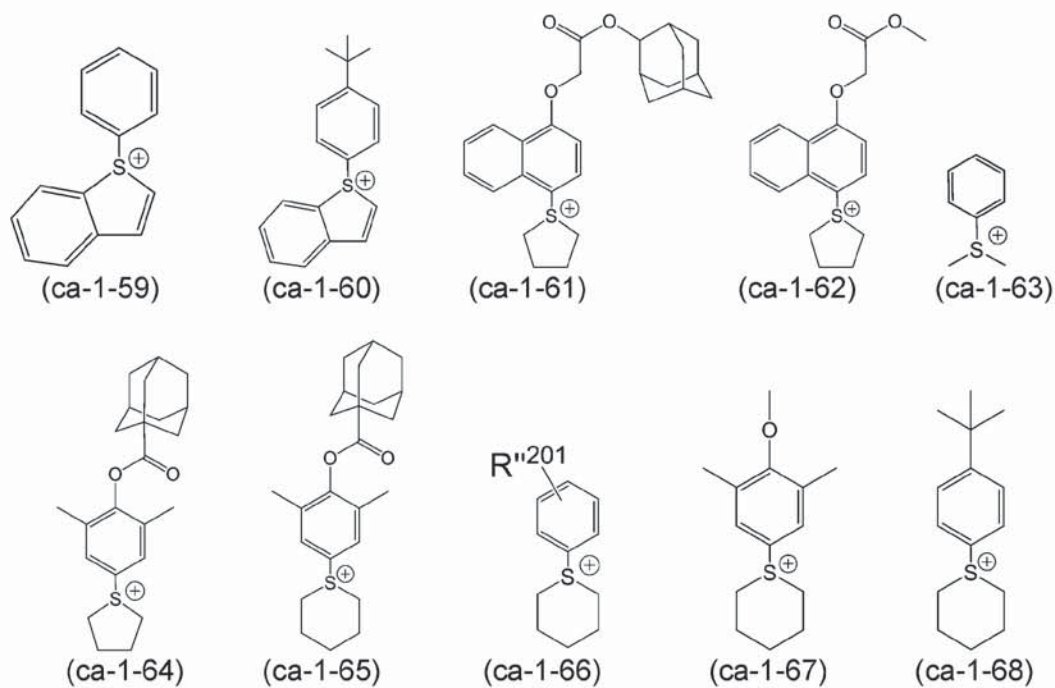
[Chemical Formula 64]



5

[0306]

[Chemical Formula 65]



In the formulae, R^{201} represents a hydrogen atom or a substituent, and as the substituent, the same groups as those described above for substituting R^{201} to R^{207} and R^{210} to R^{212} can be mentioned.

5 [0307]

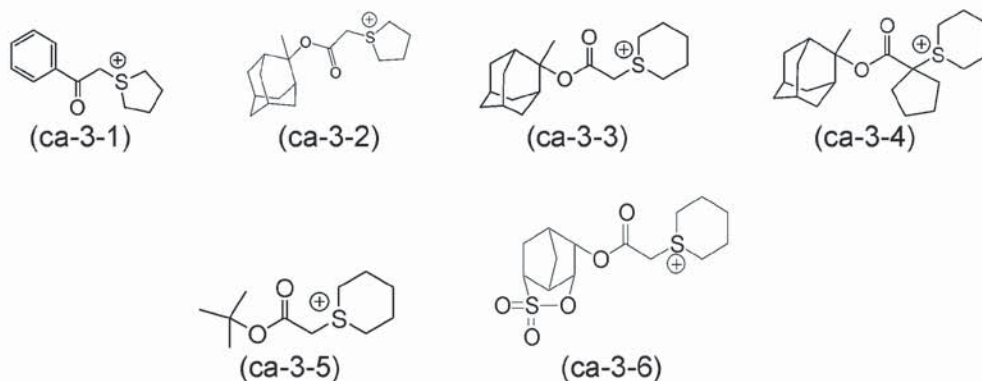
Specific examples of preferable cations represented by the formula (ca-2) include a diphenyliodonium cation and a bis(4-tert-butylphenyl)iodonium cation.

[0308]

Specific examples of preferable cations represented by formula (ca-3) include
 10 cations represented by formulae (ca-3-1) to (ca-3-6) shown below.

[0309]

[Chemical Formula 66]

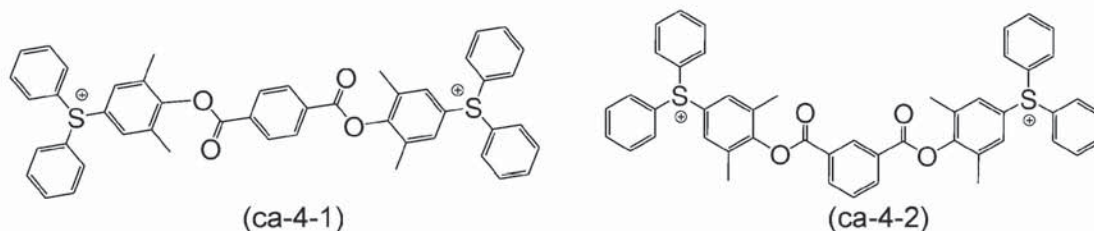


[0310]

Specific examples of preferable cations represented by formula (ca-4) include cations represented by formulae (ca-4-1) and (ca-4-2) shown below.

5 [0311]

[Chemical Formula 67]



[0312]

Among these examples, as the cation moiety $((M^{m+})_{1/m})$, a cation represented by
 10 general formula (ca-1) is preferable. In terms of maintaining the transparency of the thick-film resist film, in general formula (ca-1), it is preferable that at least one of R^{202} and R^{203} is an alkyl group or an alkenyl group, it is more preferable that 2 or more of R^{202} and R^{203} is an alkyl group or an alkenyl group, and it is still more preferable that 2 or more of R^{202} and R^{203} is an alkyl group. In the case where 2 or more of R^{202} and R^{203} is an alkyl group
 15 or an alkenyl group, R^{202} and R^{203} may be mutually bonded to form a ring together with the sulfur atom in the formula. As a cation represented by general formula (ca-1), a cation represented by any one of the aforementioned formulae (ca-1-55) to (ca-1-68) is preferable, and a cation represented by any one of the aforementioned formulae (ca-1-63) to (ca-1-68) is more preferable.

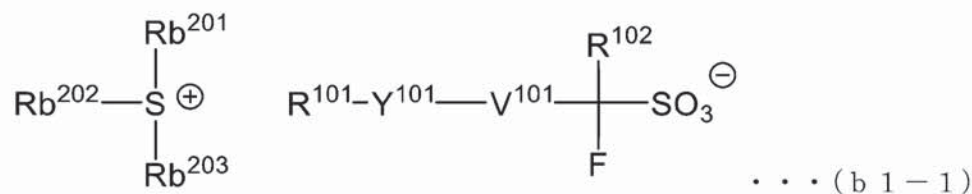
20 [0313]

Among the above examples, as the component (B1), a compound represented by

general formula (b1-1) shown below is most preferable.

[0314]

[Chemical Formula 68]



- 5 In the formula, Rb^{201} represents an aryl group which may have a substituent; Rb^{202} and Rb^{203} each independently represents an alkyl group which may have a substituent or an alkenyl group which may have a substituent; Rb^{202} and Rb^{203} may be mutually bonded to form a ring with the sulfur atom in the formula; R^{101} represent a cyclic group which may have a substituent, a chain alkyl group which may have a substituent or a chain alkenyl group which may have a substituent; R^{102} represents a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms; Y^{101} represents a single bond or a divalent group containing an oxygen atom; and V^{101} represents a single bond, an alkylene group or a fluorinated alkylene group.

[0315]

- 15 In formula (b1-1), the aryl group (which may have a substituent) represented by Rb^{201} is the same as defined for the aryl group (which may have a substituent) represented by R^{201} in the aforementioned formula (ca-1). Among these examples, as Rb^{201} , a phenyl group or a benzyl group is preferable, and a phenyl group is more preferable.

- 20 In formula (b1-1), the aryl group or alkyl group (which may have a substituent) represented by Rb^{202} or Rb^{203} is the same as defined for the aryl group or alkyl group (which may have a substituent) represented by R^{202} or R^{203} in the aforementioned formula (ca-1). Among these examples, as Rb^{202} and Rb^{203} , a linear alkyl group having 1 to 5 carbon atoms is preferable, and it is more preferable that Rb^{202} and Rb^{203} are mutually bonded to form a 5-membered ring or a 6 membered ring together with the sulfur atom in the formula.

- 25 In formula (b1-1), R^{101} , R^{102} , Y^{101} and V^{101} are the same as defined for R^{101} , R^{102} , Y^{101} and V^{101} in the aforementioned formula (b-1).

[0316]

- Component (B2)

The component (B) may contain an acid-generator component which does not fall

under the definition of the component (B1) (hereafter, sometimes referred to as "component (B2)"). The component (B2) is not particularly limited, as long as it is capable of generating acid upon exposure, and which does not fall under the definition of the component (B1), and may be arbitrarily selected from conventional compounds. Examples of the component (B2) include oxime sulfonate acid generators; diazomethane acid generators such as bisalkyl or bisaryl sulfonyl diazomethanes and poly(bis-sulfonyl)diazomethanes; nitrobenzylsulfonate acid generators; iminosulfonate acid generators; and disulfone acid generators.

[0317]

10 In the resist composition of the present embodiment, as the component (B), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

When the resist composition contains the component (B), the amount of the component (B) relative to 100 parts by weight of the component (A) is preferably less than 15 50 parts by weight, more preferably 0.1 to 40 parts by weight, and still more preferably 0.3 to 25 parts by weight.

When the amount of the component (B) is within the above-mentioned preferable range, a pattern may be satisfactorily formed. Further, by virtue of the above-mentioned range, when each of the components are dissolved in an organic solvent, a homogeneous 20 solution may be more reliably obtained and the storage stability of the resist composition becomes satisfactory.

[0318]

«Basic component (D)»

The resist composition of the present embodiment may contain, in addition to the 25 aforementioned components (A) and (Z), a basic component (component (D)) which is capable of trapping acid generated upon exposure (i.e., capable of controlling diffusion of acid). The component (D) functions as an acid diffusion control agent, i.e., a quencher which traps the acid generated in the resist composition upon exposure.

Examples of the component (D) include a photodecomposable base (D1) 30 (hereafter, referred to as "component (D1)") which is decomposed upon exposure and then loses the ability of controlling of acid diffusion, and a nitrogen-containing organic compound (D2) (hereafter, referred to as "component (D2)") which does not fall under the definition of component (D1). Among these examples, in terms of maintaining the

sensitivity of the thick-film resist film, a nitrogen-containing organic compound (D2) (component (D2)) is preferable. Among component (D2), in terms of maintaining the transparency of the thick-film resist film, a chain alkylamine is more preferable.

[0319]

5 - Component (D1)

When a resist pattern is formed using a resist composition containing the component (D1), the contrast between exposed portions and unexposed portions of the resist film is further improved. The component (D1) is not particularly limited, as long as it is decomposed upon exposure and then loses the ability of controlling of acid diffusion.

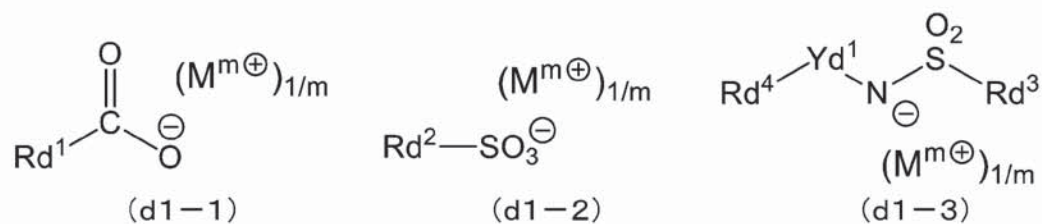
10 As the component (D1), at least one compound selected from the group consisting of a compound represented by general formula (d1-1) shown below (hereafter, referred to as “component (d1-1)”), a compound represented by general formula (d1-2) shown below (hereafter, referred to as “component (d1-2)”) and a compound represented by general formula (d1-3) shown below (hereafter, referred to as “component (d1-3)”) is preferably used.

At exposed portions of the resist film, the components (d1-1) to (d1-3) are decomposed and then lose the ability of controlling of acid diffusion (i.e., basicity), and therefore the components (d1-1) to (d1-3) cannot function as a quencher, whereas at unexposed portions of the resist film, the components (d1-1) to (d1-3) functions as a

20 quencher.

[0320]

[Chemical Formula 69]



In the formulae, Rd¹ to Rd⁴ represent a cyclic group which may have a substituent, a chain alkyl group which may have a substituent or a chain alkenyl group which may have a substituent, provided that, the carbon atom adjacent to the sulfur atom within the Rd² in the 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 more; and each M^{m+} independently represents an organic cation having a valency of m.

25

[0321]

{Component (d1-1)}

- Anion moiety

In formula (d1-1), Rd^1 represents a cyclic group which may have a substituent, a chain alkyl group which may have a substituent or a chain alkenyl group which may have a substituent, and is the same groups as those defined above for R^{201} .

Among these, as the group for Rd^1 , 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 for these groups include a hydroxy group, an oxo group, an alkyl group, an aryl group, a fluorine atom, a fluorinated alkyl group, a lactone-containing cyclic group represented by any one of the aforementioned formulae (a2-r-1) to (a2-r-7), an ether bond, an ester bond, and a combination thereof. In the case where an ether bond or an ester bond is included as the substituent, the substituent may be bonded via an alkylene group, and a linking group represented by any one of the aforementioned formulae (y-al-1) to (y-al-5) is preferable as the substituent.

Preferable examples of the aromatic hydrocarbon group include a phenyl group, a naphthyl group, and a polycyclic structure containing a bicyclooctane skeleton (a polycyclic structure constituted of a bicyclooctane skeleton and a ring structure other than bicyclooctane).

Examples of the aliphatic cyclic group include groups in which one or more hydrogen atoms have been removed from a polycycloalkane such as adamantane, norbornane, isobornane, tricyclodecane or tetracyclododecane.

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 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.

[0322]

In the case where the chain-like alkyl group is a fluorinated alkyl group having a fluorine atom or a fluorinated alkyl group, 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 fluorine. Examples of the atom other than fluorine include an oxygen atom, a sulfur atom and a nitrogen atom.

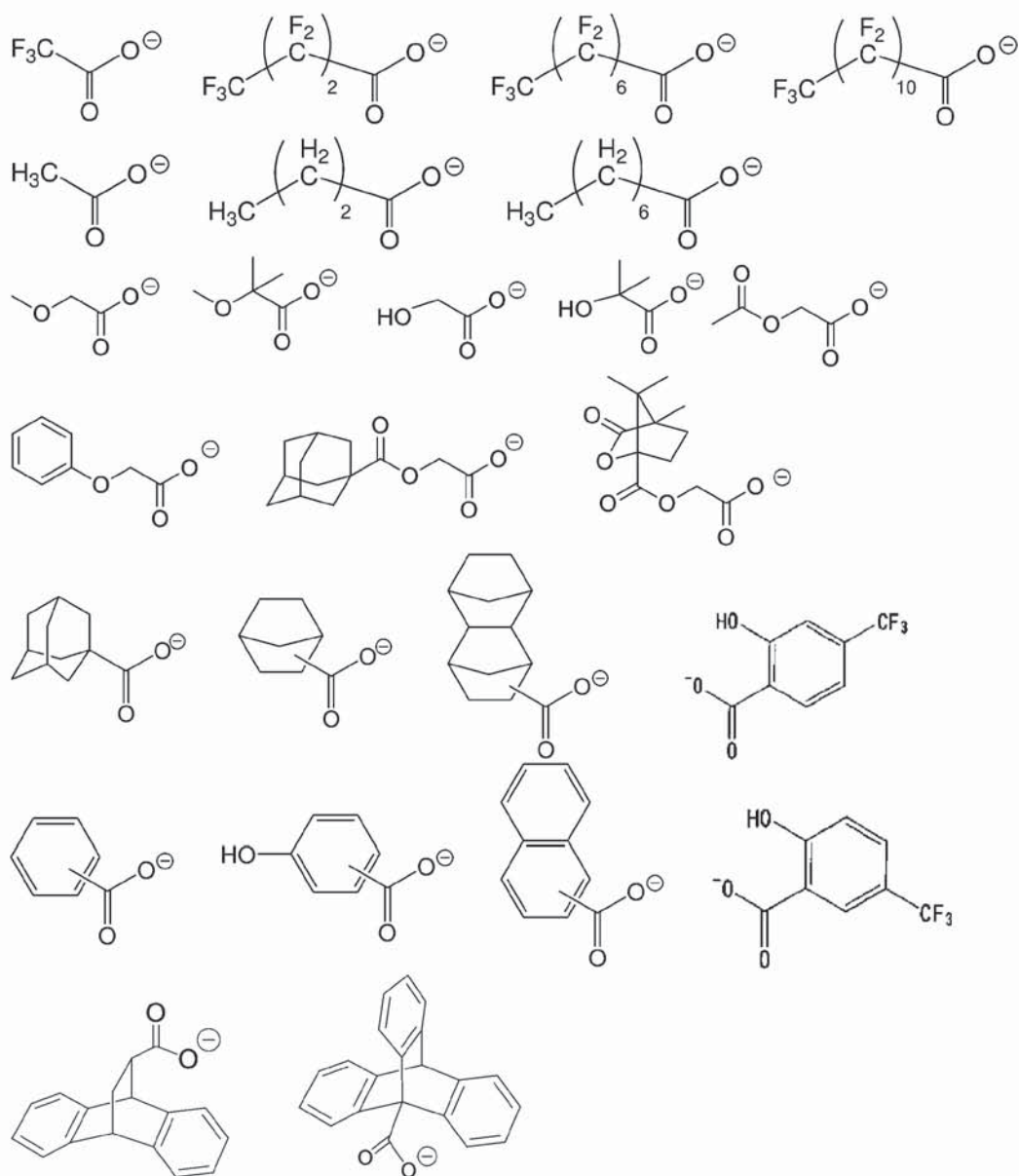
- 5 As Rd¹, a fluorinated alkyl group in which part or all of the hydrogen atoms constituting a linear alkyl group have been substituted with fluorine atom(s) is preferable, and a fluorinated alkyl group in which all of the hydrogen atoms constituting a linear alkyl group have been substituted with fluorine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

- 10 [0323]

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

[0324]

[Chemical Formula 70]



[0325]

- Cation moiety

In formula (d1-1), M^{m+} represents an organic cation having a valency of m.

- 5 As the organic cation for M^{m+} , for example, the same cation moieties as those represented by the aforementioned formulae (ca-1) to (ca-4) are preferable, cation moieties represented by the aforementioned general formulae (ca-1) is preferable, and cation moieties represented by the aforementioned formulae (ca-1-1) to (ca-1-70) are still more preferable.

As the component (d1-1), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

[0326]

{Component (d1-2)}

5 - Anion moiety

In formula (d1-2), Rd^2 represents a cyclic group which may have a substituent, a chain alkyl group which may have a substituent or a chain alkenyl group which may have a substituent, and is the same groups as those defined above for R'^{201} .

10 However, the carbon atom adjacent to the sulfur atom within the Rd^2 has no fluorine atom bonded thereto. 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, tetracyclododecane or camphor (which may have a substituent) is more preferable.

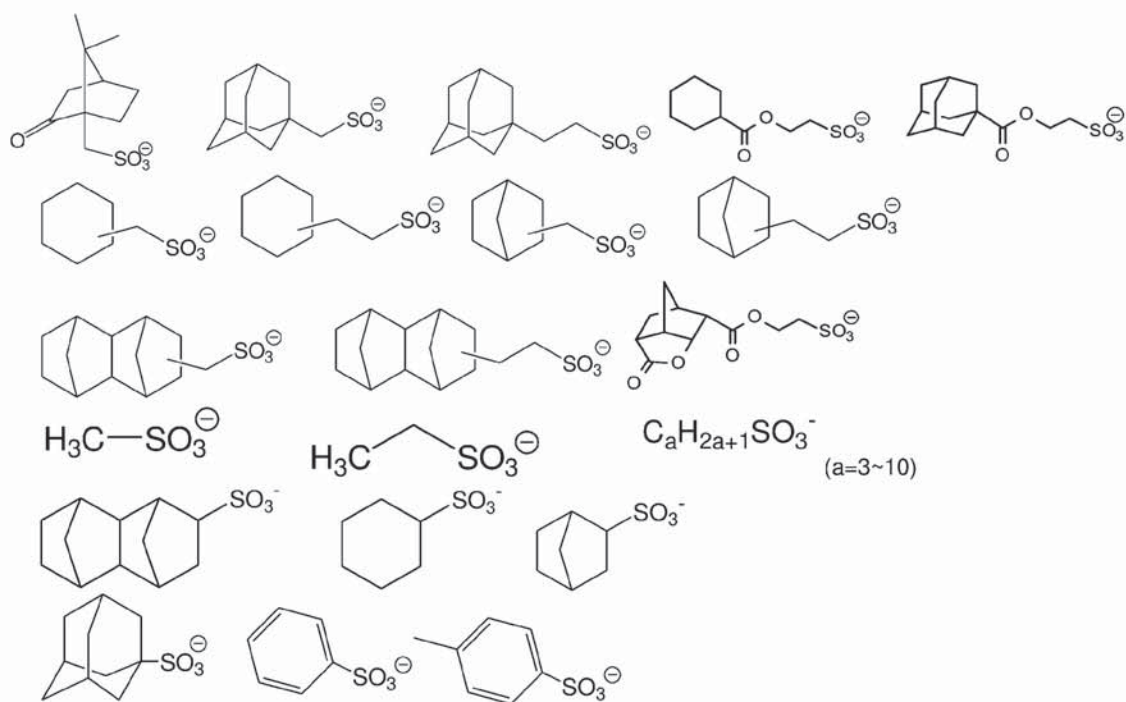
20 The hydrocarbon group for Rd^2 may have a substituent. As the substituent, the same groups as those described above for substituting the hydrocarbon group (e.g., aromatic hydrocarbon group, aliphatic cyclic group, chain-like alkyl group) for Rd^1 in the formula (d1-1) can be mentioned.

[0327]

25 Specific examples of preferable anion moieties for the component (d1-2) are shown below.

[0328]

[Chemical Formula 71]



[0329]

- Cation moiety

In formula (d1-2), M^{m+} is an organic cation having a valency of m, and is the same as defined for M^{m+} in the aforementioned formula (d1-1).

As the component (d1-2), one type of compound may be used, or two or more types of compounds may be used in combination.

[0330]

{Component (d1-3)}

10

- 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 is the same groups as those defined above for R^{*201} , and a cyclic group containing a fluorine atom, a chain alkyl group or a chain alkenyl group is preferable. Among these, a fluorinated alkyl group is preferable, and more preferably the same fluorinated alkyl groups as those described above for Rd^1 .

15

[0331]

In formula (d1-3), Rd^4 represents a cyclic group which may have a substituent, a chain alkyl group which may have a substituent or a chain alkenyl group which may have

a substituent, and is the same groups as those defined above for R'^{201} .

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

5 The alkyl group for Rd^4 is preferably a linear or branched alkyl group of 1 to 5 carbon atoms, and specific examples 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. Part of the hydrogen atoms within the alkyl group for Rd^4 may be substituted with a hydroxy group, a cyano group or the like.

10 The alkoxy group for Rd^4 is preferably an alkoxy group of 1 to 5 carbon atoms, and specific examples thereof 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.

[0332]

15 The alkenyl group for Rd^4 is the same as defined for the alkenyl group for R'^{201} , and a vinyl group, a propenyl group (an allyl group), a 1-methylpropenyl group or a 2-methylpropenyl group is preferable. These groups may have an alkyl group of 1 to 5 carbon atoms or a halogenated alkyl group of 1 to 5 carbon atoms as a substituent.

[0333]

20 As the cyclic group for Rd^4 , the same groups as those described above for R'^{201} may be mentioned. Among these, as the cyclic group, an alicyclic group (e.g., a group in 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 (e.g., a phenyl group or a naphthyl group) is
25 preferable. When Rd^4 is an alicyclic group, the resist composition can be satisfactorily dissolved in an organic solvent, thereby improving the lithographic properties. Alternatively, when Rd^4 is an aromatic group, the resist composition exhibits an excellent photoabsorption efficiency in a lithography process using EUV or the like as the exposure source, thereby resulting in the improvement of the sensitivity and the lithographic
30 properties.

[0334]

In formula (d1-3), Yd^1 represents a single bond or a divalent linking group.

The divalent linking group for Yd^1 is not particularly limited, and examples

thereof include a divalent hydrocarbon group (aliphatic hydrocarbon group, or 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 defined for the divalent hydrocarbon group which may have a substituent and the divalent linking group containing
 5 a hetero atom explained above as the divalent linking group for Y_a^{21} in the aforementioned formula (a2-1).

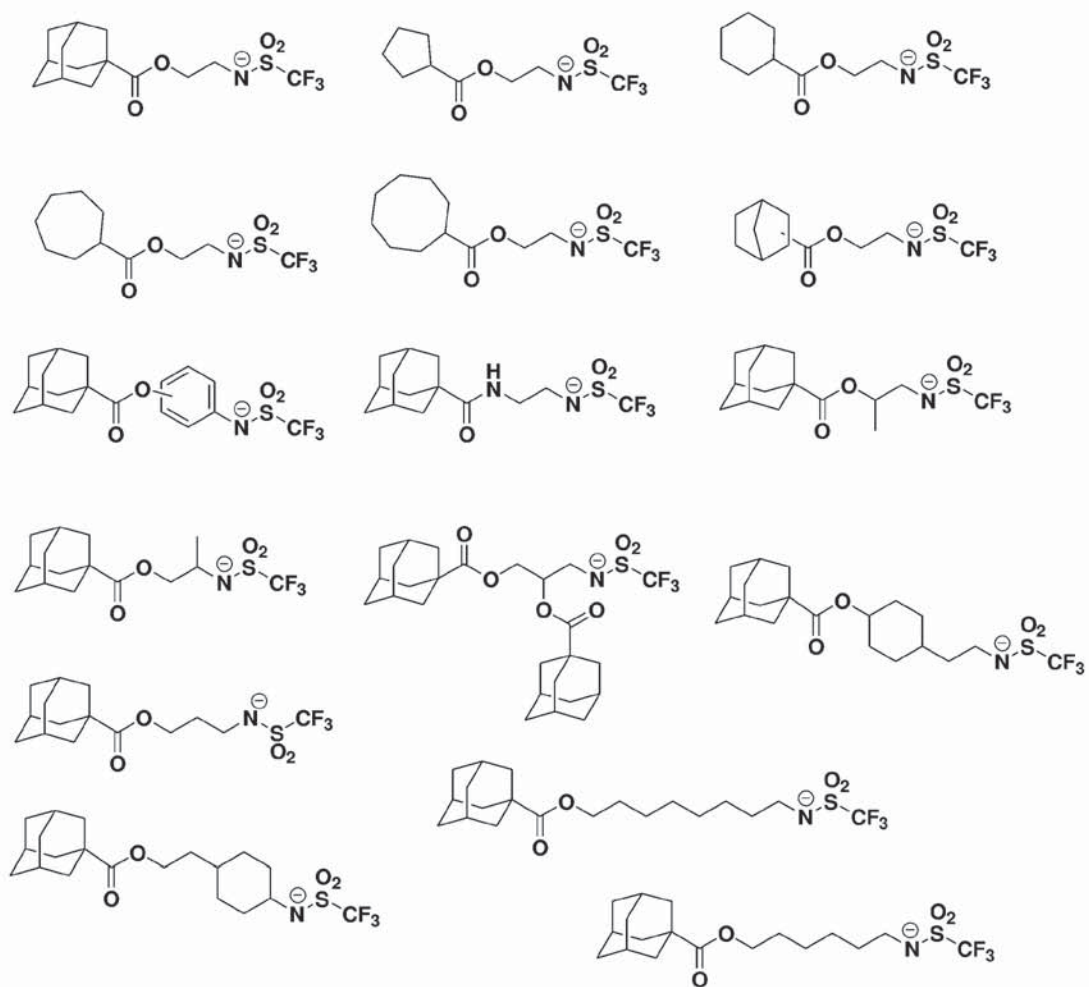
As Y_d^1 , a carbonyl group, an ester bond, an amide bond, an alkylene group or a combination of these is preferable. As the alkylene group, a linear or branched alkylene group is more preferable, and a methylene group or an ethylene group is still more
 10 preferable.

[0335]

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

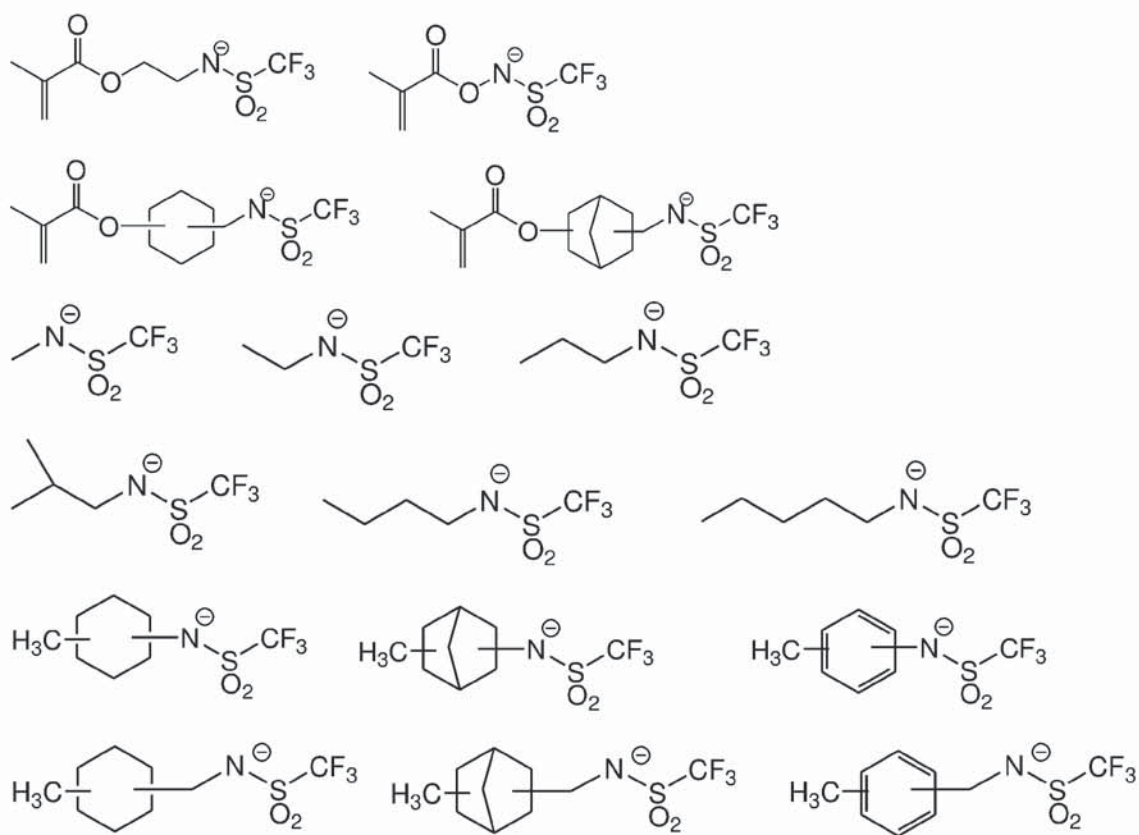
[0336]

15 [Chemical Formula 72]



[0337]

[Chemical Formula 73]



[0338]

- Cation moiety

In formula (d1-3), M^{m+} is an organic cation having a valency of m, and is the same as defined for M^{m+} in the aforementioned formula (d1-1).

As the component (d1-3), one type of compound may be used, or two or more types of compounds may be used in combination.

[0339]

As the component (D1), one type of the aforementioned components (d1-1) to (d1-3), or at least two types of the aforementioned components (d1-1) to (d1-3) can be used in combination.

In the case where the resist composition contains the component (D1), the amount of the component (D1) relative to 100 parts by weight of the component (A) is preferably within a range from 0.5 to 20 parts by weight, more preferably from 1 to 15 parts by weight, and still more preferably from 5 to 10 parts by weight.

When the amount of the component (D1) is at least as large as the lower limit of the above-mentioned range, excellent lithographic properties and excellent resist pattern

shape may be more reliably obtained. On the other hand, when the amount of the component (D1) is no more than the upper limit of the above-mentioned range, sensitivity can be maintained at a satisfactory level, and through-put becomes excellent.

[0340]

5 Production method of 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 conventional methods.

Further, the production method of the component (d1-3) is not particularly limited, and the component (d1-3) can be produced in the same manner as disclosed in

10 US2012-0149916.

[0341]

- Component (D2)

The component (D) preferably contains a nitrogen-containing organic compound (D2) (hereafter, referred to as component (D2)) which does not fall under the definition of
15 component (D1).

The component (D2) is not particularly limited, as long as it functions as an acid diffusion control agent, and does not fall under the definition of the component (D1). As the component (D2), any of the conventionally known compounds may be selected for use. Among these, an aliphatic amine is preferable, and a secondary aliphatic amine or tertiary
20 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 (NH₃) has been substituted with an alkyl group or hydroxyalkyl group
25 of no more than 12 carbon atoms (i.e., 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,
30 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 desirable.

[0342]

- 5 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).

10 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.

[0343]

- 15 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.

20 [0344]

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

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

25 [0345]

- As the component (D2), in terms of maintaining the transparency of the thick-film resist film, an aliphatic amine is preferable, a chain aliphatic amine is more preferable, and a chain alkylamine is still more preferable. The chain alkyl group within the chain alkylamine preferable has 5 to 10 carbon atoms. Among the above examples, a dialkylamine or a trialkylamine containing a linear alkyl group having 5 to 10 carbon atoms is preferable, and a trialkylamine is more preferable.
- 30

[0346]

As the component (D2), one kind of compound may be used, or two or more kinds

of compounds may be used in combination. When the resist composition contains the component (D2), the amount of the component (D2) is typically used in an amount within a range from 0.005 to 5 parts by weight, relative to 100 parts by weight of the component (A). When the amount of the component (D) is within the above-mentioned range, the shape of the resist pattern and the post exposure stability of the latent image formed by the pattern-wise exposure of the resist layer are improved.

[0347]

<<At least one compound (E) selected from the group consisting of an organic carboxylic acid, or a phosphorus oxo acid or derivative thereof>>

In the resist composition of the present embodiment, for preventing any deterioration in sensitivity, and improving the resist pattern shape and the post exposure stability of the latent image formed by the pattern-wise exposure of the resist layer, at least one compound (E) (hereafter referred to as the component (E)) selected from the group consisting of an organic carboxylic acid, or a phosphorus oxo acid or derivative thereof may be added.

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 acids include phosphoric acid, phosphonic acid and phosphinic acid. Among these, phosphonic acid is particularly desirable.

Examples of oxo acid derivatives include esters in which a hydrogen atom within the above-mentioned oxo acids is substituted with a hydrocarbon group. Examples of the hydrocarbon group include an alkyl group of 1 to 5 carbon atoms and an aryl group of 6 to 15 carbon atoms.

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

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.

In the resist composition of the present embodiment, as the component (E), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

When the resist composition contains the component (E), the amount of the component (E) is typically used in an amount within a range from 0.01 to 5 parts by weight, relative to 100 parts by weight of the component (A).

[0348]

5 <<Fluorine additive (F)>>

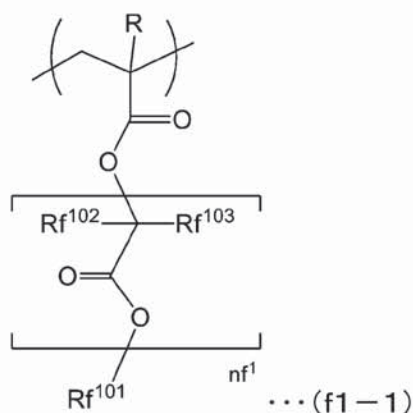
In the present embodiment, the resist composition may further include a fluorine additive (hereafter, referred to as "component (F)") for imparting water repellency to the resist film, or improving lithography properties.

As the component (F), for example, a fluorine-containing polymeric compound
10 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 Unexamined Patent Application, First Publication No. 2011-128226 can be used.

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

[0349]

25 [Chemical Formula 74]



In the formula, R is the same as defined above; Rf^{102} and Rf^{103} each independently represents a hydrogen atom, a halogen atom, an alkyl group of 1 to 5 carbon atoms, or a halogenated alkyl group of 1 to 5 carbon atoms, provided that Rf^{102} and Rf^{103} may be the same or different; nf^1 represents an integer of 1 to 5; and Rf^{101} represents an organic group containing a fluorine atom.

[0350]

In formula (f1-1), R bonded to the carbon atom on the α -position is the same as defined above. As R, a hydrogen atom or a methyl group is preferable.

In formula (f1-1), examples of the halogen atom for 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 desirable. Examples of the alkyl group of 1 to 5 carbon atoms for Rf^{102} and Rf^{103} include the same alkyl group of 1 to 5 carbon atoms as those described above for R, and a methyl group or an ethyl group is preferable. Specific examples of the halogenated alkyl group of 1 to 5 carbon atoms represented by Rf^{102} or Rf^{103} include groups in which part or all of the hydrogen atoms of the aforementioned 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 desirable. Among these, as Rf^{102} and Rf^{103} , a hydrogen atom, a fluorine atom or an alkyl group of 1 to 5 carbon atoms is preferable, and a hydrogen atom, a fluorine atom, a methyl group or an ethyl group is more preferable.

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

[0351]

In formula (f1-1), Rf^{101} represents an organic group containing a fluorine atom,

and is preferably a hydrocarbon group containing a fluorine atom.

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 most preferably 1 to 10 carbon atoms.

5 It is preferable that the hydrocarbon group having a fluorine atom has 25% or more of the hydrogen atoms within the hydrocarbon group fluorinated, more preferably 50% or more, and most preferably 60% or more, as the hydrophobicity of the resist film during immersion exposure is enhanced.

Among these, as Rf¹⁰¹, a fluorinated hydrocarbon group of 1 to 6 carbon atoms is
10 preferable, and a trifluoromethyl group, -CH₂-CF₃, -CH₂-CF₂-CF₃, -CH(CF₃)₂, -CH₂-CH₂-CF₃, and -CH₂-CH₂-CF₂-CF₂-CF₃ are most preferable.

[0352]

The weight average molecular weight (Mw) (the polystyrene equivalent value determined by gel permeation chromatography) of the component (F) is preferably 1,000
15 to 50,000, more preferably 5,000 to 40,000, and most preferably 10,000 to 30,000. When the weight average molecular weight (Mw) is no more than the upper limit of the above-mentioned range, the resist may exhibit satisfactory solubility in a resist solvent. On the other hand, when the weight average molecular weight (Mw) is at least as large as the lower limit of the above-mentioned range, the water repellency of the resist film may
20 become satisfactory.

Further, the dispersity (Mw/Mn) of the component (F) is preferably 1.0 to 5.0, more preferably 1.0 to 3.0, and most preferably 1.0 to 2.5.

[0353]

In the resist composition of the present embodiment, as the component (F), one
25 kind of compound may be used, or two or more kinds of compounds may be used in combination.

When the resist composition contains the component (F), the component (F) is used in an amount within a range from 0.5 to 10 parts by weight, relative to 100 parts by weight of the component (A).

30 [0354]

<<Organic solvent (S)>>

The resist composition of the present embodiment may be prepared by dissolving the resist materials for the resist composition in an organic solvent (hereafter, referred to

as "component (S)").

The component (S) may be any organic solvent which can dissolve the respective components to give a homogeneous solution, and any organic solvent can be appropriately selected from those which have been conventionally known as solvents for a chemically amplified resist composition.

Examples thereof include lactones such as γ -butyrolactone; 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 including compounds having an ether bond, such as a monoalkylether (e.g., 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 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 dimethylsulfoxide (DMSO).

In the resist composition of the present embodiment, as the component (S), one kind of solvent may be used, or two or more kinds of compounds may be used as a mixed solvent. Among these examples, at least one member selected from the group consisting of PGMEA, PGME, γ -butyrolactone, EL, butyl acetate and cyclohexanone is preferable, and at least one member selected from the group consisting of PGMEA, PGME and butyl acetate is more preferable.

[0355]

Further, as the component (S), a mixed solvent obtained by mixing PGMEA with a polar solvent is preferable. The mixing ratio (weight 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, more preferably from 2:8 to

8:2.

Specifically, when EL, butyl acetate or cyclohexanone is mixed as the polar solvent, the PGMEA:EL, butyl acetate or cyclohexanone weight ratio is preferably from 1:9 to 9:1, and more preferably from 2:8 to 8:2. Alternatively, when PGME is mixed as the
 5 polar solvent, the PGMEA:PGME weight ratio is preferably from 1:9 to 9:1, more preferably from 2:8 to 8:2, and still more preferably 3:7 to 7:3. Furthermore, a mixed solvent of PGMEA, PGME and butyl acetate is also preferable.

Further, as the component (S), a mixed solvent of at least one of PGMEA and EL with γ -butyrolactone is also preferable. The mixing ratio (former:latter) of such a mixed
 10 solvent is preferably from 70:30 to 95:5.

[0356]

The amount of the component (S) is adjusted such that the solid content of the resist composition becomes 25% by weight or more. In the present specification, the solid component of the resist composition refers to components other than the component (S).
 15 The solid content of the resist composition is calculated as follows.

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

[0357]

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

[0358]

By making the solid content of the resist composition to be 25% by weight or more, in the case where the resist composition is applied to a substrate to form a resist film, a thick-film resist film (for example, a film thickness of 5 μm or more, preferably 7 μm or more) may be reliably formed. The solid content of the resist composition is not particularly limited as long as it is 25% by weight or more, and may be appropriately
 25 selected depending on the desired film thickness of the resist film. In general, as the solid
 30 content becomes higher, the film thickness of the resist film becomes larger.

The upper limit of the solid content of the resist composition is not particularly limited, as long as the solid components are soluble. The solid content of the resist

composition is, for example, 60% by weight or less, preferably 55% by weight or less, and more preferably 50% by weight or less.

The range of the solid content of the resist composition may be, for example, 25 to 60% by weight, 25 to 55% by weight, or 25 to 50% by weight.

5 [0359]

If desired, other miscible additives can also be added to the resist composition of the present invention. Examples of such miscible additives include additive resins for improving the performance of the resist film, dissolution inhibitors, plasticizers, stabilizers, colorants, halation prevention agents, and dyes.

10 [0360]

After dissolving the resist materials in the organic solvent (S), the resist composition of the present embodiment may have impurities or the like removed by using a polyimide porous film, a polyamide-imide porous film, or the like. For example, the resist composition may be subjected to filtration using a filter formed of a polyimide porous membrane, a filter formed of a polyamide-imide porous film, or a filter formed of a polyimide porous membrane and a polyamide-imide porous film. Examples of the polyimide porous membrane and the polyamide-imide porous film include those described in Japanese Unexamined Patent Application, First Publication No. 2016-155121.

[0361]

20 The resist composition according to the present embodiment described above has a solid content of 25% by weight or more, and contains an ion liquid (Z).

Since the resist composition according to the present embodiment has a solid content of 25% by weight or more, when the resist composition is applied to a substrate to form a resist film, a thick-film resist film (for example, a film thickness of 5 μ m or more) may be formed. In the case of such a thick-film resist film, crack is likely to occur in the resist pattern. Further, since it is difficult for the light to reach the bottom portion of the resist film, is difficult to maintain the sensitivity during exposure, and such that it becomes difficult to form a resist pattern having a good shape.

30 In the resist composition of according to the present embodiment, by virtue of including the ion liquid (Z), both crack resistance and high sensitivity may be achieved. It is presumed that, by virtue of the ion liquid (Z) being present within the resist film formed using the resist composition, the stress of the resist film may be relaxed.

[0362]

(Method of forming a resist pattern)

The method of forming a resist pattern according to the second aspect of the present invention includes: using a resist composition according to the first aspect to form a resist film on a substrate; exposing the resist film; and developing the exposed resist film to form a resist pattern.

The method for forming a resist pattern according to the present embodiment can be performed, for example, as follows.

[0363]

Firstly, a resist composition of the first aspect is applied to a substrate using a spinner or the like, and a bake treatment (post applied bake (PAB)) is conducted at a temperature of 80 to 150°C for 40 to 120 seconds, preferably 60 to 90 seconds, to form a resist film.

Following selective exposure of the thus formed resist film, either by exposure through a mask having a predetermined pattern formed thereon (mask pattern) using an exposure apparatus such as an electron beam lithography apparatus or an EUV exposure apparatus, or by patterning via direct irradiation with an electron beam without using a mask pattern, baking treatment (post exposure baking (PEB)) is conducted under temperature conditions of 80 to 150°C for 40 to 120 seconds, and preferably 60 to 90 seconds.

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

[0364]

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

In the 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. If desired, bake treatment (post bake) can be conducted following the developing.

In this manner, a resist pattern can be formed.

[0365]

The substrate is not specifically limited and a conventionally known substrate can be used. For example, substrates for electronic components, and such substrates having
5 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 substrate, any one of the above-mentioned substrates provided with an inorganic and/or organic film on the surface thereof may be used. As the inorganic film,
10 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, a “multilayer resist method” is method in which at least one layer of an organic film (lower-layer organic film) and at least one layer of a resist film (upper resist
15 film) are provided on a substrate, and a resist pattern formed on the upper 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
20 extremely fine pattern with a high aspect ratio can be formed.

The multilayer resist method is broadly 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
25 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).

[0366]

In the method of forming a resist pattern according to the present embodiment, since the aforementioned resist composition of the present embodiment, is used, a thick-
30 film resist film is formed in step (i). The film 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 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 may be adjusted by the solid content of the resist film used in step (i). That is, the higher the solid content of the resist film, a resist film having a larger film thickness may be formed.

5 [0367]

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

15 [0368]

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

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

The immersion medium preferably exhibits a refractive index larger than the refractive index of air but smaller than the refractive index of the resist film to be exposed. The refractive index of the immersion medium is not particularly limited as long as it satisfies the above-mentioned requirements.

Examples of this immersion medium 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, silicon-based solvents and hydrocarbon-based solvents.

Specific examples of the fluorine-based inert liquids include liquids containing a fluorine-based compound such as C₃HCl₂F₅, C₄F₉OCH₃, C₄F₉OC₂H₅ or C₅H₃F₇ as the main component, which have a boiling point within a range from 70 to 180°C and

preferably from 80 to 160°C. A fluorine-based inert liquid having a boiling point within the above-mentioned range is advantageous in that the removal of the immersion medium after the exposure can be conducted by a simple method.

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

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

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

[0369]

As an example of the alkali developing solution used in an alkali developing
15 process, a 0.1 to 10% by weight aqueous solution of tetramethylammonium hydroxide (TMAH) can be given.

As the organic solvent contained in the organic developing solution used 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
20 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 within the structure thereof. An ester solvent is an organic solvent containing C-C(=O)-O-C within the structure thereof. An alcohol solvent is an organic solvent containing an alcoholic hydroxy
25 group in the structure thereof. An "alcoholic hydroxy group" refers to a hydroxy 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 within the structure thereof. An ether solvent is an organic solvent containing C-O-C within the structure thereof.

30 Some organic solvents have a plurality of the functional groups which characterizes the aforementioned solvents within the structure thereof. In such a case, the organic solvent can be classified as any type of the solvent having the characteristic functional group. For example, diethylene glycol monomethyl ether may 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.

[0370]

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, as a ketone solvent, methyl amyl ketone (2-heptanone) is preferable.

[0371]

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 monoethyl 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. Among these examples, as an ester solvent, butyl acetate is preferable.

[0372]

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

[0373]

If 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 silicon surfactant may be used. As the surfactant, a non-ionic surfactant is preferable, and a non-ionic fluorine surfactant or a non-ionic silicon surfactant is more preferable.

When a surfactant is added, the amount thereof based on the total amount of the organic developing solution is generally 0.001 to 5 % by weight, preferably 0.005 to 2% by weight, and more preferably 0.01 to 0.5% by weight.

[0374]

The developing treatment may be performed by a conventional developing method. Examples thereof include a method in which the substrate is immersed in the developing solution for a predetermined time (a dip method), a method in which the developing solution is cast up on the surface of the substrate by surface tension and maintained for a predetermined period (a puddle method), a method in which the developing solution is sprayed onto the surface of the substrate (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 substrate while rotating the substrate at a constant rate (dynamic dispense method).

[0375]

As the organic solvent contained in the rinse liquid used in the rinse treatment after the developing treatment in the case of a solvent developing process, any of the aforementioned organic solvents contained in the organic developing solution can be used which hardly dissolves the resist pattern. In general, at least one solvent selected from the

group consisting of hydrocarbon solvents, ketone solvents, ester solvents, alcohol solvents, amide solvents and ether solvents is used. Among these, at least one solvent selected from the group consisting of hydrocarbon solvents, ketone solvents, ester solvents, alcohol solvents and amide solvents is preferable, more preferably at least one solvent selected from the group consisting of alcohol solvents and ester solvents, and an alcohol solvent is particularly desirable.

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 aforementioned examples or water may be mixed together. However, in consideration of the development characteristics, the amount of water within the rinse liquid, based on the total amount of the rinse liquid is preferably 30% by weight or less, more preferably 10% by weight or less, still more preferably 5% by weight or less, and most preferably 3% by weight or less.

If desired, the rinse solution may have a conventional additive blended. Examples of the additive include surfactants. Examples of the additive include surfactants. As the surfactant, the same surfactants as those described above can be mentioned, a non-ionic surfactant is preferable, and a non-ionic fluorine surfactant or a non-ionic silicon surfactant is more preferable.

When a surfactant is added, the amount thereof based on the total amount of the rinse liquid is generally 0.001 to 5 % by weight, preferably 0.005 to 2% by weight, and more preferably 0.01 to 0.5% by weight.

[0376]

The rinse treatment using a rinse liquid (washing treatment) can be conducted by a conventional rinse method. Examples of the rinse method include a method in which the rinse liquid is continuously applied to the substrate while rotating it at a constant rate (rotational coating method), a method in which the substrate 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 substrate (spray method).

[0377]

In the method forming a resist pattern according to the present embodiment described above, by virtue of using the resist composition according to the first
5 embodiment, sensitivity may be improved, and a resist pattern having a good shape may be formed.

[0378]

The method of forming a resist pattern is useful for producing a three-dimensional structure device.

10

EXAMPLES

[0379]

As follows is a description of examples of the present invention, although the scope of the present invention is by no way limited by these examples.

15

[0380]

<Production of resist composition>

(Examples 1 to 12, Comparative Examples 1 and 2)

The components shown in Table 1 were mixed together and dissolved to obtain each resist composition.

20

[0381]

[Table 1]

	Component (A)	Component (B)	Component (D)	Component (Z)	Component (S)			Solid content (wt%)
Example 1	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-1 [5.0]	(S)-1 [127]	(S)-2 [127]	(S)-3 [64]	25
Example 2	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-1 [5.0]	(S)-1 [64]	(S)-2 [64]	(S)-3 [32]	40
Example 3	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-1 [5.0]	(S)-1 [52]	(S)-2 [52]	(S)-3 [26]	45
Example 4	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-2 [5.0]	(S)-1 [64]	(S)-2 [64]	(S)-3 [32]	40
Example 5	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-1 [10.0]	(S)-1 [67]	(S)-2 [67]	(S)-3 [33]	40
Example 6	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-3 [5.0]	(S)-1 [64]	(S)-2 [64]	(S)-3 [32]	40
Example 7	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-4 [5.0]	(S)-1 [64]	(S)-2 [64]	(S)-3 [32]	40
Example 8	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-5 [5.0]	(S)-1 [64]	(S)-2 [64]	(S)-3 [32]	40
Example 9	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-6 [5.0]	(S)-1 [64]	(S)-2 [64]	(S)-3 [32]	40
Example 10	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-7 [5.0]	(S)-1 [64]	(S)-2 [64]	(S)-3 [32]	40
Example 11	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-8 [5.0]	(S)-1 [64]	(S)-2 [64]	(S)-3 [32]	40
Example 12	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	(Z)-9 [5.0]	(S)-1 [64]	(S)-2 [64]	(S)-3 [32]	40
Comparative Example 1	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	—	(S)-1 [61]	(S)-2 [61]	(S)-3 [30]	40
Comparative Example 2	(A)-1 [100]	(B)-1 [0.9]	(D)-1 [0.01]	—	(S)-1 [121]	(S)-2 [121]	(S)-3 [61]	25

[0382]

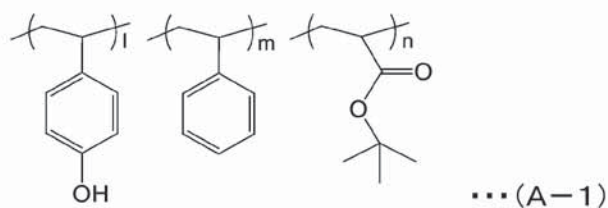
In Table 1, the reference characters indicate the following. The values in brackets [] indicate the amount (in terms of parts by weight) of the component added. The solid content was calculated as follows: solid content (% by weight) = [(component (A) + component (B) + component (D) + component (Z))/(component (A) + component (B) + component (D) + component (Z) + component (S))]×100.

[0383]

(A)–1: Polymeric compound represented by chemical formula (A–1) shown below. The weight average molecular weight (M_w) and the dispersity (M_w/M_n) in terms of the polystyrene equivalent value measured by gel permeation chromatography (GPC) were 10,000 and 1.4, respectively. The composition of the copolymer (ratio (molar ratio) of the respective structural units within the structural formula) as determined by ¹³C–NMR was l/m/n = 60/15/25.

[0384]

[Chemical Formula 75]



[0385]

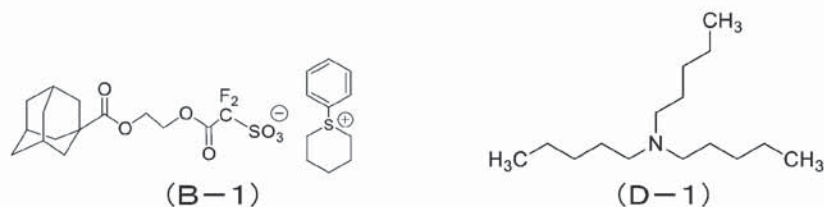
(B)-1: an acid generator represented by chemical formula (B-1) shown below.

(D)-1: Nitrogen-containing organic compound represented by chemical formula

5 (D-1) shown below.

[0386]

[Chemical Formula 76]

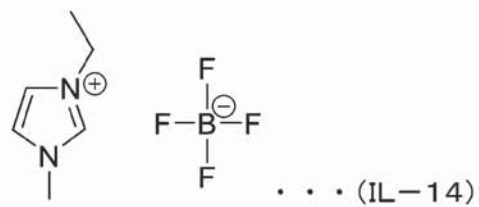
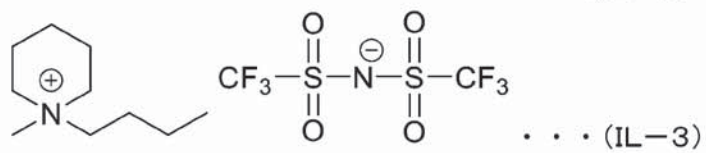
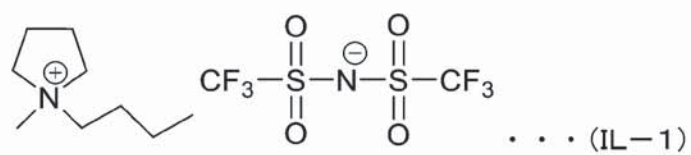


[0387]

- 10 (Z)-1: compound represented by the following chemical formula (IL)-1
 (Z)-2: compound represented by the following chemical formula (IL)-3
 (Z)-3: compound represented by the following chemical formula (IL)-14
 (Z)-4: compound represented by the following chemical formula (IL)-15
 (Z)-5: compound represented by the following chemical formula (IL)-16
 15 (Z)-6: compound represented by the following chemical formula (IL)-17
 (Z)-7: compound represented by the following chemical formula (IL)-18
 (Z)-8: compound represented by the following chemical formula (IL)-19
 (Z)-9: compound represented by the following chemical formula (IL)-20

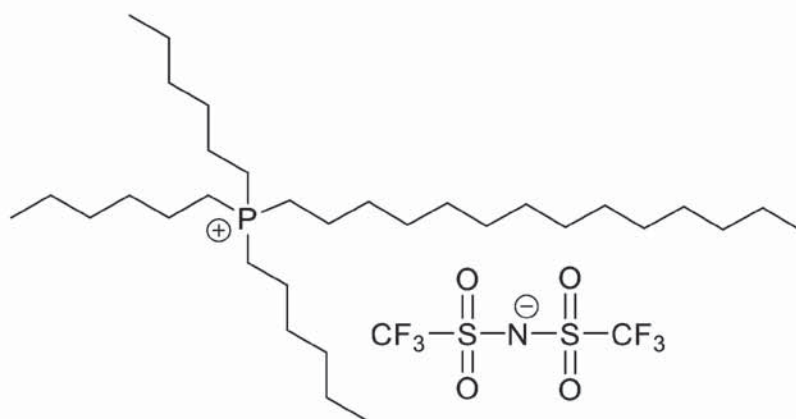
[0388]

20 [Chemical Formula 77]

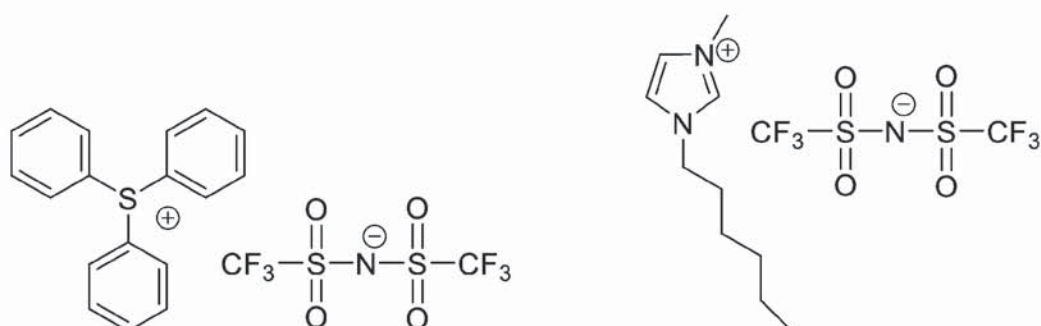


[0389]

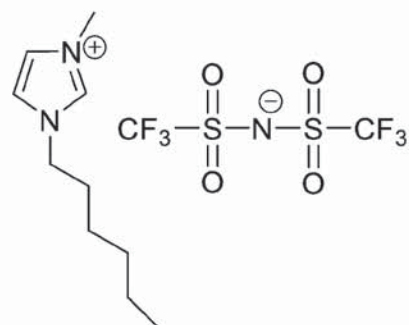
[Chemical Formula 78]



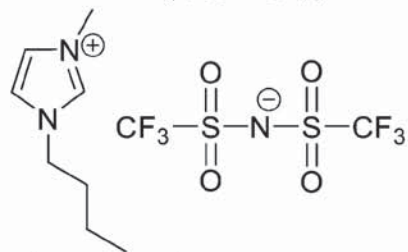
(I L - 1 5)



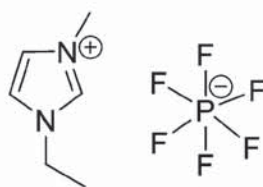
(I L - 1 6)



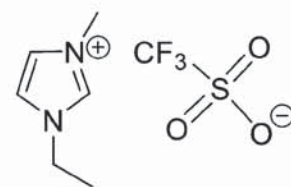
(I L - 1 7)



(I L - 1 8)



(I L - 1 9)



(I L - 2 0)

[0390]

(S)-1: propylene glycol monomethyl ether

(S)-2: propylene glycol monomethyl ether acetate

5 (S)-3: butyl acetate

[0391]

<Formation of resist pattern>

Step (i):

Using a spinner, each of the resist compositions of examples and comparative
 10 examples was applied to an 8-inch silicon substrate which had been subjected to a
 hexamethyldisilazane (HMDS) treatment at 110°C for 60 seconds. Then, a prebake (PAB)

treatment was conducted on a hot plate at 140°C for 90 seconds, followed by drying, so as to form a resist film having a film thickness of 15 μm .

Step (ii):

Subsequently, the resist film was selectively irradiated with a KrF excimer laser (248 nm) through a mask pattern (binary mask), using a KrF exposure apparatus NSR-S203 (manufactured by Nikon Corporation, NA (numerical aperture) = 0.68, $\sigma = 0.40$).

Then, a post exposure bake (PEB) treatment was conducted at 110°C for 90 seconds.

Step (iii)

Thereafter, alkali developing was conducted for 60 seconds at 23°C in a 2.38% by weight aqueous solution of tetramethylammonium hydroxide (TMAH) (product name: NMD-3; manufactured by Tokyo Ohka Kogyo Co., Ltd.).

Then, post bake was conducted at 100°C for 60 seconds.

As a result, an isolated space pattern (hereafter, referred to as "IS pattern") having a space width of 5 μm and a pitch of 30 μm was formed.

[0392]

[Evaluation of crack resistance]

The silicon wafer having an IS pattern by the above "Formation of resist pattern" was placed in a chamber of a scanning electron microscope S-9380 (manufactured by Hitachi High-Technologies Corporation), and a vacuum treatment was conducted under a pressure of 0.0001 Pa or less for 60 seconds. Using an optical microscope, the silicon wafer after the vacuum treatment was observed, and the number of cracks were counted. The number of cracks was evaluated by the following criteria. The results are indicated under "Crack" in Table 2.

Criteria:

A: 0 crack

B: 1 to 5 cracks

C: 6 or more cracks

[0393]

[Evaluation of sensitivity]

The optimum exposure dose E_{op} (mJ/cm^2) with which an IS pattern having a space width of 5 μm and a pitch of 30 μm was formed in the above "Formation of resist pattern" was determined. The results are indicated under " E_{op} (mJ/cm^2)" in Table 2.

[0394]

[Table 2]

	Crack	Eop (mJ/cm ²)
Example 1	A	67
Example 2	B	107
Example 3	B	135
Example 4	A	98
Example 5	A	87
Example 6	B	165
Example 7	B	137
Example 8	A	101
Example 9	B	112
Example 10	B	124
Example 11	B	147
Example 12	B	153
Comparative Example 1	C	193
Comparative Example 2	C	103

[0395]

- 5 As seen from the results shown in Table 2, it was confirmed that the resist compositions of Examples 1 to 12 exhibited good cracking resistance and good sensitivity.

[0396]

- 10 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.

CLAIMS

1. A resist composition which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid, the resist composition comprising:
5 a base component (A) which exhibits changed solubility in a developing solution under action of acid, and
an ion liquid (Z),
wherein a solid content of the resist composition is 25% by weight or more.
- 10 2. The resist composition according to Claim 1, wherein the amount of the ion liquid (Z) relative to 100 parts by weight of the base component (A) is more than 0% by weight to less than 25 parts by weight.
3. A method of forming a resist pattern, comprising:
15 using a resist composition according to Claim 1 or 2 to form a resist film,
exposing the resist film, and
developing the exposed resist film to form a resist pattern.