RESIST COMPOSITION AND METHOD OF FORMING RESIST PATTERN

BACKGROUND OF THE INVENTION

Field of the Invention

[0001]

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

Priority is claimed on Japanese Patent Application No. 2019-223096, filed on December 10, 2019, the content of which is incorporated herein by reference.

Description of Related Art

[0002]

In the lithography techniques, for example, a resist film which is constituted of a resist material is formed on a substrate, and the resist film is selectively exposed and then subjected to a developing treatment to form a resist pattern having a predetermined shape on the resist film. In a case where an exposed portion of a resist film is dissolved in a developing solution due to the change of characteristics of the exposed portion of the resist film, a resist material is called a positive-tone resist material, and in a case where an exposed portion of a resist film is not dissolved in a developing solution due to the change of characteristics of the exposed portion of the resist film, a resist material called a negative-tone resist material.

In recent years, in the production of semiconductor elements and liquid crystal display elements, with advances in lithography techniques, rapid progress in the field of pattern miniaturization has been achieved. Typically, these miniaturization techniques involve shortening the wavelength (increasing the energy) of the light source for exposure. Specifically, ultraviolet radiation typified by g-line and i-line radiation has been used in the related art, but nowadays KrF excimer lasers and ArF excimer lasers are used in the mass production of semiconductor elements. Furthermore, research is also being performed into lithography techniques that use an exposure light source having a wavelength shorter (energy higher) than these excimer lasers, such as electron beams (EB), extreme ultraviolet (EUV) rays, and X rays.

[0003]

Resist materials for use with these types of light sources for exposure require

lithography characteristics such as a high resolution capable of reproducing patterns of fine dimensions, and a high level of sensitivity to these types of light sources for exposure.

As a resist material that satisfies these requirements, a chemical amplification-type resist composition which contains a base material component having solubility in a developing solution, which is changed by action of an acid, and an acid generator component that generates an acid upon exposure has been conventionally used.

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

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

[0004]

Up till now, as a base resin of a chemical amplification-type resist composition, for example, for KrF excimer laser (248 nm), a resin having high transparency such as polyhydroxystyrene (PHS) and a resin (a PHS-based resin) in which a hydroxyl group of PHS is protected by an acid-dissociable and dissolution-inhibiting group has been used. In addition, for example, for ArF excimer laser (193 nm), a resin (a (meth)acrylic resin)

in which a hydroxyl group of a carboxy group of (meth)acrylic acid is protected by an acid-dissociable and dissolution-inhibiting group has been used (for example, Japanese Unexamined Patent Application, First Publication No. 2003-241385).

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

[0005]

In addition, a wide variety of acid generators have been proposed as the acid generator component used in the chemical amplification-type resist composition, and for example, onium salt-based acid generators such as iodonium salts and sulfonium salts, oxime sulfonate-based acid generators, diazomethane-based acid generators, nitrobenzylsulfonate-based acid generators, iminosulfonate-based acid generators, disulfone-based acid generators, and the like are known.

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

[0006]

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

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

SUMMARY OF THE INVENTION

[0008]

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

[0009]

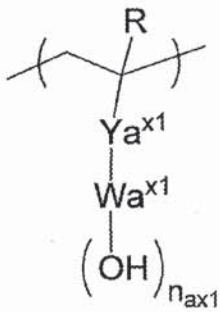
The present invention has been made in consideration of the above circumstances, and an object of the present invention is to provide a resist composition with which a thick resist film can be formed, which does not easily cause cracking, and which does not easily cause surface roughness during etching, and a method of forming a resist pattern by using the resist composition.

[0010]

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

The first aspect of the present invention is a resist composition that generates an acid upon exposure and has solubility in a developing solution, which is changed by action of an acid. The resist composition contains a resin component (A1) that has a constitutional unit (a1) containing an acid-decomposable group having a polarity which is increased by action of an acid and a constitutional unit (a10) represented by General Formula (a10-1), and a plasticizer component (Z) that has a constitutional unit (z1) represented by General Formula (z1-1) and does not contain an acid-dissociable group. In the resist composition, a content of the plasticizer component (Z) is 50 parts by mass or less with respect to 100 parts by mass of the resin component (A1), and a solid content concentration is 25% by mass or more.

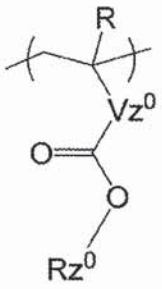
[0011]



... (a10-1)

[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Ya^{x1} represents a single bond or a divalent linking group. Wa^{x1} represents an aromatic hydrocarbon group which may have a substituent. n_{ax1} represents an integer of 1 or greater.]

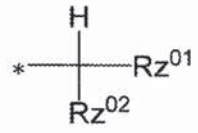
[0012]



... (z1-1)

[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Vz^0 represents a single bond or a divalent hydrocarbon group which may contain a hetero atom. However, in a case where Vz^0 represents a divalent hydrocarbon group which may contain a hetero atom, Vz^0 does not contain an acid-dissociable group. Rz^0 represents a hydrogen atom or a group represented by General Formula (z1-r-1).]

[0013]



... (z1-r-1)

[In the formula, Rz^{01} represents a hydrocarbon group which may have a substituent. Rz^{02} represents a hydrogen atom or a hydrocarbon group which may have a substituent. Rz^{01} and Rz^{02} may be bonded to each other to form a ring structure. However, Rz^{01} and Rz^{02} do not contain an acid-dissociable group. * represents a bond.]

[0014]

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

[0015]

According to the present invention, it is possible to provide a resist composition with which a thick resist film can be formed, which does not easily cause cracking, and which does not easily cause surface roughness during etching, and a method of forming a resist pattern by using the resist composition.

DETAILED DESCRIPTION OF THE INVENTION

[0016]

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

The term "alkyl group" includes a monovalent saturated hydrocarbon group that is linear, branched, or cyclic, unless otherwise specified. The same applies to the alkyl group of an alkoxy group.

The term "alkylene group" includes a divalent saturated hydrocarbon group that is linear, branched, or cyclic, unless otherwise specified.

A "halogenated alkyl group" is a group in which part or all of hydrogen atoms of an alkyl group are substituted with halogen atoms.

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

A "fluorinated alkyl group" or a "fluorinated alkylene group" is a group in which part or all of hydrogen atoms of an alkyl group or an alkylene group have been substituted with fluorine atoms.

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

The expression "may have a substituent" means a case where a hydrogen atom (-H) is substituted with a monovalent group or a case where a methylene group ($-CH_2-$) is

substituted with a divalent group.

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

[0017]

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

[0018]

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

The "acrylic acid ester" indicates a compound in which the terminal hydrogen atom of the carboxy group of acrylic acid (CH_2=CH-COOH) has been substituted with an organic group.

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

specified.

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

[0019]

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

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

Examples of the substituent that is substituted for the hydrogen atom at the α-position of hydroxystyrene include the same substituent as that described above as the substituent at the α-position of the above-described α-substituted acrylic acid ester can be mentioned.

[0020]

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

The term “vinylbenzoic acid derivative” includes compounds in which the hydrogen atom at the α-position of vinylbenzoic acid has been substituted with another substituent such as an alkyl group or a halogenated alkyl group; and derivatives thereof. Examples of the derivatives thereof include vinylbenzoic acid in which the hydrogen atom of the carboxy group has been substituted with an organic group and may have the

hydrogen atom at the α-position substituted with a substituent; and vinylbenzoic acid which has a substituent other than a hydroxyl group and a carboxy group bonded to the benzene ring and may have the hydrogen atom at the α-position substituted with a substituent. Further, the α-position (carbon atom at the α-position) indicates the carbon atom having the benzene ring bonded thereto, unless otherwise specified.

[0021]

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

Specific examples of the halogenated alkyl group as the substituent at the α-position include groups in which part or all of hydrogen atoms of the above-described "alkyl group as the substituent at the α-position" are substituted with halogen atoms. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom and, an iodine atom, and a fluorine atom is particularly preferable.

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

[0022]

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

[0023]

(Resist composition)

The resist composition according to the first aspect of the present invention is a resist composition generating an acid upon exposure and having solubility in a developing solution, which is changed by action of an acid, which includes a base material component (A) (hereinafter also referred to as component (A)) having solubility

in a developing solution, which is changed by action of an acid, and a plasticizer component (Z) (hereinafter, also referred to as a "component (Z)"). In the resist composition according to the present embodiment, the content of the component (Z) is 50 parts by mass or less with respect to 100 parts by mass of the component (A). In addition, in a case where a resist film is formed using such a resist composition, a thick resist film (for example, a film having a thickness of 5 μm or more) can be formed.

[0024]

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

[0025]

In the present specification, a resist composition which forms a positive-tone resist pattern by dissolving and removing the exposed portion of the resist film is called a positive-tone resist composition, and a resist composition which forms a negative-tone resist pattern by dissolving and removing the unexposed portion of the resist film is called a negative-tone resist composition. The resist composition according to the present embodiment may be a positive-tone resist composition or a negative-tone resist composition. Further, during the formation of a resist pattern, the resist composition according to the present embodiment can be applied to an alkali developing process using an alkali developing solution in the developing treatment, or a solvent developing process using a developing solution containing an organic solvent (organic developing solution) in the developing treatment.

[0026]

The resist composition according to the present embodiment has a function of

generating an acid upon exposure, the component (A) may generate an acid upon exposure, and an additive component that is separately blended from the component (A) may generate an acid upon exposure.

Specifically, the resist composition according to the present embodiment may (1) further contain an acid generator component (B) (hereinafter, referred to as a "component (B)") that generates an acid upon exposure; (2) have a component (A) that generates an acid upon exposure; and (3) have a component (A) that generates an acid upon exposure and further contains component (B). That is, in the cases of (2) and (3) described above, the component (A) becomes a "base material component which generates an acid upon exposure and has solubility in a developing solution, which is changed by action of an acid". In a case where the component (A) is a base material component which generates an acid upon exposure and has solubility in a developing solution, which is changed by action of an acid, it is preferable that the component (A1) described below be a high-molecular-weight compound which generates an acid upon exposure and has solubility in a developing solution, which is changed by action of an acid. As such a high-molecular-weight compound, a resin having a constitutional unit that generates an acid upon exposure can be used. As the constitutional unit that generates an acid upon exposure, a conventionally known constitutional unit can be used. Among them, the resist composition according to the present embodiment is particularly preferably the case of the above (1).

[0027]

<Component (A)>

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

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

[0028]

In a case of applying an alkali developing process, a base material component containing the component (A1) is substantially insoluble in an alkali developing solution prior to exposure, but in a case where an acid is generated from the component (B) upon exposure, the action of this acid causes an increase in the polarity of the base material component, thereby increasing the solubility of the base material component in an alkali developing solution. Therefore, in the formation of a resist pattern, by performing selective exposure of a resist film formed by applying the resist composition onto a support, the exposed portion of the resist film changes from an insoluble state to a soluble state in an alkali developing solution, whereas the unexposed portion of the resist film remains insoluble in an alkali developing solution, and thus, a positive-tone resist pattern is formed by alkali developing.

[0029]

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

[0030]

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

[0031]

· In regard to component (A1)

The component (A1) is a resin component having solubility in a developing solution, which is changed by action of an acid. The component (A1) has a constitutional unit (a1) containing an acid-decomposable group having a polarity which is increased by action of an acid and a constitutional unit (a10) represented by General

Formula (a10-1).

The component (A1) may have other constitutional units as necessary in addition to the constitutional unit (a1) and the constitutional unit (a10).

[0032]

<<Constitutional unit (a1)>>

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

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

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

Examples of the polar group include a carboxy group, a hydroxyl group, an amino group, and a sulfo group ($-SO_3H$). Among these, a polar group containing -OH in the structure thereof (hereinafter, also referred to as an "OH-containing polar group") is preferable, a carboxy group or a hydroxyl group is more preferable, and a carboxy group is particularly preferable.

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

[0033]

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

It is necessary that the acid-dissociable group that constitutes the acid-decomposable group be a group that exhibits a lower polarity than the polar group generated by the dissociation of the acid-dissociable group. Thus, in a case where the acid-dissociable group is dissociated by action of an acid, a polar group exhibiting a

higher polarity than the acid-dissociable group is generated, thereby increasing the polarity. As a result, the polarity of the entire component (A1) is increased. The solubility in a developing solution relatively changes in a case where the polarity is increased. The solubility in an alkali developing solution is increased in a case where the developing solution is an alkali developing solution, whereas the solubility in an organic developing solution is decreased in a case where the developing solution is an alkali developing solution.

[0034]

Examples of the acid-dissociable group are the same as those which have been proposed as acid-dissociable groups for the base resin for a chemical amplification-type resist composition.

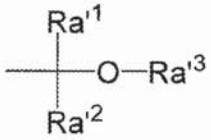
Specific examples of acid-dissociable groups of the base resin proposed for a chemical amplification-type resist composition contains an "acetal-type acid-dissociable group", a "tertiary alkyl ester-type acid-dissociable group", and a "tertiary alkyloxycarbonyl acid-dissociable group" described below.

[0035]

Acetal-type acid-dissociable group:

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

[0036]



(a 1 − r − 1)

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

[0037]

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

In a case where Ra'^1 or Ra'^2 represents an alkyl group, examples of the alkyl

group include the same alkyl group as that mentioned as the substituent which may be bonded to the carbon atom at the α-position in the description on the α-substituted acrylic acid ester, and the alkyl group preferably has 1 to 5 carbon atoms. Specific examples thereof preferably include a linear or branched alkyl group. More 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. Among these, a methyl group or an ethyl group is preferable, and a methyl group is particularly preferable.

[0038]

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

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

[0039]

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

[0040]

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

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

The aliphatic hydrocarbon group which is a polycyclic group is preferably a group in which one hydrogen atom has been removed from a polycycloalkane. The polycycloalkane preferably has 7 to 12 carbon atoms, and specific examples thereof

include adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane.

[0041]

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

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

Specific examples of the aromatic hydrocarbon group as Ra'^3 include a group in which one hydrogen atom has been removed from the above-described aromatic hydrocarbon ring or aromatic heterocyclic ring (an aryl group or a heteroaryl group); a group in which one hydrogen atom has been removed from an aromatic compound having two or more aromatic rings (biphenyl, fluorene or the like); and a group in which one hydrogen atom of the above-described aromatic hydrocarbon ring or aromatic heterocyclic ring has been substituted with an alkylene group (an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group). The number of carbon atoms in the alkylene group bonded to the aromatic hydrocarbon ring or aromatic heterocyclic ring is preferably in a range of 1 to 4, more preferably 1 or 2, and particularly preferably 1.

[0042]

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

Here, R^{P1} represents a monovalent chain-like saturated hydrocarbon group

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

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

Examples of the monovalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms include monocyclic aliphatic saturated hydrocarbon groups such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclodecyl group, and cyclododecyl group; and polycyclic aliphatic saturated hydrocarbon groups such as a bicyclo[2.2.2]octanyl group, a tricyclo[5.2.1.02,6]decanyl group, a tricyclo [3.3.1.13,7]decanyl group, a tetracyclo[6.2.1.13,6.02,7] dodecanyl group, and an adamantyl group.

Examples of the monovalent aromatic hydrocarbon group having 6 to 30 carbon atoms include a group in which one hydrogen atom has been removed from an aromatic hydrocarbon ring such as benzene, biphenyl, fluorene, naphthalene, anthracene, or phenanthrene.

[0043]

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

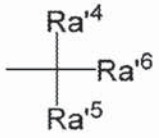
[0044]

Tertiary alkyl ester-type acid-dissociable group:

Among the above polar groups, examples of the acid-dissociable group for protecting the carboxy group include the acid-dissociable group represented by General Formula (a1-r-2) shown below.

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 a "tertiary alkyl ester-type acid-dissociable group".

[0045]



(a 1 — r — 2)

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

[0046]

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

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

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

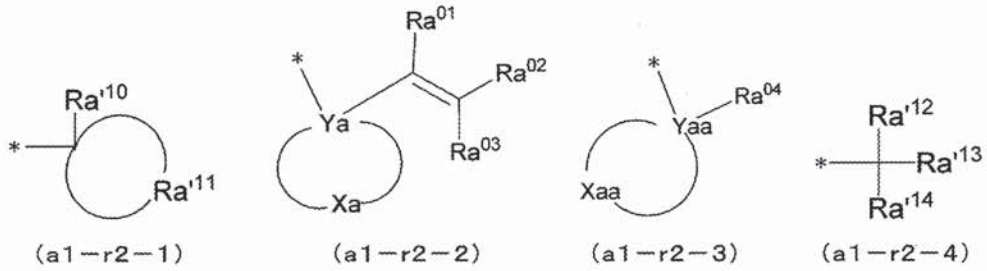
Examples of the hydrocarbon groups as Ra'^5 and Ra'^6 include the same groups as those mentioned above as Ra'^3.

[0047]

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

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

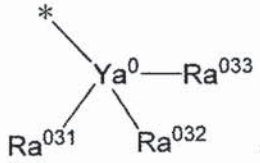
[0048]



(a1−r2−1) (a1−r2−2) (a1−r2−3) (a1−r2−4)

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

[0049]



・・・(a1−r2−r1)

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

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

[0050]

In General Formula (a1-r2-1), the alkyl group having 1 to 10 carbon atoms as Ra'^{10} is preferably the group exemplified as the linear or branched alkyl group as Ra'^{3} in General Formula (a1-r-1). Ra'^{10} is preferably an alkyl group having 1 to 5 carbon atoms.

[0051]

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

[0052]

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

[0053]

The linear alkyl groups as Ra^{031}, Ra^{032}, and Ra^{033} preferably have 1 to 5 carbon atoms, more preferably 1 to 4 carbon atoms, and still more preferably 1 or 2 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, an n-propyl group, an n-butyl group, and an n-pentyl group. Among these, a methyl group, an ethyl group, or an n-butyl group is preferable, and a methyl group or an ethyl group is more preferable.

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

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

[0054]

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

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

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

[0055]

The aromatic hydrocarbon groups as Ra^{031}, Ra^{032}, and Ra^{033} are a hydrocarbon group having at least one aromatic ring. The aromatic ring is not particularly limited as long as it is a cyclic conjugated system having $(4n + 2)$ π electrons, and may be monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, still more preferably 6 to 15 carbon atoms, and particularly preferably 6 to 12 carbon atoms. Specific examples of the aromatic ring include aromatic hydrocarbon rings such as benzene, naphthalene, anthracene, and phenanthrene; and an aromatic heterocyclic ring in which a part of carbon atoms constituting the above-described aromatic hydrocarbon ring have been substituted with a hetero atom. Examples of the hetero atom in the aromatic heterocyclic rings include an oxygen atom, a sulfur atom, and a nitrogen atom. Specific examples of the aromatic heterocyclic ring include a pyridine ring and a thiophene ring. Specific examples of the aromatic hydrocarbon group include a group in which one hydrogen atom has been removed from the above-described aromatic hydrocarbon ring or aromatic heterocyclic ring (an aryl group or a heteroaryl group); a group in which one hydrogen atom has been removed from an aromatic compound having two or more aromatic rings (biphenyl, fluorene or the like); and a group in which one hydrogen atom of the above-described aromatic hydrocarbon ring or aromatic heterocyclic 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 aromatic hydrocarbon ring or aromatic heterocyclic ring preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and particularly preferably 1 carbon atom.

[0056]

In a case where the hydrocarbon groups represented by Ra^{031}, Ra^{032}, and Ra^{033} are substituted, examples of the substituent include a hydroxy group, a carboxy group, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, and the like), an alkoxy group (a methoxy group, an ethoxy group, a propoxy group, a butoxy group, and the like), an alkyloxycarbonyl group.

[0057]

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

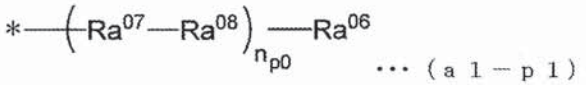
[0058]

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

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

Such a "hydrocarbon group having a polar group" is preferably a functional group represented by General Formula (a1-p1).

[0059]



... (a1-p1)

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

[0060]

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

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

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

Among the above, an alkanediyl group is preferable, and a linear alkanediyl group is more preferable.

[0061]

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

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

Among these, Ra^{08} is preferably -O-, -C(= O)-O-, -C(=O)-, or -O-C(=O)-O-, and more preferably -O- or -C(=O)- from the viewpoint of the solubility in a developing solution.

[0062]

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 and preferably has 1 to 8 carbon atoms, more preferably 1 to 5 carbon atoms, still more preferably 1 to 3 carbon atoms, particularly preferably 1 or 2 carbon atoms, and most preferably 1 carbon atoms, from the viewpoint of the solubility in a developing solution.

[0063]

Examples of the hydrocarbon group as Ra^{06} include a chain-like hydrocarbon group or a cyclic hydrocarbon group, or a hydrocarbon group obtained by combining a chain-like hydrocarbon group or a cyclic hydrocarbon group.

Examples of the chain-like hydrocarbon group include a methyl group, an ethyl

group, an n-propyl group, an isopropyl group, an n-butyl group, a sec-butyl group, a tert-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, a 2-ethylhexyl group, an n -octyl group, an n-nonyl group, an n-decyl group, an n-undecyl group, and an n-dodecyl group.

[0064]

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

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

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

[0065]

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

[0066]

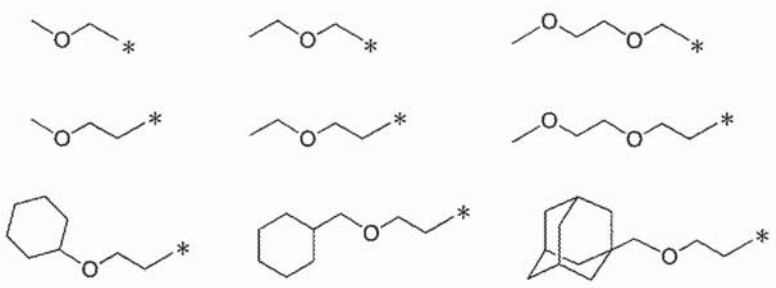
In Formula (a1-p1) n_{p0} represents an integer in a range of 1 to 6, is preferably an integer in a range of 1 to 3, more preferably an integer of 1 or 2, and still more preferably 1.

[0067]

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

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

[0068]



[0069]

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

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

[0070]

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

[0071]

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

[0072]

In General Formula (a1-r2-2), examples of the cyclic hydrocarbon group formed by Xa together with Ya include a group in which one or more hydrogen atoms are further removed from a cyclic monovalent hydrocarbon group (an aliphatic hydrocarbon group) as Ra'^{3} in General Formula (a1-r-1).

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

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

Examples of the monovalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms, as Ra^{01} to Ra^{03}, include monocyclic aliphatic saturated hydrocarbon groups such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclodecyl group, and cyclododecyl group; and polycyclic aliphatic saturated hydrocarbon groups such as a bicyclo[2.2.2]octanyl group, a tricyclo[5.2.1.02,6]decanyl group, a tricyclo[3.3.1.13,7]decanyl group, a tetracyclo[6.2.1.13,6.02,7] dodecanyl group, and an adamantyl group.

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

[0073]

Examples of the substituent which the chain-like saturated hydrocarbon group represented by Ra^{01} to Ra^{03} or the aliphatic cyclic saturated hydrocarbon group has include the same groups as Ra^{05} described above.

[0074]

Examples of the group containing a carbon-carbon double bond generated by forming a cyclic structure, in which two or more of Ra^{01} to Ra^{03} are bonded to each other, include a cyclopentenyl group, a cyclohexenyl group, a methylcyclopentenyl group, a methylcyclohexenyl group, a cyclopentylideneethenyl group, and a cyclohexylideneethenyl group. Among these, a cyclopentenyl group, a cyclohexenyl group, and a cyclopentylideneethenyl group are preferable from the viewpoint of easy synthesis of a monomer compound from which the constitutional unit (a1) is derived.

[0075]

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

In General Formula (a1-r2-3), Examples of the aromatic hydrocarbon group as Ra^{04} include a group in which one or more hydrogen atoms have been removed from an aromatic hydrocarbon ring having 5 to 30 carbon atoms. Among them, Ra^{04} is preferably a group in which one or more hydrogen atoms have been removed from an aromatic hydrocarbon ring having 6 to 15 carbon atoms, more preferably a group in which one or more hydrogen atoms have been removed from benzene, naphthalene, anthracene, or phenanthrene, still more preferably a group in which one or more hydrogen atoms have been removed from benzene, naphthalene, or anthracene, particularly preferably a group in which one or more hydrogen atoms have been removed from benzene or naphthalene, and most preferably a group in which one or more hydrogen atoms have been removed from benzene.

[0076]

Examples of the substituent which Ra^{04} in General Formula (a1-r2-3) may have include a methyl group, an ethyl group, propyl group, a hydroxy group, a carboxy group, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, and the like), an alkoxy group (a methoxy group, an ethoxy group, a propoxy group, a butoxy group, and the like), and an alkyloxycarbonyl group.

[0077]

In General Formula (a1-r2-4), Ra'^{12} and Ra'^{13} each independently represent a monovalent chain-like saturated hydrocarbon group having 1 to 10 carbon atoms or a hydrogen atom. Examples of the monovalent chain-like saturated hydrocarbon group having 1 to 10 carbon atoms as Ra'^{12} and Ra'^{13} include the same monovalent chain-like saturated hydrocarbon groups as those having 1 to 10 carbon atoms as Ra^{01} to Ra^{03} as described above. Part or all of the hydrogen atoms which the chain-like saturated hydrocarbon group has may be substituted.

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

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

[0078]

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

[0079]

The linear alkyl group as Ra'^{14} preferably has 1 to 5 carbon atoms, more preferably 1 to 4 carbon atoms, and still more preferably 1 or 2 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, an n-propyl group, an n-butyl group, and an n-pentyl group. Among these, a methyl group, an ethyl group, or an n-butyl group is preferable, and a methyl group or an ethyl group is more preferable.

[0080]

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

[0081]

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

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

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

[0082]

Examples of the aromatic hydrocarbon group as Ra'^{14} include the same group as the aromatic hydrocarbon group as Ra^{04}. Among them, Ra'^{14} is preferably a group in which one or more hydrogen atoms have been removed from an aromatic hydrocarbon ring having 6 to 15 carbon atoms, more preferably a group in which one or more hydrogen atoms have been removed from benzene, naphthalene, anthracene, or

phenanthrene, still more preferably a group in which one or more hydrogen atoms have been removed from benzene, naphthalene, or anthracene, particularly preferably a group in which one or more hydrogen atoms have been removed from naphthalene or anthracene, and most preferably a group in which one or more hydrogen atoms have been removed from naphthalene.

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

[0083]

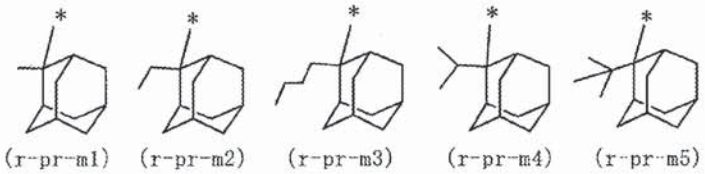
In a case where Ra'^{14} in General Formula (a1-r2-4) is a naphthyl group, the position at which the tertiary carbon atom in General Formula (a1-r2-4) is bonded is any one of the 1- or the 2-position of the naphthyl group.

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

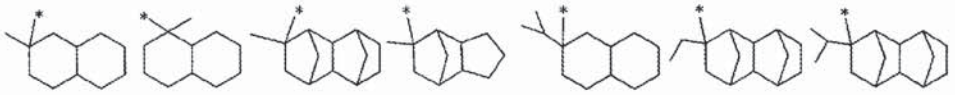
[0084]

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

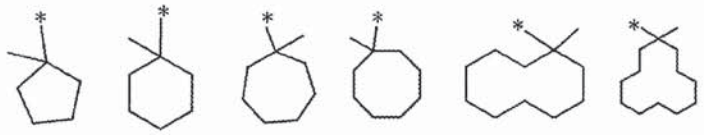
[0085]


(r-pr-m1) (r-pr-m2) (r-pr-m3) (r-pr-m4) (r-pr-m5)

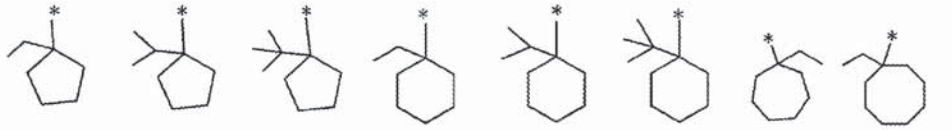

(r-pr-m6) (r-pr-m7) (r-pr-m8) (r-pr-m9) (r-pr-m10)


(r-pr-m11) (r-pr-m12) (r-pr-m13) (r-pr-m14) (r-pr-m15) (r-pr-m16) (r-pr-m17)

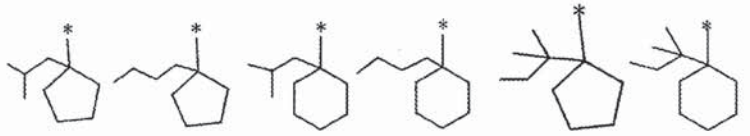
[0086]



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

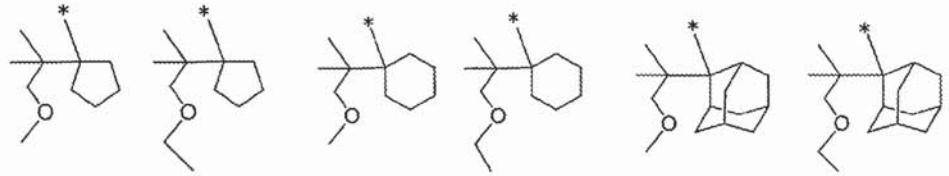


(r-pr-s7) (r-pr-s8) (r-pr-s9) (r-pr-s10) (r-pr-s11) (r-pr-s12) (r-pr-s13) (r-pr-s14)



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

[0087]

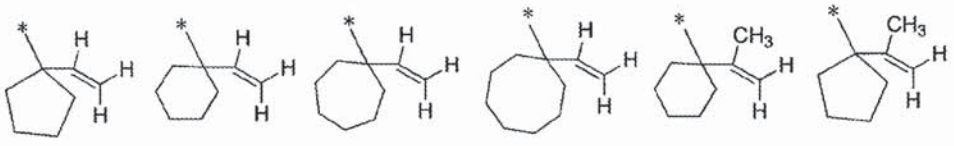


(r-pr-sp1) (r-pr-sp2) (r-pr-sp3) (r-pr-sp4) (r-pr-mp1) (r-pr-mp2)

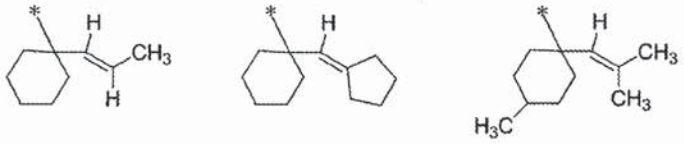
[0088]

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

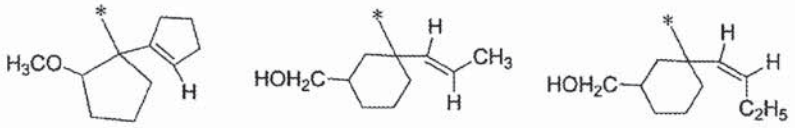
[0089]



(r-pr-sv1) (r-pr-sv2) (r-pr-sv3) (r-pr-sv4) (r-pr-sv5) (r-pr-sv6)

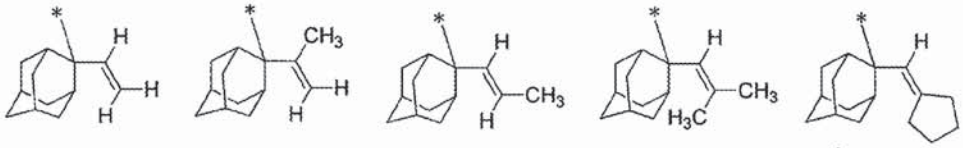


(r-pr-sv7) (r-pr-sv8) (r-pr-sv9)

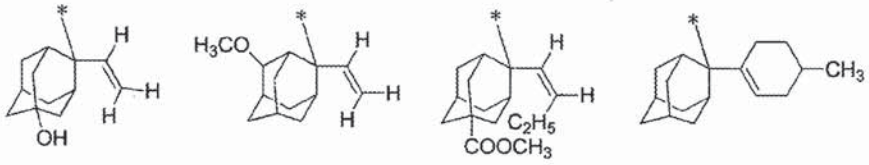


(r-pr-sv10) (r-pr-sv11) (r-pr-sv12)

[0090]

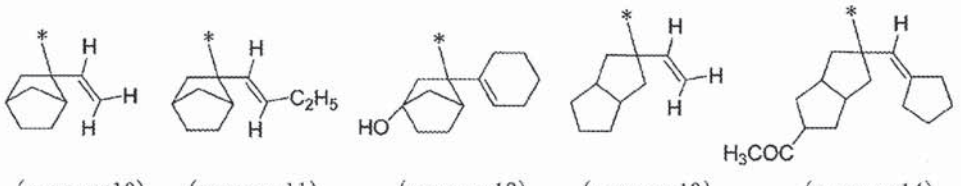


(r-pr-mv1) (r-pr-mv2) (r-pr-mv3) (r-pr-mv4) (r-pr-mv5)

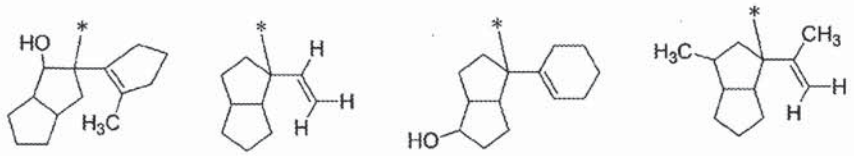


(r-pr-mv6) (r-pr-mv7) (r-pr-mv8) (r-pr-mv9)

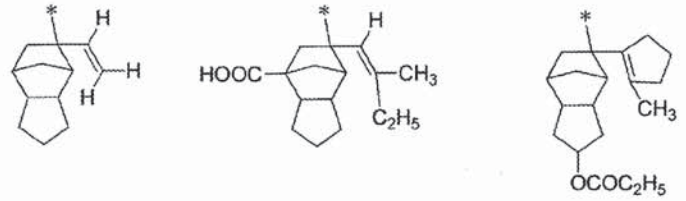
[0091]



(r-pr-mv10) (r-pr-mv11) (r-pr-mv12) (r-pr-mv13) (r-pr-mv14)



(r-pr-mv15) (r-pr-mv16) (r-pr-mv17) (r-pr-mv18)

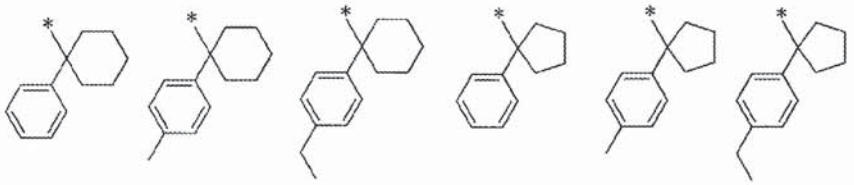


(r-pr-mv19) (r-pr-mv20) (r-pr-mv21)

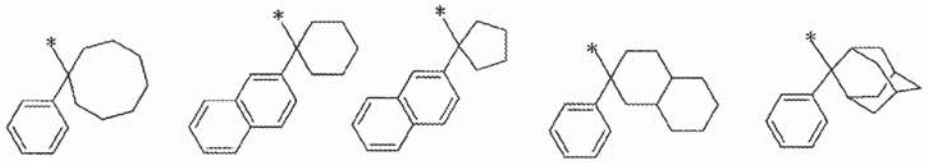
[0092]

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

[0093]



(r-pr-sa1) (r-pr-sa2) (r-pr-sa3) (r-pr-sa4) (r-pr-sa5) (r-pr-sa6)

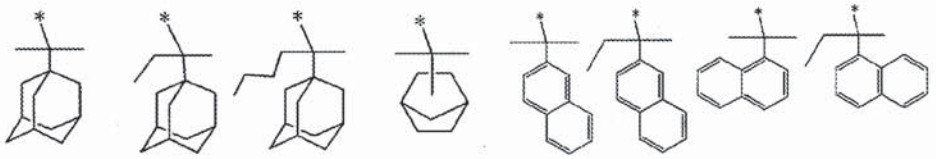


(r-pr-sa7) (r-pr-sa8) (r-pr-sa9) (r-pr-ma1) (r-pr-ma2)

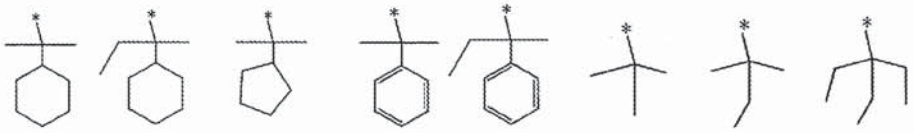
[0094]

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

[0095]



(r-pr-cm1) (r-pr-cm2) (r-pr-cm3) (r-pr-cm4) (r-pr-cm5) (r-pr-cm6) (r-pr-cm7) (r-pr-cm8)



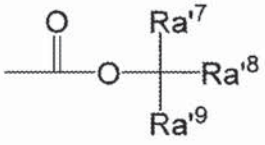
(r-pr-cs1) (r-pr-cs2) (r-pr-cs3) (r-pr-cs4) (r-pr-cs5) (r-pr-c1) (r-pr-c2) (r-pr-c3)

[0096]

Tertiary alkyloxycarbonyl acid-dissociable group:

Among the polar groups, examples of the acid-dissociable group for protecting a hydroxyl group include an acid-dissociable group (hereinafter, for convenience, also referred to as a "tertiary alkyloxycarbonyl acid-dissociable group") represented by General Formula (a1-r-3) shown below.

[0097]



(a1-r-3)

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

[0098]

In General Formula (a1-r-3), Ra'^{7} to Ra'^{9} are each independently 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 each alkyl group is preferably in a range of 3 to 7, more preferably in a range of 3 to 5, and most preferably 3 or 4.

[0099]

The constitutional unit (a1) is preferably a unit including an acid-dissociable group represented by General Formula (a1-r-2) and more preferably a unit including an acid-dissociable group represented by General Formula (a1-r2-4), from the viewpoint of suppressing the decrease in light transmittance of a thick resist film. In General Formula (a1-r2-4), Ra'^{12} and Ra'^{13} are each independently 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 particularly preferably a methyl group. In General Formula (a1-r2-4), Ra'^{14} is 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 particularly preferably a methyl group.

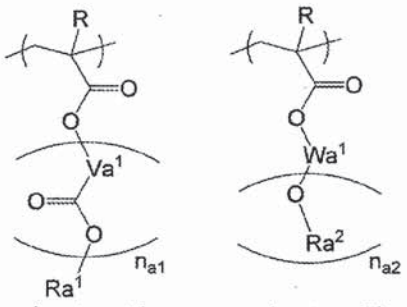
[0100]

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

[0101]

Among the above, the constitutional unit (a1) is preferably a constitutional unit derived from acrylic acid ester in which the hydrogen atom bonded to the carbon atom at the α-position may be substituted with a substituent. Preferred specific examples of such a constitutional unit (a1) include constitutional units represented by General Formula (a1-1) or (a1-2).

[0102]



(a 1 − 1) (a 1 − 2)

[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Va^1 represents

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

[0103]

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

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

[0104]

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

[0105]

The aliphatic hydrocarbon group as the divalent hydrocarbon group represented by Va^1 may be saturated or unsaturated. In general, it is preferable that the aliphatic hydrocarbon group be saturated.

Specific examples of the aliphatic hydrocarbon group include a linear or branched aliphatic hydrocarbon group, and an aliphatic hydrocarbon group containing a ring in the structure thereof.

[0106]

The linear aliphatic hydrocarbon group described above 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. The linear aliphatic hydrocarbon group is preferably a linear alkylene group, and specific examples thereof include a

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

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

[0107]

Examples of the aliphatic hydrocarbon group containing a ring in the structure thereof include an alicyclic hydrocarbon group (a group in which two hydrogen atoms have been removed from an aliphatic hydrocarbon ring), a group in which the alicyclic hydrocarbon group is bonded to the terminal of the linear or branched aliphatic hydrocarbon group, and a group in which the alicyclic hydrocarbon group is interposed in the linear or branched aliphatic hydrocarbon group. The linear or branched aliphatic hydrocarbon group is the same as that defined for the above-described linear aliphatic hydrocarbon group or the above-described branched aliphatic hydrocarbon group.

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

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

[0108]

The aromatic hydrocarbon group as the divalent hydrocarbon group represented by 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 carbon atoms, still more preferably 5 to 20 carbon atoms, particularly preferably 6 to 15 carbon atoms, and most preferably 6 to 12 carbon atoms. Here, the number of carbon atoms in a substituent is not included in the number of carbon atoms. Specific examples of the aromatic ring which the aromatic hydrocarbon group has include aromatic hydrocarbon rings such as benzene, biphenyl, fluorene, naphthalene, anthracene, and phenanthrene; and aromatic heterocyclic rings in which a part of carbon atoms constituting the above-described aromatic hydrocarbon rings have been substituted with a hetero atom. Examples of the hetero atom in the aromatic heterocyclic 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 above-described aromatic hydrocarbon ring (an arylene group); and a group in which one hydrogen atom of a group (an aryl group) formed by removing one hydrogen atom from the aromatic hydrocarbon ring has been substituted with an alkylene group (a group formed by removing one more hydrogen atom from an aryl group in arylalkyl groups such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group). The alkylene group (an alkyl chain in the arylalkyl group) preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and particularly preferably 1 carbon atom.

[0109]

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

[0110]

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

[0111]

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

saturated or unsaturated. In general, it is preferable that the aliphatic hydrocarbon group be saturated. Examples of the aliphatic hydrocarbon group include a linear or branched aliphatic hydrocarbon group, an aliphatic hydrocarbon group containing a ring in the structure thereof, and a combination of the linear or branched aliphatic hydrocarbon group and the aliphatic hydrocarbon group containing a ring in the structure thereof. The valency of $(n_{a2}+1)$ is preferably divalent, trivalent, or tetravalent, and more preferably divalent or trivalent.

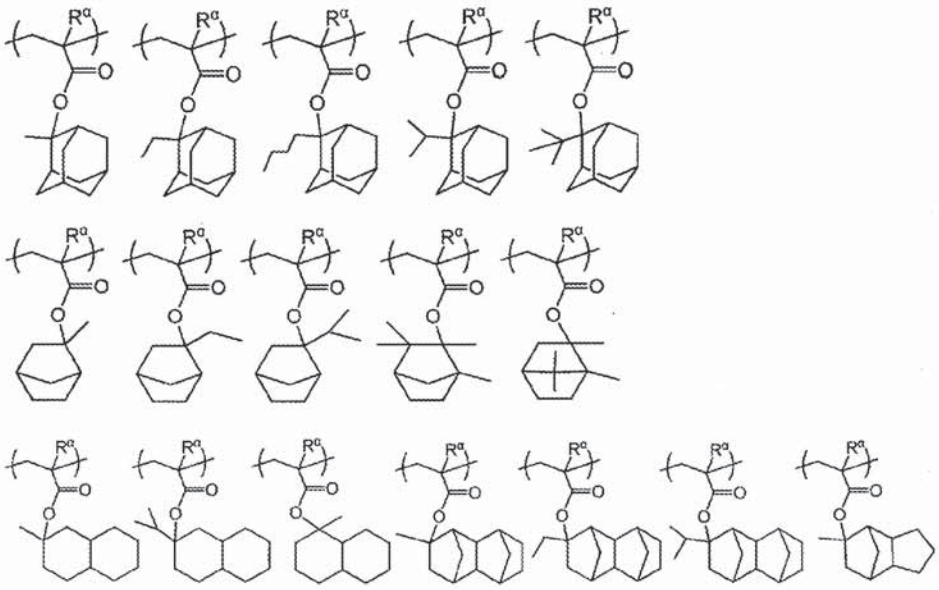
[0112]

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

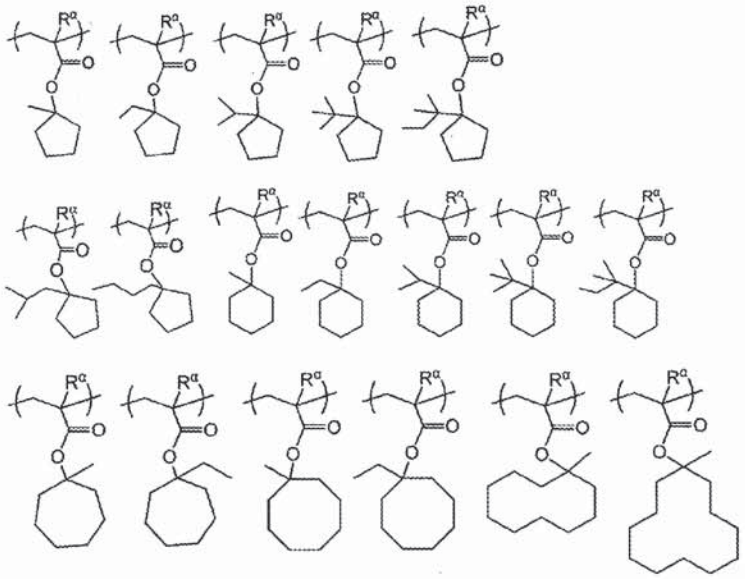
[0113]

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

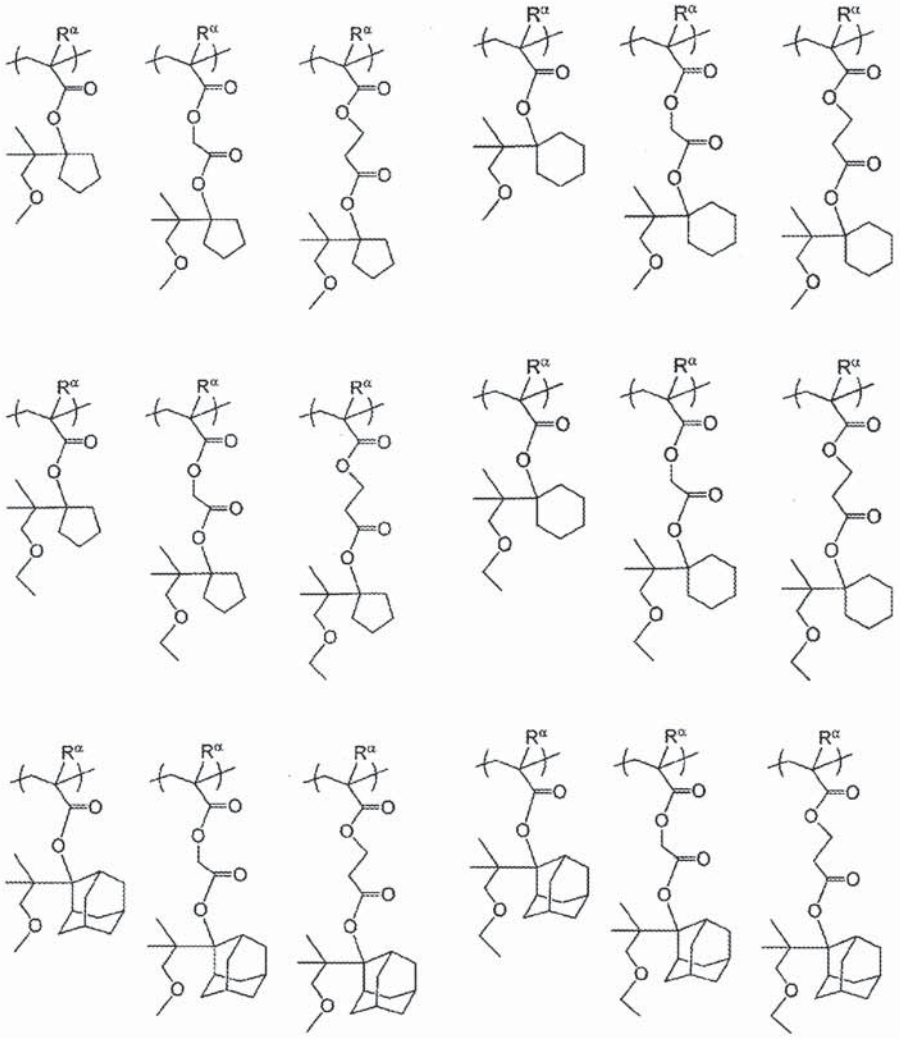
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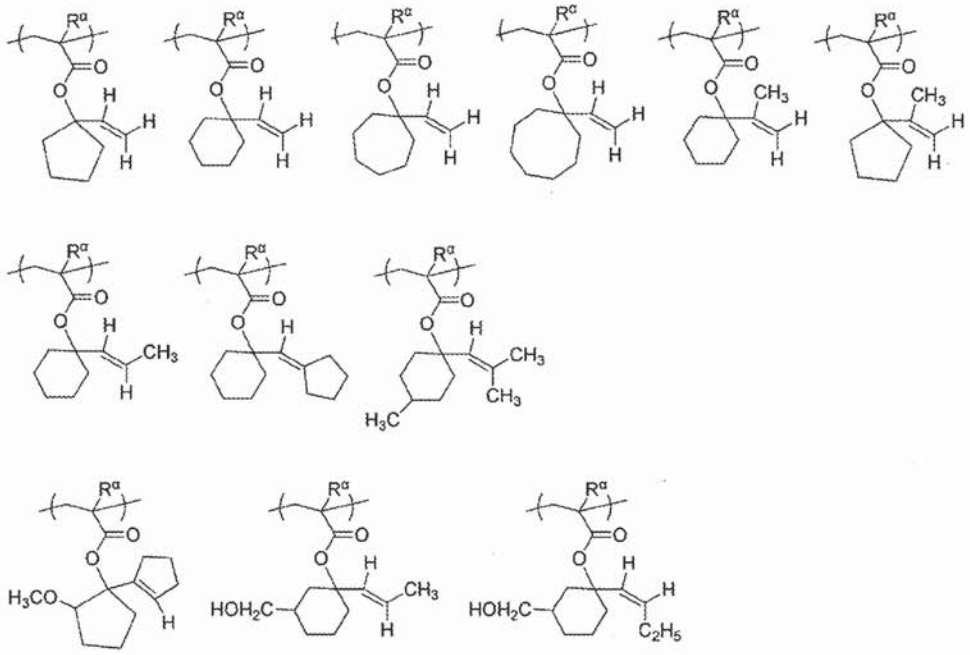
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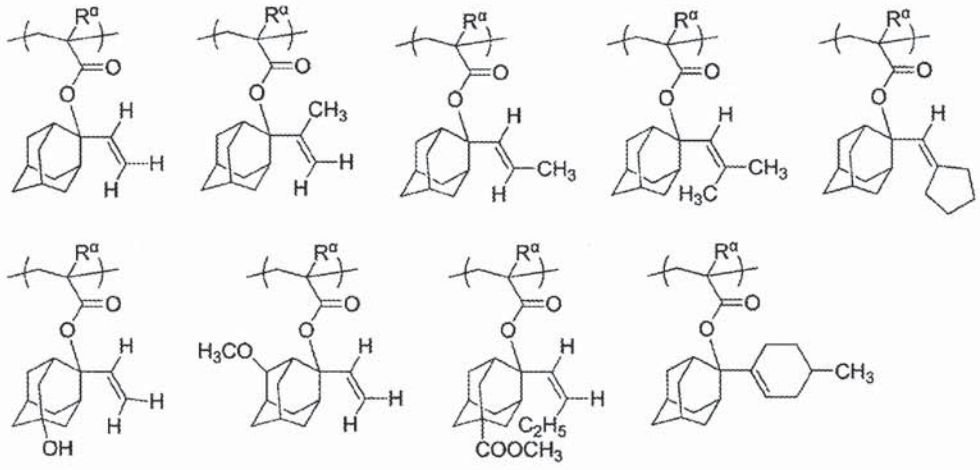
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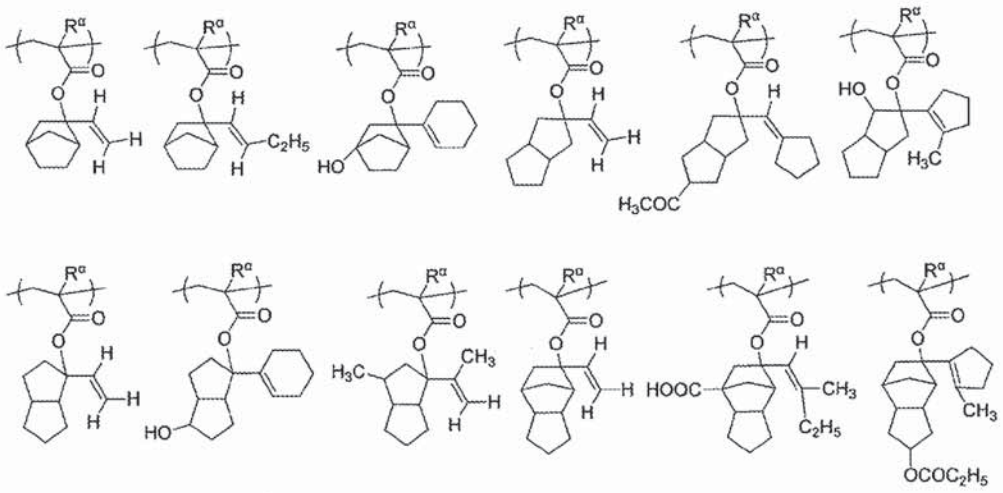
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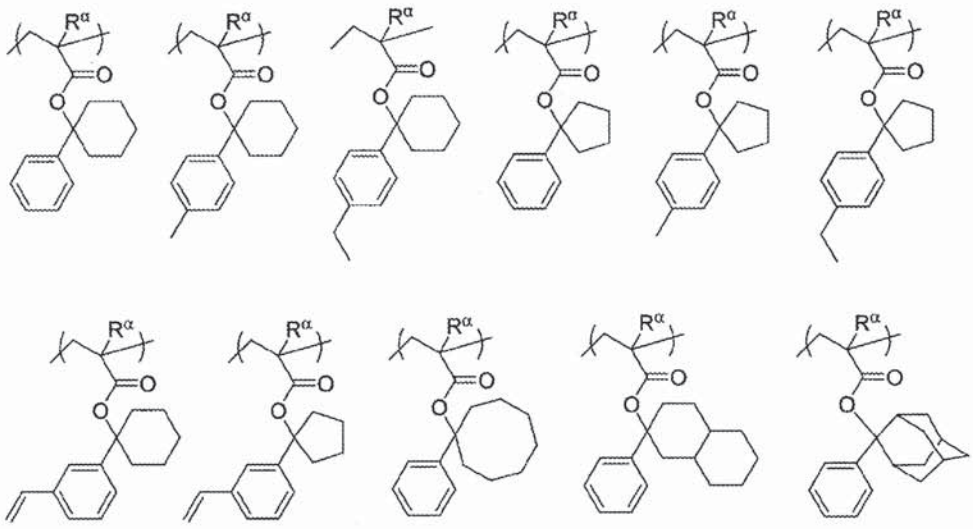
[0118]



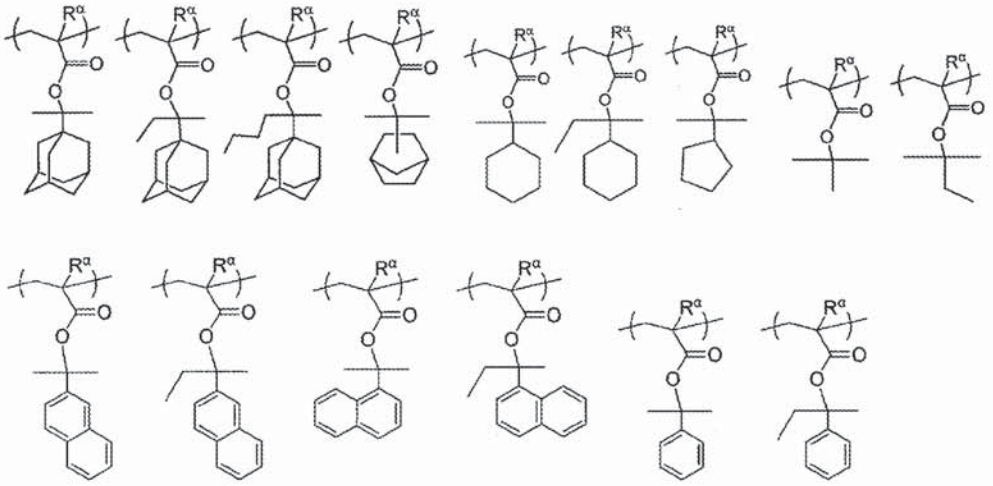
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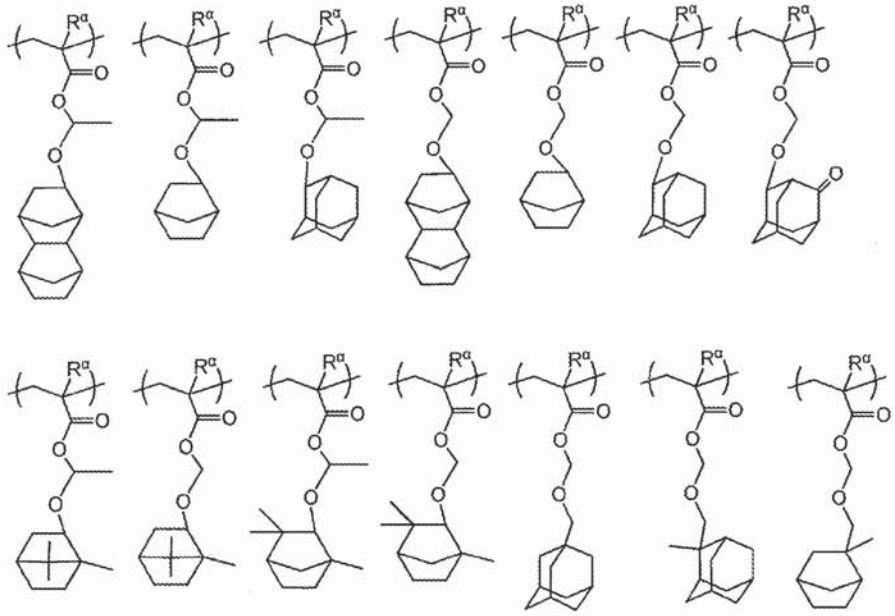
[0120]



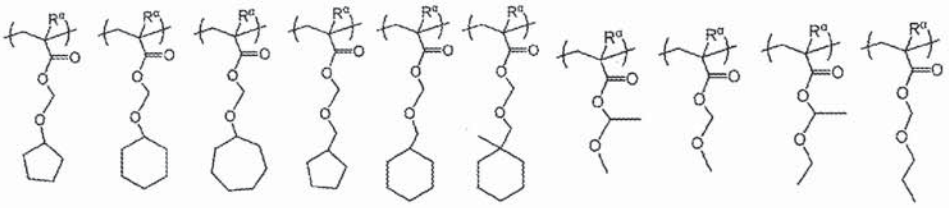
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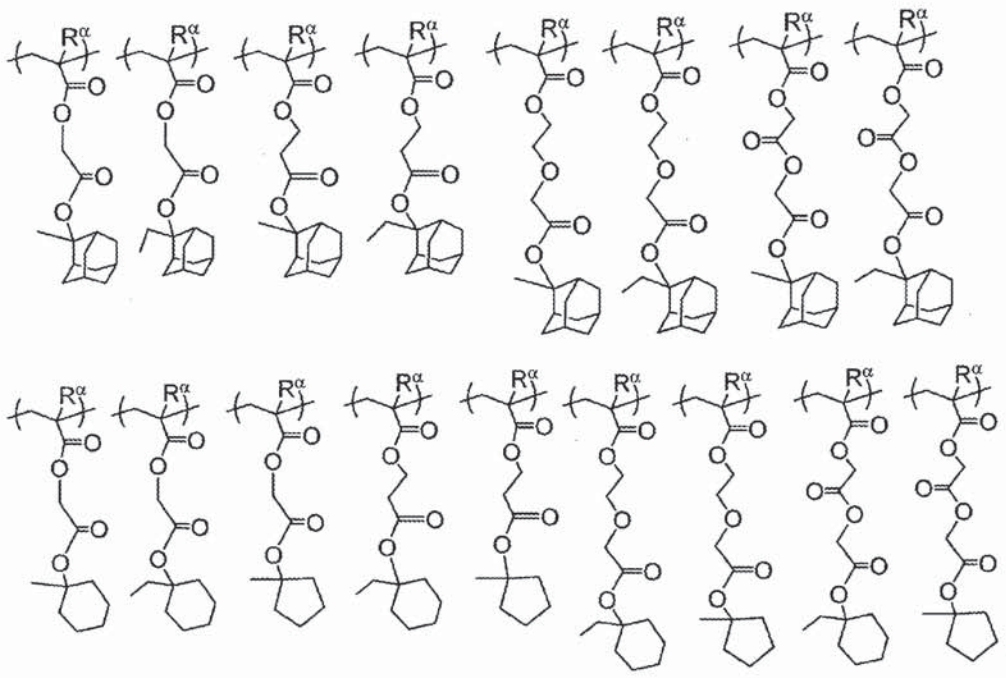
[0122]



[0123]



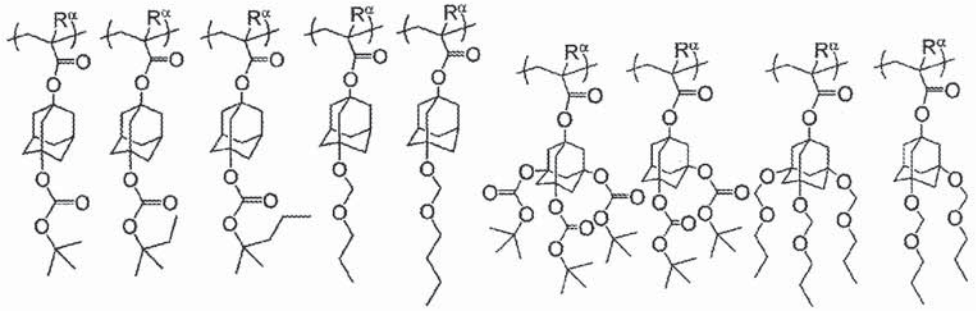
[0124]



[0125]

Specific examples of the constitutional unit represented by General Formula (a1-2) are shown below.

[0126]



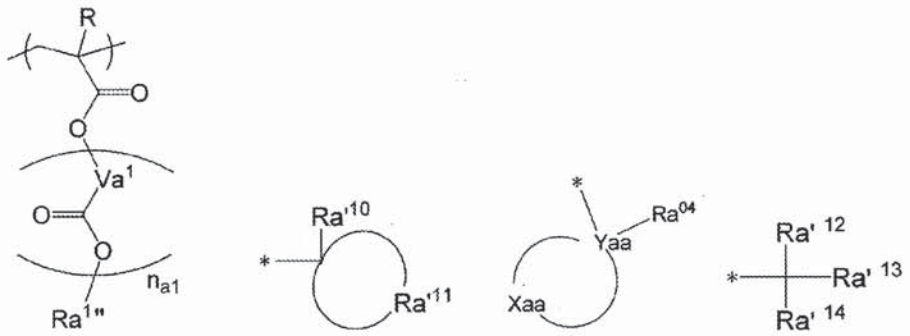
[0127]

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

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

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

[0128]



(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).]

[0129]

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

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

[0130]

The proportion of the constitutional unit (a1) in the component (A1) is preferably in a range of 5% to 80% by mole, more preferably in a range of 5% to 75% by mole, still more preferably in a range of 10% to 70% by mole, even still more preferably in a range of 10% to 60% by mole, and particularly preferably 10% to 30% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

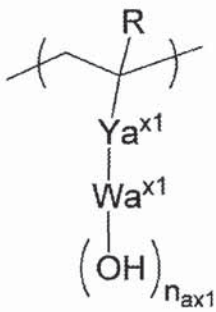
In a case where the proportion of the constitutional unit (a1) is equal to or more than the lower limit of the preferred range described above, lithography characteristics such as sensitivity, resolution, and roughness amelioration are improved. On the other hand, in a case where the proportion is equal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

[0131]

In regard to constitutional unit (a10):

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

[0132]



... (a10-1)

[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Ya^{x1} represents a single bond or a divalent linking group. Wa^{x1} represents an $(n_{ax1} + 1)$-valent aromatic hydrocarbon group. n_{ax1} represents an integer of 1 or greater.]

[0133]

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

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

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

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

more preferably a hydrogen atom or a methyl group, and particularly preferably a methyl group.

[0134]

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

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

[0135]

· Divalent hydrocarbon group which may have substituent:

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

[0136]

·· Aliphatic hydrocarbon group as Ya^{x1}

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

[0137]

··· Linear or branched aliphatic hydrocarbon group

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

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

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

The branched aliphatic hydrocarbon group is preferably a branched alkylene

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

[0138]

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

[0139]

··· Aliphatic hydrocarbon group containing ring in structure thereof

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

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

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

atoms. Specific examples of the polycyclic alicyclic hydrocarbon group include adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane.

[0140]

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

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

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

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

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

In the cyclic aliphatic hydrocarbon group, a part of carbon atoms constituting the ring structure thereof may be substituted with a substituent containing a hetero atom. The substituent containing a hetero atom is preferably -O-, -C(=O)-O-, -S-, $-S(=O)_2-$, or $-S(=O)_2-O-$.

[0141]

·· Aromatic hydrocarbon group as Ya^{x1}

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

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

Specific examples of the aromatic ring include aromatic hydrocarbon rings such

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

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

[0142]

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

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

Examples of the alkoxy group, the halogen atom, and the halogenated alkyl group, as the substituent, include the same groups as those exemplified as the substituent that is substituted for a hydrogen atom which the cyclic aliphatic hydrocarbon group has.

[0143]

· Divalent linking group containing hetero atom

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

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

In General Formula $-Y^{21}-O-Y^{22}-$, $-Y^{21}-O-$, $-Y^{21}-C(=O)-O-$, $-C(=O)-O-Y^{21}-$, $-[Y^{21}-C(=O)-O]_{m"}-Y^{22}-$, $-Y^{21}-O-C(=O)-Y^{22}-$, or $-Y^{21}-S(=O)_2-O-Y^{22}-$, Y^{21}, and Y^{22} each independently represent a divalent hydrocarbon group which may have a substituent. Examples of the divalent hydrocarbon group include those (mentioned as the divalent hydrocarbon group which may have a substituent) in the description of the above-described divalent linking group as Ya^{x1}.

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

Y^{22} is preferably a linear or branched aliphatic hydrocarbon group and more preferably a methylene group, an ethylene group, or an alkylmethylene group. The alkyl group in the alkylmethylene group is preferably a linear alkyl group having 1 to 5 carbon atoms, more preferably a linear alkyl group having 1 to 3 carbon atoms, and most preferably a methyl group.

In the group represented by Formula $-[Y^{21}-C(=O)-O]_{m"}-Y^{22}-$, m" represents an integer in a range of 0 to 3, preferably an integer in a range of 0 to 2, more preferably 0 or 1, and particularly preferably 1. In other words, it is particularly preferable that the group represented by Formula $-[Y^{21}-C(=O)-O]_{m"}-Y^{22}-$ represent a group represented by

Formula $-Y^{21}-C(=O)-O-Y^{22}-$. Among these, a group represented by Formula $-(CH_2)_{a'}-C(=O)-O-(CH_2)_{b'}-$ is preferable. In the formula, a' represents an integer in a range of 1 to 10, preferably an integer in a range of 1 to 8, more preferably an integer in a range of 1 to 5, still more preferably 1 or 2, and most preferably 1. b' represents an integer in a range of 1 to 10, preferably an integer in a range of 1 to 8, more preferably an integer in a range of 1 to 5, still more preferably 1 or 2, and most preferably 1.

[0144]

Among the above, Ya^{x1} is preferably 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 thereof, more preferably a single bond or an ester bond [-C(=O)-O-, -O-C(=O)-], and still more preferably a single bond.

[0145]

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

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

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

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

been removed from benzene.

[0146]

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

[0147]

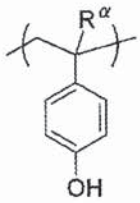
In General Formula (a10-1), n_{ax1} represents an integer of 1 or greater, preferably an integer in a range of 1 to 10, more preferably an integer in a range of 1 to 5, still more preferably 1, 2, or 3, and particularly preferably 1 or 2. Among them, n_{ax1} is preferably 1.

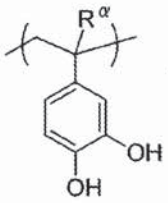
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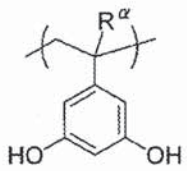
Specific examples of the constitutional unit (a10) represented by General Formula (a10-1) are shown below.

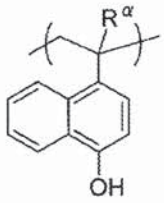
In the formulae shown below, R^{α} represents a hydrogen atom, a methyl group, or a trifluoromethyl group.

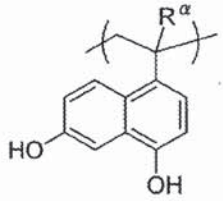
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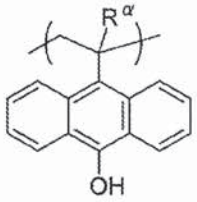

(a10−1−11)

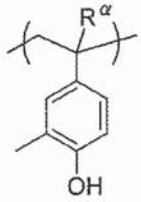

(a10−1−12)

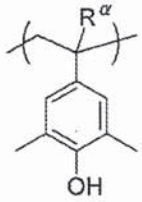

(a10−1−13)


(a10−1−14)

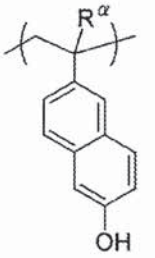

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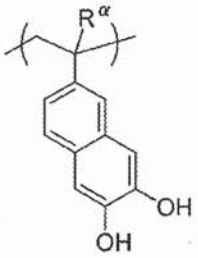

(a10−1−16)

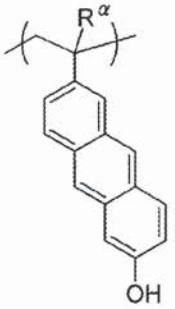

(a10−1−17)

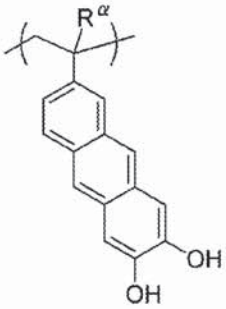

(a10−1−18)

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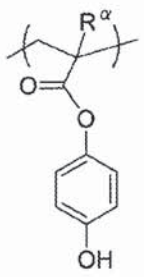

(a10−1−21)

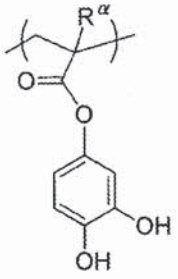

(a10−1−22)

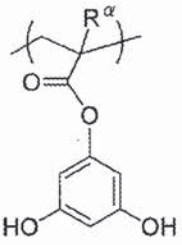

(a10−1−23)

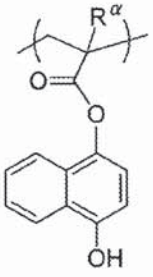

(a10−1−24)

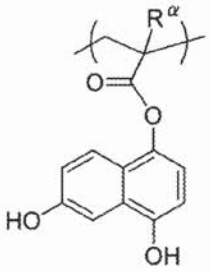
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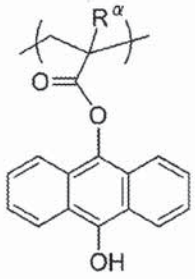

(a10−1−31)


(a10−1−32)

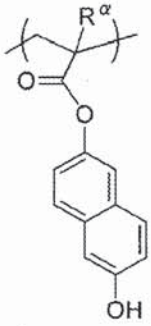

(a10−1−33)

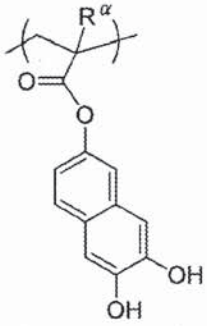

(a10−1−34)

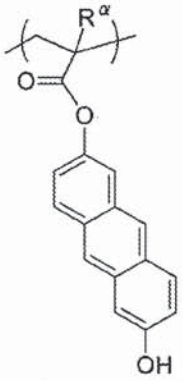

(a10−1−35)

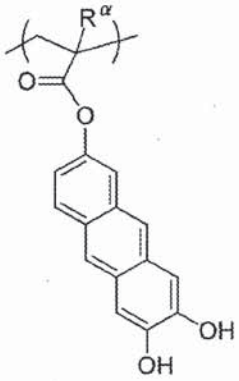

(a10−1−36)

[0152]


(a10−1−41)


(a10−1−42)


(a10−1−43)


(a10−1−44)

[0153]

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

In a case where the component (A1) has the constitutional unit (a10), the proportion of the constitutional unit (a10) in the component (A1) is preferably in a range of 5% to 80% by mole, more preferably in a range of 5% to 75% by mole, and still more preferably in a range of 10% to 70% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

In a case where the proportion of the constitutional unit (a10) is equal to or more

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

[0154]

<<Other constitutional units>>

The component (A1) may have other constitutional units as necessary in addition to the constitutional unit (a1) and the constitutional unit (a10) described above.

Examples of other constitutional units include a constitutional unit (a2) containing a lactone-containing cyclic group, a -SO_2--containing cyclic group, or a carbonate-containing cyclic group; a constitutional unit (a3) containing a polar group-containing aliphatic hydrocarbon group; a constitutional unit (a4) containing an acid non-dissociable aliphatic cyclic group; and a constitutional unit (st) derived from styrene or a derivative thereof.

[0155]

In regard to constitutional unit (a2):

The component (A1) may further have, as necessary, a constitutional unit (a2) (provided that a group having the constitutional unit (a1) is excluded) containing a lactone-containing cyclic group, a -SO_2--containing cyclic group, or a carbonate-containing cyclic group, in addition to the constitutional unit (a1).

In a case where the component (A1) is used for forming a resist film, the lactone-containing cyclic group, the -SO_2--containing cyclic group, or the carbonate-containing cyclic group in the constitutional unit (a2) is effective for improving the adhesiveness of the resist film to the substrate. Further, due to having the constitutional unit (a2), lithography characteristics can be improved, for example, by the effects obtained by appropriately adjusting the acid diffusion length, increasing the adhesiveness of the resist film to the substrate, and appropriately adjusting the solubility during development.

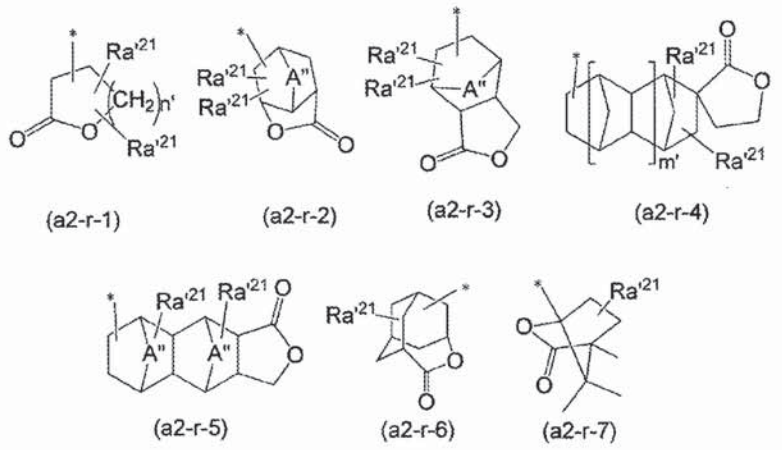
[0156]

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

structures. The lactone-containing cyclic group may be a monocyclic group or a polycyclic group.

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

[0157]



[In the formulae, Ra'^{21}s each independently represent a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, -COOR", -OC(=O)R", a hydroxyalkyl group, or a cyano group; R" represents a hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group, or a -SO_2--containing cyclic group; A" represents an oxygen atom, a sulfur atom, or an alkylene group having 1 to 5 carbon atoms, which may contain an oxygen atom (-O-)or a sulfur atom (-S-); and n' represents an integer in a range of 0 to 2, and m' is 0 or 1.]

[0158]

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

The alkoxy group as Ra'^{21} is preferably an alkoxy group having 1 to 6 carbon atoms. Further, the alkoxy group is preferably a linear or branched alkoxy group. Specific examples of the alkoxy groups include a group formed by linking the above-described alkyl group mentioned as the alkyl group represented by Ra'^{21} to an oxygen atom (-O-).

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

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

[0159]

In -COOR" and -OC(=O)R" as Ra'^{21}, R" represents a hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group, or a $-SO_2-$-containing cyclic group.

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

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

In a case where R" represents a cyclic alkyl group, the cyclic alkyl group preferably has 3 to 15 carbon atoms, more preferably 4 to 12 carbon atoms, and particularly preferably 5 to 10 carbon atoms. Specific examples thereof include a group in which one or more hydrogen atoms have been removed from a monocycloalkane, which may or may not be substituted with a fluorine atom or a fluorinated alkyl group; and a group in which one or more hydrogen atoms have been removed from polycycloalkanes such as bicycloalkane, tricycloalkane, or tetracycloalkane. More specific examples thereof include a group in which one or more hydrogen atoms have been removed from a monocycloalkane such as cyclopentane or cyclohexane; and a group 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 as R" include the same groups as those respectively represented by General Formulae (a2-r-1) to (a2-r-7).

The carbonate-containing cyclic group as R" has the same definition as that for the carbonate-containing cyclic group described below.

Specific examples of the carbonate-containing cyclic group include groups respectively represented by General Formulae (ax3-r-1) to (ax3-r-3).

The -SO_2--containing cyclic group as R" has the same definition as that for the -SO_2--containing cyclic group described below. Specific examples thereof include groups respectively represented by General Formulae (a5-r-1) to (a5-r-4).

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

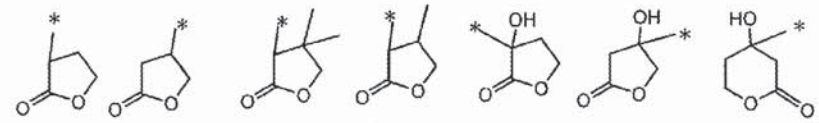
[0160]

In General Formulae (a2-r-2), (a2-r-3) and (a2-r-5), as the alkylene group having 1 to 5 carbon atoms as A", a linear or branched alkylene group is preferable, and examples thereof include a methylene group, an ethylene group, an n-propylene group, and an isopropylene group. Specific examples of the alkylene groups that contain an oxygen atom or a sulfur atom include groups in which -O- or -S- is interposed in the terminal of the alkylene group or between the carbon atoms of the alkylene group, and examples thereof include -O-CH_2-, -CH_2-O-CH_2-, -S-CH_2-, and -CH_2-S-CH_2-. A" is preferably an alkylene group having 1 to 5 carbon atoms or -O-, more preferably an alkylene group having 1 to 5 carbon atoms, and most preferably a methylene group.

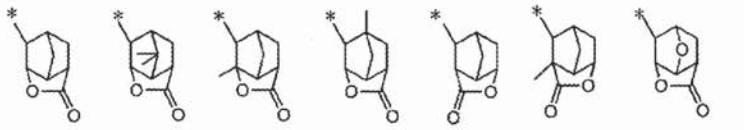
[0161]

Specific examples of the groups respectively represented by General Formulae (a2-r-1) to (a2-r-7) are shown below.

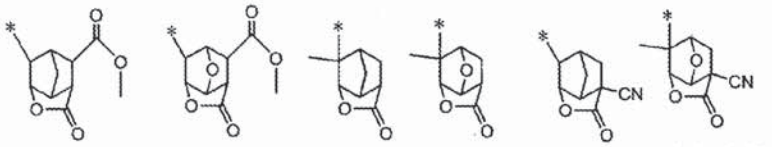
[0162]



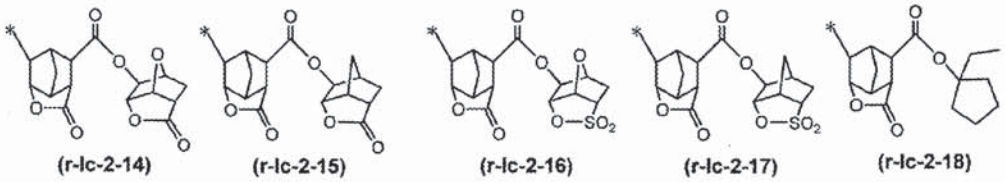
(r-lc-1-1) (r-lc-1-2) (r-lc-1-3) (r-lc-1-4) (r-lc-1-5) (r-lc-1-6) (r-lc-1-7)



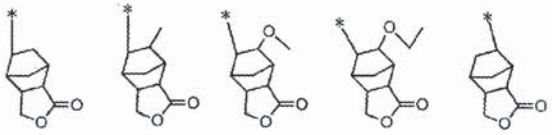
(r-lc-2-1) (r-lc-2-2) (r-lc-2-3) (r-lc-2-4) (r-lc-2-5) (r-lc-2-6) (r-lc-2-7)



(r-lc-2-8) (r-lc-2-9) (r-lc-2-10) (r-lc-2-11) (r-lc-2-12) (r-lc-2-13)

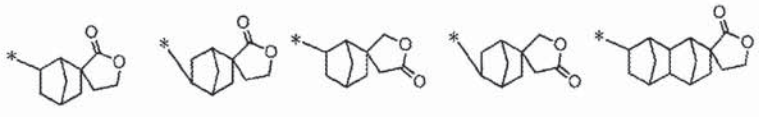


(r-lc-2-14) (r-lc-2-15) (r-lc-2-16) (r-lc-2-17) (r-lc-2-18)

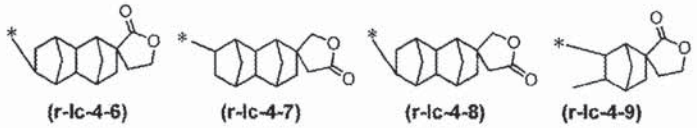


(r-lc-3-1) (r-lc-3-2) (r-lc-3-3) (r-lc-3-4) (r-lc-3-5)

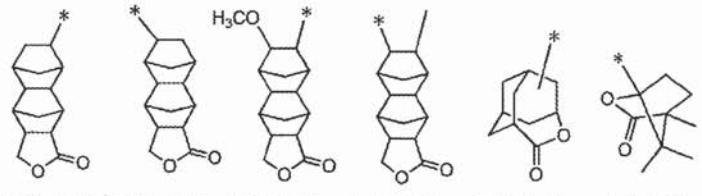
[0163]



(r-lc-4-1) (r-lc-4-2) (r-lc-4-3) (r-lc-4-4) (r-lc-4-5)



(r-lc-4-6) (r-lc-4-7) (r-lc-4-8) (r-lc-4-9)



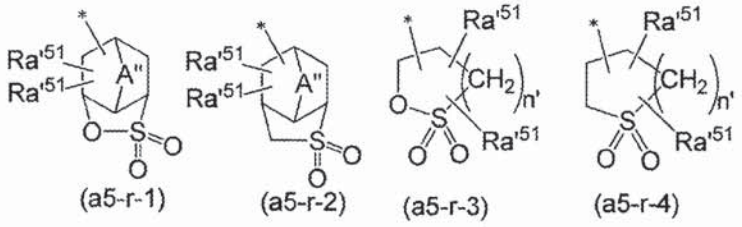
(r-lc-5-1) (r-lc-5-2) (r-lc-5-3) (r-lc-5-4) (r-lc-6-1) (r-lc-7-1)

[0164]

The "-SO_2--containing cyclic group" indicates a cyclic group having a ring containing -SO_2- in the ring skeleton thereof. Specifically, the -SO_2--containing cyclic group is a cyclic group in which the sulfur atom (S) in -SO_2- forms a part of the ring skeleton of the cyclic group. In a case where the ring containing -SO_2- in the ring skeleton thereof is counted as the first ring and the group contains only the ring, the group is referred to as a monocyclic group. Further, in a case where the group has other ring structures, the group is referred to as a polycyclic group regardless of the structures. The -SO_2--containing cyclic group may be a monocyclic group or a polycyclic group. As the -SO_2--containing cyclic group, a cyclic group containing -O-SO_2- in the ring skeleton thereof, in other words, a cyclic group containing a sultone ring in which -O-S- in the -O-SO_2- group forms a part of the ring skeleton thereof is particularly preferable.

More specific examples of the -SO_2--containing cyclic group include groups respectively represented by General Formulae (a5-r-1) to (a5-r-4) shown below.

[0165]



[In the formulae, Ra'^{51}s each independently represent a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, -COOR", -OC(=O)R", a hydroxyalkyl group, or a cyano group; R" represents a hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group, or a -SO_2--containing cyclic group; A" represents an oxygen atom, a sulfur atom, or an alkylene group having 1 to 5 carbon atoms, which may contain an oxygen atom or a sulfur atom; and n' represents an integer in a range of 0 to 2.]

[0166]

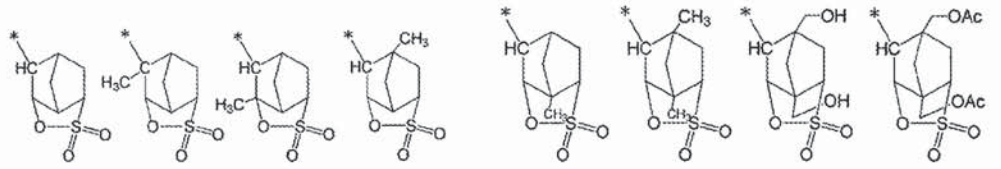
In General Formulae (a5-r-1) and (a5-r-2), A" has the same definition as that for A" in General Formulae (a2-r-2), (a2-r-3) and (a2-r-5).

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

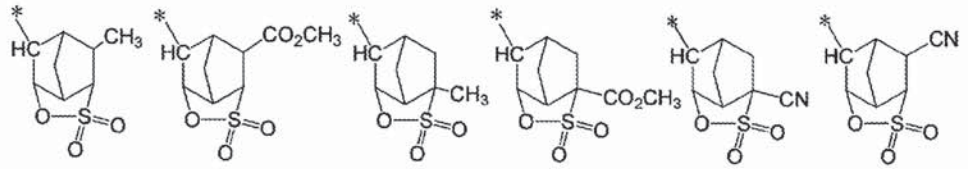
Formulae (a2-r-1) to (a2-r-7).

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

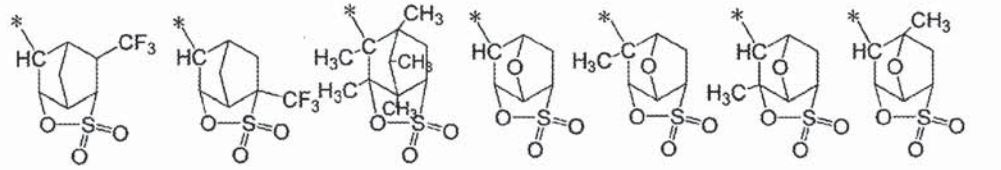
[0167]



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

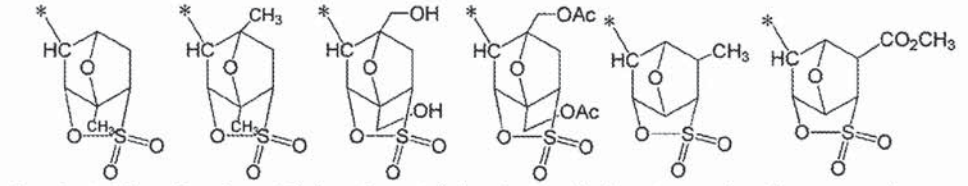


(r-sl-1-9) (r-sl-1-10) (r-sl-1-11) (r-sl-1-12) (r-sl-1-13) (r-sl-1-14)

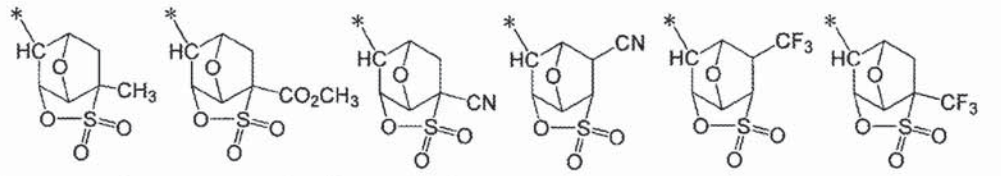


(r-sl-1-15) (r-sl-1-16) (r-sl-1-17) (r-sl-1-18) (r-sl-1-19) (r-sl-1-20) (r-sl-1-21)

[0168]

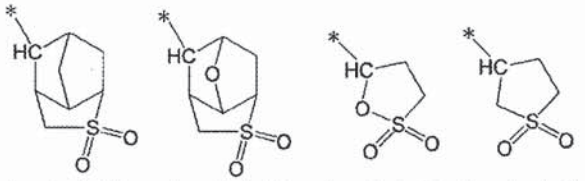


(r-sl-1-22) (r-sl-1-23) (r-sl-1-24) (r-sl-1-25) (r-sl-1-26) (r-sl-1-27)



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

[0169]



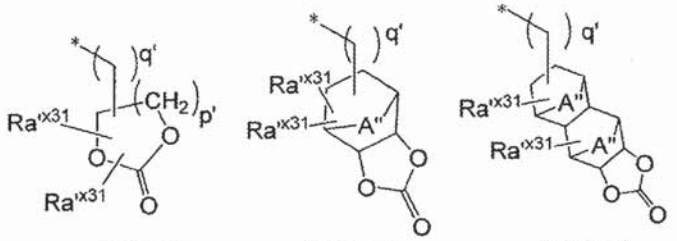
(r-sl-2-1) (r-sl-2-2) (r-sl-3-1) (r-sl-4-1)

[0170]

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

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

[0171]



(ax3-r-1) (ax3-r-2) (ax3-r-3)

[In the formulae, Ra'^{x31}s each independently represent a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, -COOR", -OC(=O)R", a hydroxyalkyl group, or a cyano group; R" represents a hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group, or a -SO_2--containing cyclic group; A" represents an oxygen atom, a sulfur atom, or an alkylene group having 1 to 5 carbon atoms, which may contain an oxygen atom or a sulfur atom; and p' represents an integer in a range of 0 to 3, and q' is 0 or 1.]

[0172]

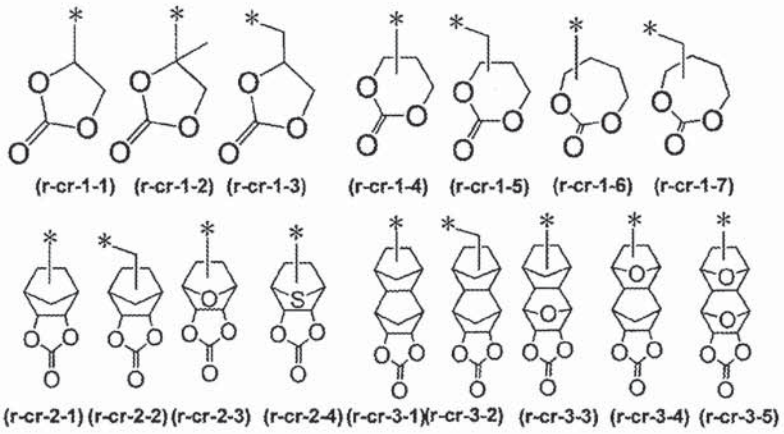
In General Formulae (ax3-r-2) and (ax3-r-3), A" has the same definition as that

for A" in General Formulae (a2-r-2), (a2-r-3) and (a2-r-5).

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

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

[0173]

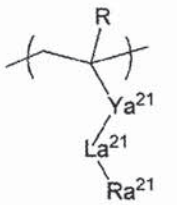


[0174]

Among them, the constitutional unit (a2) is preferably a constitutional unit derived from acrylic acid ester in which the hydrogen atom bonded to the carbon atom at the α-position may be substituted with a substituent.

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

[0175]



··· (a 2 − 1)

[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Ya^{21} represents a single bond or a divalent linking group. La^{21} represents -O-, -COO-, -CON(R')-, -

OCO-, -CONHCO- or -CONHCS-, and R' represents a hydrogen atom or a methyl group. However, in a case where La^{21} represents -O-, Ya^{21} does not represent -CO-. Ra^{21} represents a lactone-containing cyclic group, a carbonate-containing cyclic group, or a $-SO_2$--containing cyclic group.]

[0176]

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

[0177]

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

[0178]

· Divalent hydrocarbon group which may have substituent:

In a case where Ya^{21} represents a divalent hydrocarbon group which may have a substituent, the hydrocarbon group may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

[0179]

·· Aliphatic hydrocarbon group as Ya^{21}

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

[0180]

··· Linear or branched aliphatic hydrocarbon group

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

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

pentamethylene group [-$(CH_2)_5$-].

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

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

[0181]

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

[0182]

··· Aliphatic hydrocarbon group containing ring in structure thereof

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

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

The cyclic aliphatic hydrocarbon group may be a polycyclic group or a monocyclic group. The monocyclic alicyclic hydrocarbon group is preferably a group

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

[0183]

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

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

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

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

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

In the cyclic aliphatic hydrocarbon group, a part of carbon atoms constituting the ring structure thereof may be substituted with a substituent containing a hetero atom. The substituent containing a hetero atom is preferably -O-, -C(=O)-O-, -S-, $-S(=O)_2-$, or $-S(=O)_2-O-$.

[0184]

·· Aromatic hydrocarbon group as Ya^{21}

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

The aromatic ring is not particularly limited as long as it is a cyclic conjugated system having $(4n + 2)$ π electrons, and may be monocyclic or polycyclic. The

aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, still more preferably 6 to 15 carbon atoms, and particularly preferably 6 to 12 carbon atoms. Here, the number of carbon atoms in a substituent is not included in the number of carbon atoms.

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

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

[0185]

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

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

tert-butyl group is most preferable.

Examples of the alkoxy group, the halogen atom, and the halogenated alkyl group, as the substituent, include the same groups as those exemplified as the substituent that is substituted for a hydrogen atom which the cyclic aliphatic hydrocarbon group has.

[0186]

· Divalent linking group containing hetero atom

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

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

In General Formula $-Y^{21}-O-Y^{22}-$, $-Y^{21}-O-$, $-Y^{21}-C(=O)-O-$, $-C(=O)-O-Y^{21}-$, $-[Y^{21}-C(=O)-O]_{m"}-Y^{22}-$, $-Y^{21}-O-C(=O)-Y^{22}-$, or $-Y^{21}-S(=O)_2-O-Y^{22}-$, Y^{21}, and Y^{22} each independently represent a divalent hydrocarbon group which may have a substituent. Examples of the divalent hydrocarbon group include those (mentioned as the divalent hydrocarbon group which may have a substituent) in the description of the above-described divalent linking group as Ya^{21}.

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

Y^{22} is preferably a linear or branched aliphatic hydrocarbon group and more preferably a methylene group, an ethylene group, or an alkylmethylene group. The alkyl group in the alkylmethylene group is preferably a linear alkyl group having 1 to 5 carbon atoms, more preferably a linear alkyl group having 1 to 3 carbon atoms, and most

preferably a methyl group.

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

[0187]

Among the above, Ya^{21} is preferably a single bond, an ester bond [-C(=O)-O-], an ether bond (-O-), a linear or branched alkylene group, or a combination thereof.

[0188]

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

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

Among them, a lactone-containing cyclic group or a -SO_2--containing cyclic group is preferable, and groups respectively represented by General Formula (a2-r-1), (a2-r-2), (a2-r-6), or (a5-r-1) are more preferable. Specifically, groups respectively represented by any of Chemical Formulae (r-lc-1-1) to (r-lc-1-7), (r-lc-2-1) to (r-lc-2-18), (r-lc-6-1), (r-sl-1-1), and (r-sl-1-18) are more preferable.

[0189]

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

In a case where the component (A1) has the constitutional unit (a2), the proportion of the constitutional unit (a2) in the component (A1) is preferably in a range of 5% to 60% by mole, more preferably in a range of 10% to 60% by mole, still more

preferably in a range of 20% to 55% by mole, and particularly preferably in a range of 30% to 50% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

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

[0190]

In regard to constitutional unit (a3):

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

[0191]

Examples of the polar group include a hydroxyl group, a cyano group, a carboxy group, or a hydroxyalkyl group in which a part of hydrogen atoms of the alkyl group have been substituted with a fluorine atom, and the polar group is particularly preferably a hydroxyl group.

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

[0192]

In a case where the cyclic group is a monocyclic group, the monocyclic group preferably has 3 to 10 carbon atoms. Among them, a constitutional unit derived from an

acrylic acid ester that includes an aliphatic monocyclic group containing a hydroxyl group, cyano group, carboxy group, or a hydroxyalkyl group in which a part of hydrogen atoms of the alkyl group have been substituted with a fluorine atom are particularly preferable. Examples of the monocyclic group include a group in which two or more hydrogen atoms have been removed from a monocycloalkane. Specific examples of the monocyclic group a include group in which two or more hydrogen atoms have been removed from a monocycloalkane such as cyclopentane, cyclohexane, or cyclooctane. Among these monocyclic groups, a group in which two or more hydrogen atoms have been removed from cyclopentane or a group in which two or more hydrogen atoms have been removed from cyclohexane are industrially preferable.

[0193]

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

[0194]

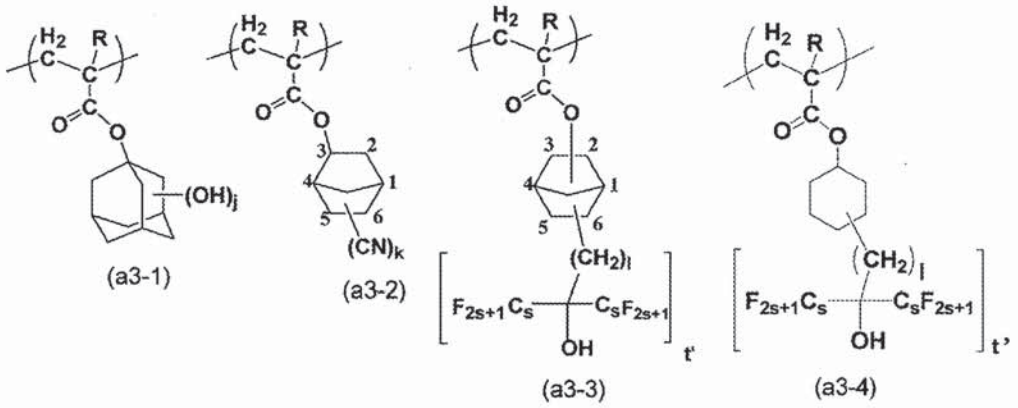
The constitutional unit (a3) is not particularly limited, and any constitutional unit may be used as long as the constitutional unit contains a polar group-containing aliphatic hydrocarbon group.

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

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

Further, preferred examples of the constitutional unit (a3) include a constitutional unit represented by General Formula (a3-1), a constitutional unit represented by General Formula (a3-2), and a constitutional unit represented by General Formula (a3-3) in a case where the hydrocarbon group in the polar group-containing aliphatic hydrocarbon group is a polycyclic group; and a constitutional unit represented by General Formula (a3-4) in a case where the hydrocarbon group is a monocyclic group.

[0195]



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

[0196]

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

[0197]

In General Formula (a3-2), k preferably represents 1. The cyano group is

preferably bonded to the 5- or 6- position of the norbornyl group.

[0198]

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

[0199]

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

[0200]

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

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

In a case where the proportion of the constitutional unit (a3) is equal to or greater than the lower limit of the preferred range, the effect obtained by allowing the component (A1) to contain the constitutional unit (a3) can be sufficiently achieved by the effect described above. In a case where the proportion of the constitutional unit (a3) is equal to or lower than the upper limit of the preferred range, balance with other constitutional units can be obtained, and various lithography characteristics are improved.

[0201]

In regard to constitutional unit (a4):

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

In a case where the component (A1) has the constitutional unit (a4), the dry etching resistance of the formed resist pattern is improved. Further, the hydrophobicity of the component (A) increases. The improvement in hydrophobicity contributes to the

improvement in resolution, a resist pattern shape, and the like, particularly in the case of a solvent developing process. The "acid non-dissociable cyclic group" in the constitutional unit (a4) is a cyclic group that remains in the constitutional unit without being dissociated even in a case where an acid acts thereto in a case where the acid is generated in the resist composition upon exposure (for example, in a case where the acid is generated from the constitutional unit that generates an acid upon exposure or the component (B)).

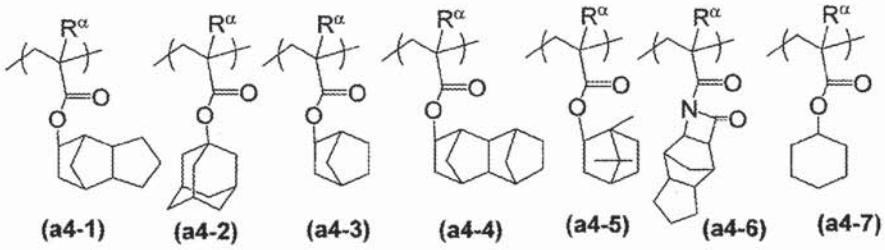
[0202]

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

The cyclic group is particularly preferably at least one selected from a tricyclodecyl group, an adamantyl group, a tetracyclododecyl group, an isobornyl group, and a norbornyl group, from the viewpoint of industrial availability. These polycyclic groups may have, as a substituent, a linear or branched alkyl group having 1 to 5 carbon atoms.

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

[0203]



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

[0204]

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

In a case where the component (A1) has the constitutional unit (a4), the proportion of the constitutional unit (a4) is preferably in a range of 1% to 40% by mole

and more preferably in a range of 5% to 20% by mole, with respect to the total (100% by mole) of all constitutional units constituting the component (A1).

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

[0205]

In regard to constitutional unit (st):

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

[0206]

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

[0207]

Examples of the substituent that is substituted for the hydrogen atom at the α-position of styrene include an alkyl group having 1 to 5 carbon atoms or a halogenated alkyl group having 1 to 5 carbon atoms.

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

The halogenated alkyl group having 1 to 5 carbon atoms is a group in which part or all of hydrogen atoms in the alkyl group having 1 to 5 carbon atoms have been

substituted with 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 particularly preferable. The substituent that is substituted for the hydrogen atom at the α-position of styrene is preferably an alkyl group having 1 to 5 carbon atoms or a fluorinated alkyl group having 1 to 5 carbon atoms, more preferably an alkyl group having 1 to 3 carbon atoms or a fluorinated alkyl group having 1 to 3 carbon atoms, and still more preferably a methyl group from the viewpoint of industrial availability.

[0208]

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

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

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

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

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

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

[0209]

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

methyl group, and still more preferably a constitutional unit derived from styrene.

[0210]

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

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

[0211]

The component (A1) contained in the resist composition may be used alone or in a combination of two or more kinds thereof.

In the resist composition according to the present embodiment, examples of the component (A1) include a high-molecular-weight compound having a repeated structure of the constitutional unit (a1) and the constitutional unit (a10).

Examples of the preferred component (A1) include a high-molecular-weight compound having a repeated structure of the constitutional unit (a1), the constitutional unit (a10), and other constitutional units. Examples of the other constitutional units include the constitutional unit (st).

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

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

[0212]

The component (A1) can be produced by dissolving, in a polymerization solvent, each monomer from which the constitutional unit is derived, adding thereto a radical polymerization initiator such as azobisisobutyronitrile (AIBN) or dimethyl

azobisisobutyrate (for example, V-601) to perform polymerization.

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

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

[0213]

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

In a case where Mw of the component (A1) is equal to or lower than the upper limit of this preferred range, the resist composition exhibits sufficient solubility in a solvent for a resist such that the resist composition can be used as a resist composition. On the other hand, in a case where Mw of the component (Aa1) is equal to or greater than the lower limit of this preferred range, dry etching resistance and the cross-sectional shape of the resist pattern become excellent.

Further, the polydispersity (Mw/Mn) of the component (A1) is not particularly limited; however, it is preferably in a range of 1.0 to 4.0, more preferably in a range of 1.0 to 3.0, and particularly preferably in a range of 1.0 to 2.0. Mn represents the number-average molecular weight.

[0214]

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

In the resist composition according to the present embodiment, a base material component having solubility in a developing solution, which is changed by action of an

acid, which does not correspond to the component (A1), may be used in combination as the component (A). The base material component which does not correspond to the component (A1) is not particularly limited, many components conventionally known as base material components for a chemical amplification-type resist composition can be randomly selected, and one kind of high-molecular-weight compound or low-molecular-weight compound may be used alone or in combination of two or more kinds thereof.

[0215]

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

[0216]

In the resist composition according to the present embodiment, the content of the component (A) is preferably 20% by mass or more with respect to the total mass (100% by mass) of the resist composition. In a case where the content of the component (A) is 20% by mass or more, a thick resist film (for example, a film having a thickness of 5 μm or more) can be easily formed. The upper limit of the content of the component (A) is not particularly limited as long as it has a concentration capable of forming a resist film, but may be, for example, 50% by mass or less. The content of the component (A) is preferably in a range of 20% to 50% by mass, more preferably in a range of 22% to 50% by mass, and still more preferably in a range of 25% to 50% by mass.

[0217]

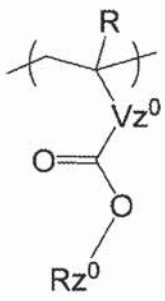
<Component (Z)>

The component (Z) is a plasticizer component that has a constitutional unit (z1) represented by General Formula (z1-1) and does not contain an acid-dissociable group. Here, the "acid-dissociable group" indicates both (i) a group in which a bond between the acid-dissociable group and an atom adjacent to the acid-dissociable group can be cleaved by action of an acid; and (ii) a group in which a part of bonds are cleaved by action of an acid, and then a decarboxylation reaction occurs, thereby cleaving the bond between the acid-dissociable group and the atom adjacent to the acid-dissociable group."

That is, all the constitutional units constituting the component (Z) do not contain an acid-dissociable group. Therefore, the component (Z) does not undergo a

deprotection reaction by action of an acid.

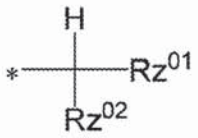
[0218]



··· (z1-1)

[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Vz^0 represents a single bond or a divalent hydrocarbon group which may contain a hetero atom. However, in a case where Vz^0 represents a divalent hydrocarbon group which may contain a hetero atom, Vz^0 does not contain an acid-dissociable group. Rz^0 represents a hydrogen atom or a group represented by General Formula (z1-r-1).]

[0219]



··· (z1-r-1)

[In the formula, Rz^{01} represents a hydrocarbon group which may have a substituent. Rz^{02} represents a hydrogen atom or a hydrocarbon group which may have a substituent. Rz^{01} and Rz^{02} may be bonded to each other to form a ring structure. However, Rz^{01} and Rz^{02} do not contain an acid-dissociable group. * represents a bond.]

[0220]

<<Constitutional unit (z1)>>

In General Formula (z1-1), R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms.

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

The halogenated alkyl group having 1 to 5 carbon atoms as R is a group in

which part or all of hydrogen atoms of the above-described alkyl group having 1 to 5 carbon atoms have been substituted with 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 particularly preferable.

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

[0221]

In General Formula (z1-1), examples of the divalent hydrocarbon group which may have a hetero atom, as Vz^0, include the divalent hydrocarbon group which may have a substituent, and the divalent linking group containing a hetero atom, as Ya^{x1} in General Formula (a10-1).

However, in a case where Vz^0 represents a divalent hydrocarbon group which may contain a hetero atom, Vz^0 does not contain an acid-dissociable group.

Among them, Vz^0 is preferably a single bond, -C(=O)-O-Y^{21}-, or -C(=O)-O-Y^{21}-O-C(=O)-Y^{22}- and more preferably a single bond. Y^{21} and Y^{22} each independently represent a divalent hydrocarbon group which may have a substituent. Examples of the divalent hydrocarbon group include those (mentioned as the divalent hydrocarbon group which may have a substituent) in the description of the above-described divalent linking group as Ya^{21}.

[0222]

In General Formula (z1-1), Rz^0 represents a hydrogen atom or a group represented by General Formula (z1-r-1).

In General Formula (z1-r-1), examples of the hydrocarbon group which may have a substituent, as Rz^{01}, include a linear or branched alkyl group or a cyclic hydrocarbon group. The linear alkyl group as Rz^{01} preferably has 1 to 10 carbon atoms and more preferably 1 to 5 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, an n-propyl group, an n-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, an n-octyl group, an n-nonyl group, and an n-decyl group.

The branched alkyl group as Rz^{01} preferably has 3 to 10 carbon atoms and more preferably 3 to 5 carbon atoms. Specific examples thereof include an isopropyl group, an isobutyl group, a tert-butyl group, an isopentyl group, a neopentyl group a 1,1-

diethylpropyl group, and a 2,2-dimethylbutyl group.

A part of the carbon atoms constituting the linear or branched alkyl group as Rz^{01} may be substituted with an oxygen atom (-O-). However, in General Formula (z1-r-1), Rz^{01} does not contain an acid-dissociable group. Accordingly, in General Formula (z1-r-1), even in a case where a part of carbon atoms constituting the linear or branched alkyl group as Rz^{01} is substituted with an oxygen atom (-O-), an acetal-type acid-dissociable group represented by General Formula (a1-r-1) is not contained.

[0223]

The cyclic hydrocarbon group as Rz^{01} may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group and may be a polycyclic group or a monocyclic group.

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

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

[0224]

In a case where the cyclic hydrocarbon group as Rz^{01} is an aromatic hydrocarbon group, the aromatic hydrocarbon group is a hydrocarbon group having at least one aromatic ring.

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

Specific examples of the aromatic hydrocarbon group as Rz^{01} include a group in which one hydrogen atom has been removed from the above-described aromatic hydrocarbon ring or aromatic heterocyclic ring (an aryl group or a heteroaryl group); a group in which one hydrogen atom has been removed from an aromatic compound having two or more aromatic rings (biphenyl, fluorene or the like); and a group in which one hydrogen atom of the above-described aromatic hydrocarbon ring or aromatic heterocyclic ring has been substituted with an alkylene group (an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group). The number of carbon atoms in the alkylene group bonded to the aromatic hydrocarbon ring or aromatic heterocyclic ring is preferably in a range of 1 to 4, more preferably 1 or 2, and particularly preferably 1.

[0225]

The cyclic hydrocarbon group in Rz^{01} may have a substituent. Examples of the substituent include the substituent "Ra^{05}" which the hydrocarbon group as Ra'^{3} in General Formula (a1-r-1) may have.

[0226]

In General Formula (z1-r-1), the hydrocarbon group which may have a substituent, as Rz^{02}, is the same as the hydrocarbon group which may have a substituent, as Rz^{01}.

[0227]

In General Formula (z1-r-1), in a case where Rz^{01} and Rz^{02} are bonded to each other to form a ring structure, examples of the ring structure include a group in which two hydrogen atoms have been removed from a monocycloalkane or a polycycloalkane. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

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

[0228]

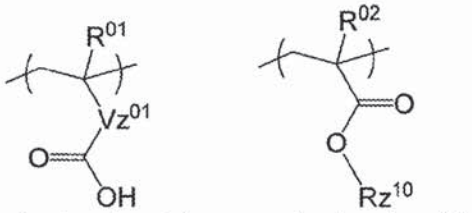
In General Formula (z1-r-1), it is preferable that Rz^{01} be a linear alkyl group or a linear alkoxy group and Rz^{02} be a hydrogen atom, or Rz^{01} and Rz^{02} be bonded to each other to form a s ring structure.

[0229]

The constitutional unit (z1) which the component (Z) has may be one kind or may be two or more kinds.

Among them, the component (Z) preferably has, as the constitutional unit (z1), a constitutional unit represented by General Formula (z1-1-1) (hereinafter, may be referred to as a "constitutional unit (z1-1-1)") and a constitutional unit represented by General Formula (z1-1-2) (hereinafter, may be referred to as a "constitutional unit (z1-1-2)").

[0230]



(z1-1-1) (z1-1-2)

[In the formula, R^{01} and R^{02} each independently represent a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Vz^{01} represents a single bond, -C(=O)-O-Y^{21}- or -C(=O)-O-Y^{21}-O-C(=O)-Y^{22}-. Y^{21} and Y^{22} each independently represent a divalent hydrocarbon group which may have a substituent, and O represents an oxygen atom. However, Vz^{01} represents -C(=O)-O-Y^{21}- or -C(=O)-O-Y^{21}-O-C(=O)-Y^{22}-, Vz^{01} does not contain an acid-dissociable group. Rz^{10} represents a linear alkyl group, -Rz^{11}-O-Rz^{12}, or a monovalent alicyclic hydrocarbon group. Rz^{11} represents a linear alkylene group, and Rz^{12} represents a linear alkyl group.]

[0231]

In General Formulae (z1-1-1) and (z1-1-2), R^{01} and R^{02} are the same as R in General Formula (z1-1). Among them, R^{01} is preferably a hydrogen atom, a methyl group, or a trifluoromethyl group, more preferably a hydrogen atom or a methyl group, and still more preferably a methyl group. R^{02} is preferably a hydrogen atom, a methyl group, or a trifluoromethyl group, more preferably a hydrogen atom or a methyl group, and still more preferably a hydrogen atom.

[0232]

In General Formula (z1-1-1), in a case where Vz^{01} represents -C(=O)-O-Y^{21}- or -C(=O)-O-Y^{21}-O-C(=O)-Y^{22}-, Y^{21} is preferably a linear aliphatic hydrocarbon group, more preferably a linear alkylene group, still more preferably a linear alkylene group

having 1 to 5 carbon atoms, and particularly preferably a methylene group or an ethylene group. Y^{22} is preferably a linear or branched aliphatic hydrocarbon group and more preferably a methylene group, an ethylene group, or an alkylmethylene group. The alkyl group in the alkylmethylene group is preferably a linear alkyl group having 1 to 5 carbon atoms, more preferably a linear alkyl group having 1 to 3 carbon atoms, and most preferably a methyl group.

Among them, Vz^{01} is preferably a single bond.

[0233]

In General Formula (z1-1-1), the linear alkyl group as Rz^{10} preferably has 1 to 10 carbon atoms and more preferably 1 to 5 carbon atoms.

In General Formula (z1-1-1), in a case where Rz^{10} represents $-Rz^{11}$-O-Rz^{12}, Rz^{10} is preferably a linear alkylene group having 1 to 5 carbon atoms and more preferably a methylene group or an ethylene group. Rz^{11} is preferably a linear alkyl group having 1 to 5 carbon atoms and more preferably a methyl group or an ethyl group.

In General Formula (z1-1-1), the monovalent alicyclic hydrocarbon group as Rz^{10} may be a polycyclic group or a monocyclic group.

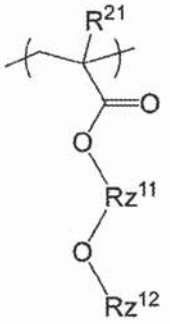
The aliphatic hydrocarbon group which is a monocyclic group is preferably a group in which one hydrogen atom has been removed from a monocycloalkane. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

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

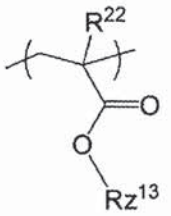
[0234]

Among them, the component (Z) preferably contains, as the constitutional unit (z1-1-2), a constitutional unit represented by General Formula (z1-2-21) (hereinafter, may be referred to as a "constitutional unit (z1-2-21)") and a constitutional unit represented by General Formula (z1-2-22) (hereinafter, may be referred to as a “constitutional unit (z1-2-22)”).

[0235]



(z1-1-21)



(z1-1-22)

[In the formula, R^{21} and R^{22} each independently represent a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Rz^{11} represents a linear alkylene group. Rz^{12} represents a linear alkyl group. Rz^{13} represents a linear alkyl group or a monovalent alicyclic hydrocarbon group.]

[0236]

In General Formulae (z1-1-21) and (z1-1-22), R^{21} and R^{22} are the same as R^{02} in General Formula (z1-1-2).

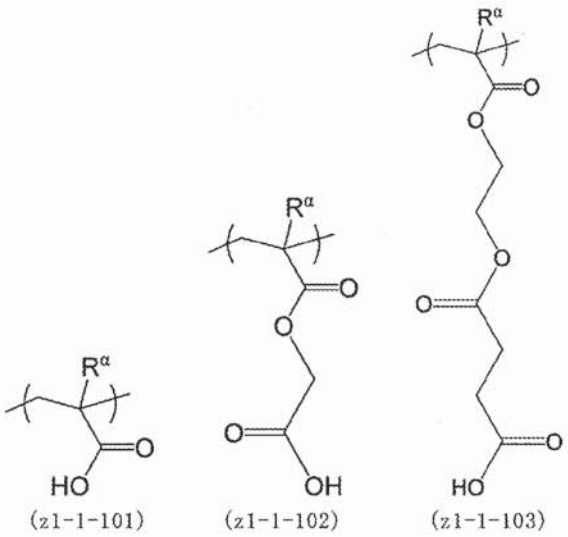
In General Formula (z1-1-21), Rz^{11} and Rz^{12} are respectively the same as Rz^{11} and Rz^{12} in General Formula (z1-1-2).

In General Formula (z1-1-21), the linear alkyl group or the monovalent alicyclic hydrocarbon group as Rz^{13} is the same as the linear alkyl group or the monovalent alicyclic hydrocarbon group as Rz^{10} in General Formula (z1-1-2).

[0237]

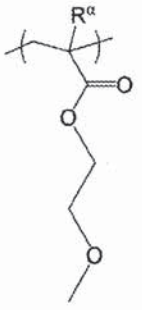
Specific examples of the constitutional unit (z1) are as follows. In the formulae shown below, R^{α} represents a hydrogen atom, a methyl group, or a trifluoromethyl group.

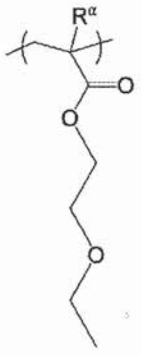
[0238]

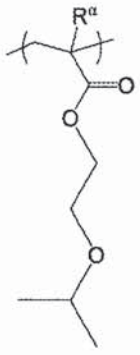

(z1-1-101)

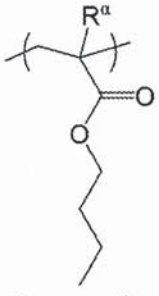
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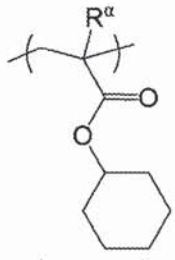
(z1-1-103)

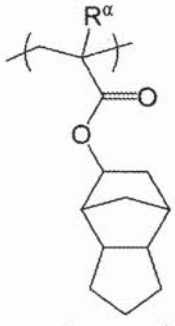

(z1-1-211)


(z1-1-212)


(z1-1-213)


(z1-1-221)


(z1-1-222)


(z1-1-223)

[0239]

The proportion of the constitutional unit (z1) in the component (Z) is preferably in a range of 50% to 100% by mole, more preferably in a range of 60% to 100% by mole, and still more preferably in a range of 70% to 100% by mole, and may be 100% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting

the component (Z).

In a case where the proportion of the constitutional unit (z1) is within the preferred range described above, the occurrence of cracking is easily suppressed and the occurrence of surface roughness is easily suppressed during etching.

[0240]

In a case where the component (Z) contains, as the constitutional unit (z1), the constitutional unit (z1-1-1) and the constitutional unit (z1-1-2), the proportion of the constitutional unit (z1-1-1) in the component (Z) is preferably in a range of 1% to 30% by mole, more preferably in a range of 3% to 25% by mole, and still more preferably in a range of 5% to 20% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (Z). The proportion of the constitutional unit (z1-1-2) in the component (Z) is preferably in a range of 70% to 99% by mole, more preferably in a range of 75% to 97% by mole, and still more preferably in a range of 80% to 95% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (Z).

In a case where the proportions of the constitutional units (z1-1-1) and the constitutional unit (z1-1-2) are within the preferred range described above, the occurrence of cracking is easily suppressed and the occurrence of surface roughness is easily suppressed during etching.

[0241]

In a case where the component (Z) contains, as the constitutional unit (z1), the constitutional unit (z1-1-1), the constitutional unit (z1-1-21), and the constitutional unit (z1-1-22), the proportion of the constitutional unit (z1-1-1) in the component (Z) is preferably in a range of 1% to 30% by mole, more preferably in a range of 3% to 25% by mole, and still more preferably in a range of 5% to 20% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (Z). In addition, the proportion of the constitutional unit (z1-1-21) in the component (Z) is preferably in a range of 10% to 99% by mole, more preferably in a range of 15% to 97% by mole, still more preferably in a range of 20% to 95% by mole, and even still more preferably in a range of 20% to 70% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (Z). In addition, the proportion of the constitutional unit (z1-1-22) in the component (Z) is preferably in a range of 0% to 80% by mole, more preferably in a range of 10% to 75% by mole, still

more preferably in a range of 15% to 70% by mole, and even still more preferably in a range of 20% to 65% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (Z).

In a case where the proportions of the constitutional units (z1-1-1), the constitutional unit (z1-1-21), and the constitutional unit (z1-1-22) are within the preferred range described above, the occurrence of cracking is easily suppressed and the occurrence of surface roughness is easily suppressed during etching.

[0242]

<<Other constitutional units>>

The component (Z) may have other constitutional units as necessary in addition to the constitutional unit (z1) described above.

Examples of the other constitutional units include the constitutional unit (a10), the constitutional unit (st), and the constitutional unit (a1).

[0243]

In a case where the component (Z) has the constitutional unit (a10), the proportion of the constitutional unit (a10) in the component (Z) is preferably in a range of 5% to 50% by mole, more preferably in a range of 5% to 40% by mole, and still more preferably in a range of 10% to 30% by mole, with respect to the total amount (100% by mole) of all constitutional units constituting the component (Z).

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

[0244]

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

[0245]

The component (Z) contained in the resist composition may be used alone or in a combination of two or more kinds thereof.

In the resist composition according to the present embodiment, examples of the component (Z) include a high-molecular-weight compound having a repeated structure of

the constitutional unit (z1).

Preferred examples of the component (Z) include a high-molecular-weight compound having a repeated structure of the constitutional unit (z1-1-1) and the constitutional unit (z1-1-21); and a high-molecular-weight compound having a repeated structure of the constitutional unit (z1-1-1), the constitutional unit (z1-1-21), and the constitutional unit (z1-1-22).

[0246]

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

Alternatively, the component (Z) can be produced by dissolving, in a polymerization solvent, a monomer from which the constitutional unit (z1) is derived and, as necessary, a monomer from which a constitutional unit other than the constitutional unit (z1) is derived, and adding thereto a radical polymerization initiator such as described above to perform polymerization. Further, a $-C(CF_3)_2-OH$ group may be introduced into the terminal of the component (Z) during the polymerization using a chain transfer agent such as $HS-CH_2-CH_2-CH_2-C(CF_3)_2-OH$ in combination. As described above, a copolymer into which a hydroxyalkyl group, formed by substitution of a part of hydrogen atoms in the alkyl group with fluorine atoms, has been introduced is effective for reducing development defects and reducing line edge roughness (LER: uneven irregularities of a line side wall).

[0247]

The weight-average molecular weight (Mw) (based on the polystyrene-equivalent value determined by gel permeation chromatography (GPC)) of the component (Z), which is not particularly limited, is preferably in a range of 5,000 to 200,000, more preferably in a range of 10,000 to 150,000, and still more preferably in a range of 15,000 to 100,000.

In a case where the weight-average molecular weight of the component (Z) is within the preferred range described above, the occurrence of cracking is easily suppressed and the occurrence of surface roughness is easily suppressed during etching.

Further, the polydispersity (Mw/Mn) of the component (Z) is not particularly limited; however, it is preferably in a range of 1.0 to 7.0, more preferably in a range of

2.0 to 6.0, and particularly preferably in a range of 3.0 to 6.0. Mn represents the number-average molecular weight.

[0248]

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

The content of the component (Z) in the resist composition according to the present embodiment is 50 parts by mass, preferably in a range of 1 to 30 parts by mass, more preferably 5 to 25 parts by mass, and still more preferably 10 to 20 parts by mass, with respect to 100 parts by mass of the component (A1).

In a case where the content of the component (Z) is 50 parts by mass or less with respect to 100 parts by mass of the component (A1), it is possible to suppress the occurrence of cracking and the occurrence of surface roughness during etching.

In addition, in a case where the content of the component (Z) is within the preferred range described above, the occurrence of cracking is easily suppressed and the occurrence of surface roughness is easily suppressed during etching.

[0249]

<Other components>

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

[0250]

<<Acid generator component (B)>>

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

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

Examples of such an acid generator are numerous and include onium salt-based acid generators such as an iodonium salt and a sulfonium salt; an oxime sulfonate-based acid generator; diazomethane-based acid generators such as bisalkyl or bisaryl sulfonyl diazomethanes and poly(bis-sulfonyl)diazomethanes; nitrobenzylsulfonate-based acid

generators; iminosulfonate-based acid generators; and disulfone-based acid generators.

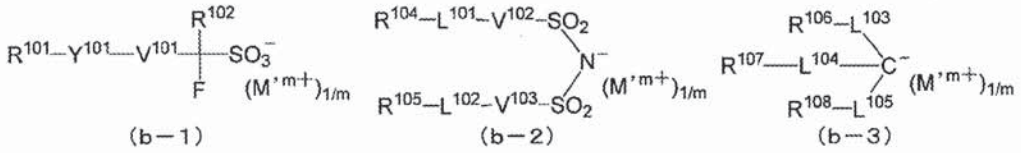
The component (B) preferably contains a compound (B1) constituted of an onium salt (hereinafter, referred to as "component (B1)").

[0251]

· In regard to component (B1)

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

[0252]



[In the formulae, R^{101} and R^{104} to R^{108} each independently represent a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent. R^{104} and R^{105} may be bonded to each other to form a ring structure. R^{102} represents a fluorinated alkyl group having 1 to 5 carbon atoms or a fluorine atom. Y^{101} represents a divalent linking group containing an oxygen atom or a single bond. V^{101} to V^{103} each independently represents a single bond, an alkylene group, or a fluorinated alkylene group. L^{101} and L^{102} each independently represent a single bond or an oxygen atom. L^{103} to L^{105} each independently represents a single bond, -CO-, or $-SO_2-$. m represents an integer of 1 or greater, and M'^{m+} represents an m-valent onium cation.]

[0253]

{Anion moiety}

· Anion in component (b-1)

In General 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.

[0254]

Cyclic group which may have substituent:

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

[0255]

The aromatic hydrocarbon group as R^{101} 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, particularly preferably 6 to 15, and most preferably 6 to 10. Here, the number of carbon atoms in a substituent is not included in the number of carbon atoms.

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

Specific examples of the aromatic hydrocarbon group as R^{101} include a group in which one hydrogen atom has been removed from the above-described aromatic ring (an aryl group such as a phenyl group or a naphthyl group) and a group in which one hydrogen atom in the aromatic ring has been substituted with an alkylene group (an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, 1-naphthylethyl group, or a 2-naphthylethyl group). The alkylene group (an alkyl chain in the arylalkyl group) preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and particularly preferably 1 carbon atom.

[0256]

Examples of the cyclic aliphatic hydrocarbon group as R^{101} include aliphatic hydrocarbon groups containing a ring in the structure thereof.

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

in a linear or branched aliphatic hydrocarbon group.

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

The alicyclic hydrocarbon group may be a polycyclic group or a monocyclic group. The monocyclic alicyclic hydrocarbon group is preferably 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 include cyclopentane and cyclohexane. The polycyclic alicyclic hydrocarbon group is preferably a group in which one or more hydrogen atoms have been removed from a polycycloalkane, and the polycycloalkane preferably has 7 to 30 carbon atoms. Among polycycloalkanes, a polycycloalkane having a bridged ring-based polycyclic skeleton, such as adamantane, norbornane, isobornane, tricyclodecane, or tetracyclododecane, and a polycycloalkane having a condensed ring-based polycyclic skeleton, such as a cyclic group having a steroid skeleton are preferable.

[0257]

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

[0258]

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

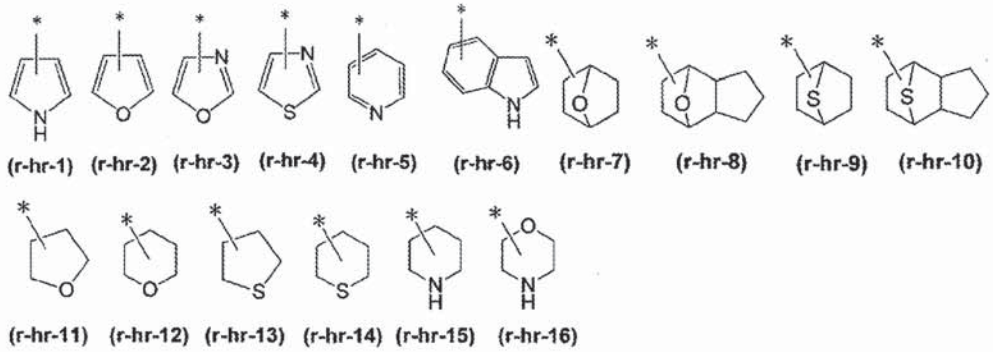
The branched aliphatic hydrocarbon group which may be bonded to the alicyclic hydrocarbon group preferably has 2 to 10 carbon atoms, more preferably 3 to 6 carbon atoms, still more preferably 3 or 4 carbon atoms, and most preferably 3 carbon atoms. The branched aliphatic hydrocarbon group is preferably a branched alkylene group, and specific examples thereof include alkylalkylene groups, for example, alkylmethylene

groups such as -$CH(CH_3)$-, -$CH(CH_2CH_3)$-, -$C(CH_3)_2$-, -$C(CH_3)(CH_2CH_3)$-, -$C(CH_3)(CH_2CH_2CH_3)$-, and -$C(CH_2CH_3)_2$-; alkylethylene groups such as -$CH(CH_3)CH_2$-, -$CH(CH_3)CH(CH_3)$-, -$C(CH_3)_2CH_2$-, -$CH(CH_2CH_3)CH_2$-, and -$C(CH_2CH_3)_2$-CH_2-; alkyltrimethylene groups such as -$CH(CH_3)CH_2CH_2$-, and -$CH_2CH(CH_3)CH_2$-; and alkyltetramethylene groups such as -$CH(CH_3)CH_2CH_2CH_2$-, and -$CH_2CH(CH_3)CH_2CH_2$-. The alkyl group in the alkylalkylene group is preferably a linear alkyl group having 1 to 5 carbon atoms.

[0259]

The cyclic hydrocarbon group as R^{101} may contain a hetero atom such as a heterocyclic ring. Specific examples thereof include lactone-containing cyclic groups respectively represented by General Formulae (a2-r-1) to (a2-r-7), -SO_2--containing cyclic groups respectively represented by General Formulae (a5-r-1) to (a5-r-4), and other heterocyclic groups respectively represented by Chemical Formulae (r-hr-1) to (r-hr-16).

[0260]



[0261]

Examples of the substituent of the cyclic group as R^{101} include an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, a carbonyl group, and a nitro group. The alkyl group as the substituent is preferably an alkyl group having 1 to 5 carbon atoms, and a methyl group, an ethyl group, a propyl group, an n-butyl group, or a tert-butyl group is most preferable.

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

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

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

The carbonyl group as a substituent is a group that is substituted for a methylene group (-CH_2-) constituting the cyclic hydrocarbon group.

[0262]

Chain-like alkyl group which may have substituent:

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

The linear alkyl group preferably has 1 to 20 carbon atoms, more preferably 1 to 15 carbon atoms, and most preferably 1 to 10 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decanyl group, an undecyl 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 nonadecil group, an icosyl group, a henicosyl 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 thereof include a 1-methylethyl group, a 1-methylpropyl group, a 2-methylpropyl group, a 1-methylbutyl group, a 2-methylbutyl group, a 3-methylbutyl group, a 1-ethylbutyl group, a 2-ethylbutyl group, a 1-methylpentyl group, a 2-methylpentyl group, a 3-methylpentyl group, and a 4-methylpentyl group.

[0263]

Chain-like alkenyl group which may have substituent:

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

methylpropenyl group.

Among the above, the chain-like alkenyl group is preferably a linear alkenyl group, more preferably a vinyl group or a propenyl group, and particularly preferably a vinyl group.

[0264]

Examples of the substituent in the chain-like alkyl group or alkenyl group as R^{101}, include an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, a carbonyl group, a nitro group, an amino group, and a cyclic group as R^{101}.

[0265]

Among the above, R^{101} is preferably a cyclic group which may have a substituent and more preferably a cyclic hydrocarbon group which may have a substituent. More specific examples of the cyclic hydrocarbon group preferably include a group in which one or more hydrogen atoms have been removed from a phenyl group, a naphthyl group, or a polycycloalkane; lactone-containing cyclic groups respectively represented by General Formulae (a2-r-1) to (a2-r-7); and $-SO_2$--containing cyclic groups respectively represented by General Formulae (a5-r-1) to (a5-r-4).

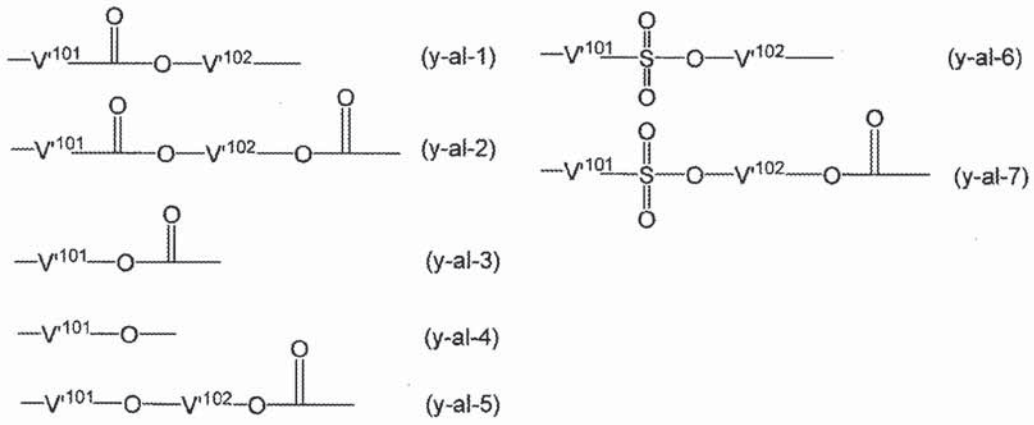
[0266]

In General Formula (b-1), Y^{101} represents a single bond or a divalent linking group containing an oxygen atom.

In a case where Y^{101} represents a divalent linking group containing an oxygen atom, Y^{101} 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-based oxygen atom-containing linking groups such as an oxygen atom (an ether bond; -O-), an ester bond (-C(=O)-O-), an oxycarbonyl group (-O-C(=O)-), an amide bond (-C(=O)-NH-), a carbonyl group (-C(=O)-), or a carbonate bond (-O-C(=O)-O-); and combinations of the above-described non-hydrocarbon-based oxygen atom-containing linking groups with an alkylene group. Furthermore, a sulfonyl group (-SO_2-) may be linked to the combination. Examples of divalent linking groups containing an oxygen atom include linking groups respectively represented by General Formulae (y-al-1) to (y-al-7) shown below.

[0267]



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

[0268]

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

[0269]

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

Specific examples of the alkylene group as V'^{101} and V'^{102} include a methylene group [-CH_2-]; an alkylmethylene group such as -$CH(CH_3)$-, -$CH(CH_2CH_3)$-, -$C(CH_3)_2$-, -$C(CH_3)(CH_2CH_3)$-, -$C(CH_3)(CH_2CH_2CH_3)$-, or -$C(CH_2CH_3)_2$-; an ethylene group [-CH_2CH_2-]; an alkylethylene group such as -$CH(CH_3)CH_2$-, -$CH(CH_3)CH(CH_3)$-, -$C(CH_3)_2CH_2$-, or -$CH(CH_2CH_3)CH_2$-; a trimethylene group (n-propylene group) [-$CH_2CH_2CH_2$-]; an alkyltrimethylene group such as -$CH(CH_3)CH_2CH_2$- or -$CH_2CH(CH_3)CH_2$-; a tetramethylene group [-$CH_2CH_2CH_2CH_2$-]; an alkyltetramethylene group such as -$CH(CH_3)CH_2CH_2CH_2$-, or -$CH_2CH(CH_3)CH_2CH_2$-; and a pentamethylene group [-$CH_2CH_2CH_2CH_2CH_2$-].

Further, a part of a methylene group in the alkylene group as V'^{101} and V'^{102} may be substituted with a divalent aliphatic cyclic group having 5 to 10 carbon atoms. The aliphatic cyclic group is preferably a divalent group in which one hydrogen atom has been removed from the cyclic aliphatic hydrocarbon group (a monocyclic aliphatic

hydrocarbon group or a polycyclic aliphatic hydrocarbon group) as Ra'^3 in General Formula (a1-r-1), and a cyclohexylene group, a 1,5-adamantylene group, or a 2,6-adamantylene group is more preferable.

[0270]

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

[0271]

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

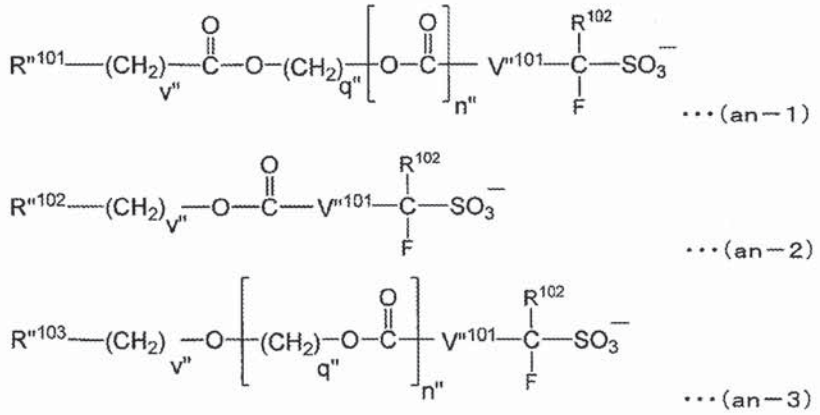
[0272]

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

[0273]

Specific examples of the anion moiety represented by General Formula (b-1) include a fluorinated alkylsulfonate anions such as a trifluoromethanesulfonate anion and a perfluorobutanesulfonate anion in a case where Y^{101} represents a single bond; and anions respectively represented by General Formulae (an-1) to (an-3) shown below in a case where Y^{101} represents a divalent linking group containing an oxygen atom.

[0274]



[In the formula, R"^{101} represents an aliphatic cyclic group which may have a substituent, monovalent heterocyclic groups respectively represented by each of Chemical Formulae (r-hr-1) to (r-hr-6), or a chain-like alkyl group which may have a substituent. R"^{102} is an aliphatic cyclic group which may have a substituent, lactone-containing cyclic groups respectively represented by General Formulae (a2-r-1) and (a2-r-3) to (a2-r-7), or -SO_2--containing cyclic groups respectively represented by General Formulae (a5-r-1) to (a5-r-4). R"^{103} represents an aromatic cyclic group which may have a substituent, an aliphatic cyclic group which may have a substituent, or a chain-like alkenyl group which may have a substituent. V"^{101} represents a single bond, an alkylene group having 1 to 4 carbon atoms, or a fluorinated alkylene group having 1 to 4 carbon atoms. R^{102} represents a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms. v"s each independently represent an integer in a range of 0 to 3, q"s each independently represent an integer in a range of 0 to 20, and n" represents 0 or 1.]

[0275]

The aliphatic cyclic group as R"^{101}, R"^{102}, and R"^{103} which may have a substituent is preferably the group exemplified as the cyclic aliphatic hydrocarbon group as R^{101} in General Formula (b-1). Examples of the substituent include the same group as the substituent with which the cyclic aliphatic hydrocarbon group as R^{101} in General Formula (b-1) may be substituted.

[0276]

The aromatic cyclic group as R"^{103} in General Formula (b-1), which may have a substituent, is preferably the group exemplified as the aromatic hydrocarbon group for the cyclic hydrocarbon group as R^{101} in General Formula (b-1). Examples of the substituent include the same groups as the substituent with which the aromatic

hydrocarbon group as R^{101} in General Formula (b-1) may be substituted.

[0277]

The chain-like alkyl group as R''^{101}, which may have a substituent, is preferably the group exemplified as the chain-like alkyl group as R^{101} in General Formula (b-1).

The chain-like alkenyl group as R''^{103}, which may have a substituent, is preferably the group exemplified as the chain-like alkenyl group as R^{101} in General Formula (b-1).

[0278]

· Anion in component (b-2)

In General Formula (b-2), R^{104} and R^{105} each independently represent 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 has the same definition as that for R^{101} in General Formula (b-1). However, R^{104} and R^{105} may be bonded to each other to form a ring.

R^{104} and R^{105} are preferably a chain-like alkyl group which may have a substituent and more preferably a linear or branched alkyl group or a linear or branched fluorinated alkyl group.

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

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

In General Formula (b-2), L^{101} and L^{102} each independently represent a single

bond or an oxygen atom.

[0279]

· Anion in component (b-3)

In General Formula (b-3), R^{106} to R^{108} each independently represent 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 has the same definition as that for R^{101} in General Formula (b-1).

In General Formula (b-3), L^{103} to L^{105} each independently represents a single bond, -CO-, or $-SO_2-$.

[0280]

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

[0281]

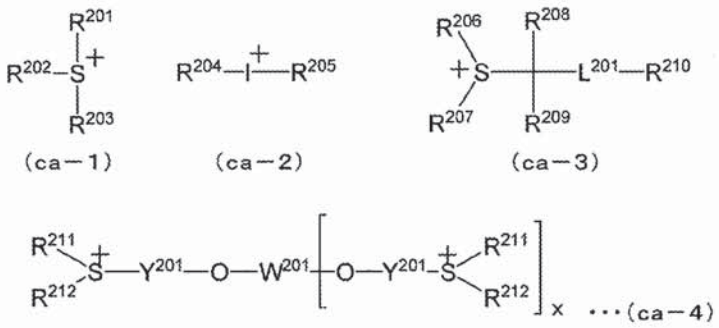
{Cation moiety}

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

[0282]

Preferred examples of the cation moiety ($(M'^{m+})_{1/m}$) include organic cations respectively represented by General Formulae (ca-1) to (ca-4).

[0283]



(ca-1) (ca-2) (ca-3)

(ca-4)

[In the formula, R^{201} to R^{207}, R^{211}, and R^{212} each independently represent an aryl

group, an alkyl group, or an alkenyl group, each of which may have a substituent. R^{201} to R^{203}, R^{206} and R^{207}, or R^{211} and R^{212} may be bonded to each other to form a ring together with the sulfur atom in the formula. R^{208} and R^{209} each independently represent a hydrogen atom or an alkyl group having 1 to 5 carbon atoms. R^{210} represents an aryl group which may have a substituent, an alkyl group which may have a substituent, an alkenyl group which may have a substituent, or a $-SO_2$--containing cyclic group which may have a substituent. L^{201} represents -C(=O)- or -C(=O)-O-. Y^{201}s each independently represent an arylene group, an alkylene group, or an alkenylene group. x represents 1 or 2. W^{201} represents an (x+1)-valent linking group.]

[0284]

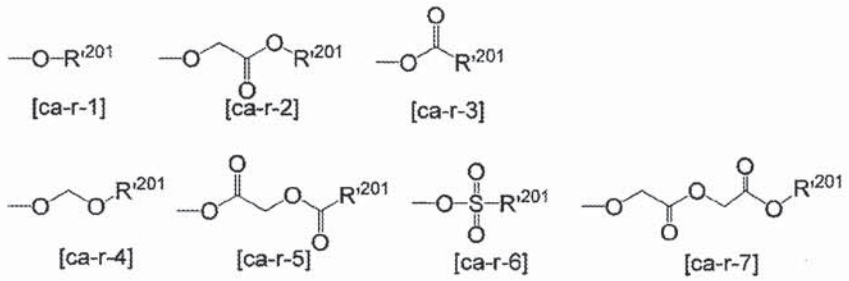
In General Formulae (ca-1) to (ca-4), examples of the aryl group as R^{201} to R^{207}, R^{211}, and R^{212} include an unsubstituted aryl group having 6 to 20 carbon atoms, and a phenyl group or a naphthyl group is preferable.

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

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

Examples of the substituent which may be included in R^{201} to R^{207} and R^{210} to R^{212} 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 respectively represented by General Formulae (ca-r-1) to (ca-r-7).

[0285]



[In the formulae, R'^{201}s each independently represent 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.]

[0286]

Cyclic group which may have substituent:

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

[0287]

The aromatic hydrocarbon group as 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, particularly preferably 6 to 15 carbon atoms, and most preferably 6 to 10 carbon atoms. Here, the number of carbon atoms in a substituent is not included in the number of carbon atoms.

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

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

[0288]

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

Examples of the aliphatic hydrocarbon group containing a ring in the structure thereof include an alicyclic hydrocarbon group (a group in which one hydrogen atom has been removed from an aliphatic hydrocarbon ring), a group in which the alicyclic

hydrocarbon group is bonded to the terminal of a linear or branched aliphatic hydrocarbon group, and a group in which the alicyclic hydrocarbon group is interposed in a linear or branched aliphatic hydrocarbon group.

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

The alicyclic hydrocarbon group may be a polycyclic group or a monocyclic group. The monocyclic alicyclic hydrocarbon group is preferably 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 include cyclopentane and cyclohexane. The polycyclic alicyclic hydrocarbon group is preferably a group in which one or more hydrogen atoms have been removed from a polycycloalkane, and the polycycloalkane preferably has 7 to 30 carbon atoms. Among polycycloalkanes, a polycycloalkane having a bridged ring-based polycyclic skeleton, such as adamantane, norbornane, isobornane, tricyclodecane, or tetracyclododecane, and a polycycloalkane having a condensed ring-based polycyclic skeleton, such as a cyclic group having a steroid skeleton are preferable.

[0289]

Among them, the cyclic aliphatic hydrocarbon group as R'^{201} is preferably a group in which one or more hydrogen atoms have been removed from a monocycloalkane or a polycycloalkane, more preferably a group in which one hydrogen atom has been removed from a polycycloalkane, particularly preferably an adamantyl group or a norbornyl group, and most preferably an adamantyl group.

[0290]

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

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

The branched aliphatic hydrocarbon group is preferably a branched alkylene group, and specific examples thereof include alkylalkylene groups, for example,

alkylmethylene groups such as -$CH(CH_3)$-, -$CH(CH_2CH_3)$-, -$C(CH_3)_2$-, -$C(CH_3)(CH_2CH_3)$-, -$C(CH_3)(CH_2CH_2CH_3)$-, and -$C(CH_2CH_3)_2$-; alkylethylene groups such as -$CH(CH_3)CH_2$-, -$CH(CH_3)CH(CH_3)$-, -$C(CH_3)_2CH_2$-, -$CH(CH_2CH_3)CH_2$-, and -$C(CH_2CH_3)_2$-CH_2-; alkyltrimethylene groups such as -$CH(CH_3)CH_2CH_2$-, and -$CH_2CH(CH_3)CH_2$-; and alkyltetramethylene groups such as -$CH(CH_3)CH_2CH_2CH_2$-, and -$CH_2CH(CH_3)CH_2CH_2$-. The alkyl group in the alkylalkylene group is preferably a linear alkyl group having 1 to 5 carbon atoms.

[0291]

The cyclic hydrocarbon group as R'^{201} may contain a hetero atom such as a heterocyclic ring. Specific examples thereof include lactone-containing cyclic groups respectively represented by General Formulae (a2-r-1) to (a2-r-7), -SO_2--containing cyclic groups respectively represented by General Formulae (a5-r-1) to (a5-r-4), and other heterocyclic groups respectively represented by Chemical Formulae (r-hr-1) to (r-hr-16).

[0292]

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

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

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

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

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

The carbonyl group as a substituent is a group that is substituted for a methylene group (-CH_2-) constituting the cyclic hydrocarbon group.

[0293]

Chain-like alkyl group which may have substituent:

The chain-like alkyl group as R'^{201} may be linear or branched.

The linear alkyl group preferably has 1 to 20 carbon atoms, more preferably 1 to 15 carbon atoms, and most preferably 1 to 10 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decanyl group, an undecyl 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 nonadecil group, an icosyl group, a henicosyl group, and a docosyl group.

The branched alkyl group preferably has 3 to 20 carbon atoms, more preferably 3 to 15 carbon atoms, and most preferably 3 to 10 carbon atoms. Specific examples thereof include a 1-methylethyl group, a 1-methylpropyl group, a 2-methylpropyl group, a 1-methylbutyl group, a 2-methylbutyl group, a 3-methylbutyl group, a 1-ethylbutyl group, a 2-ethylbutyl group, a 1-methylpentyl group, a 2-methylpentyl group, a 3-methylpentyl group, and a 4-methylpentyl group.

[0294]

Chain-like alkenyl group which may have substituent:

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

Among the above, the chain-like alkenyl group is preferably a linear alkenyl group, more preferably a vinyl group or a propenyl group, and particularly preferably a vinyl group.

[0295]

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

[0296]

Examples of the cyclic group which may have a substituent, the chain-like alkyl group which may have a substituent, or the chain-like alkenyl group which may have a substituent, as R'^{201}, include, in addition to the groups described above, the same group as the acid-dissociable group represented by General Formula (a1-r-2), as the cyclic group which may have a substituent or the chain-like alkyl group which may have a substituent.

[0297]

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

[0298]

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

[0299]

R^{208} and R^{209} each independently represent a hydrogen atom or an alkyl group having 1 to 5 carbon atoms and are preferably a hydrogen atom or an alkyl group having 1 to 3 carbon atoms. In a case where R^{208} and R^{209} each independently represent an alkyl group, R^{208} and R^{209} may be bonded to each other to form a ring.

[0300]

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

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

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

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

[0301]

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

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

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

[0302]

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

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

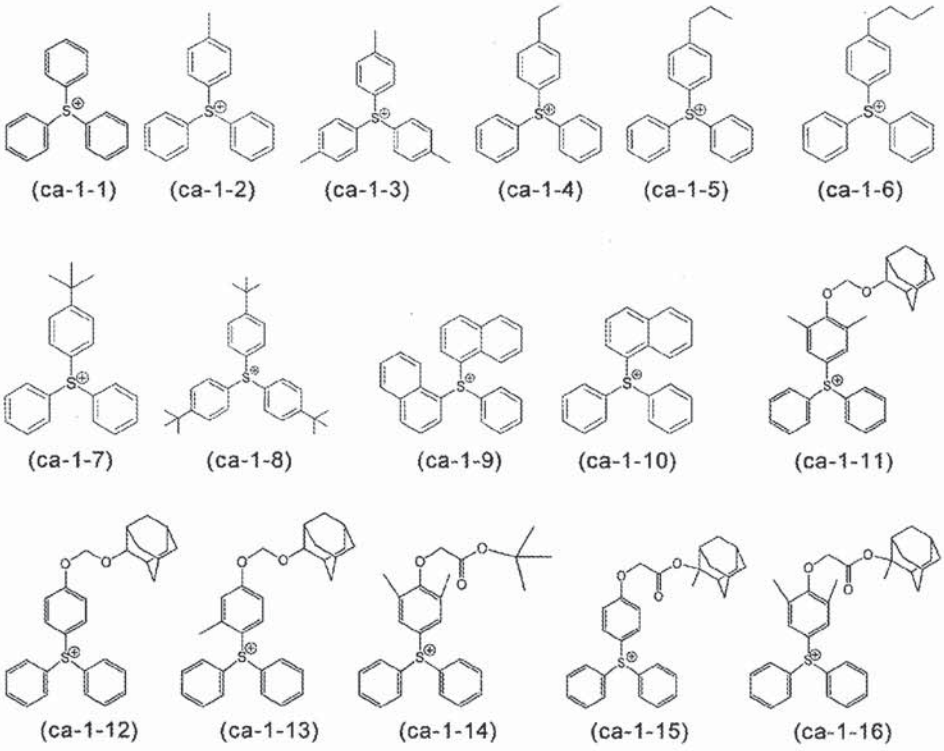
The divalent linking group as W^{201} is preferably a divalent hydrocarbon group which may have a substituent, and as examples thereof include the same divalent hydrocarbon group, which may have a substituent, as Ya^{21} in General Formula (a2-1). The divalent linking group as W^{201} may be linear, branched, or cyclic and is preferably cyclic. Among them, an arylene group having two carbonyl groups, each bonded to both the terminals thereof is preferable. Examples of the arylene group include a phenylene group and a naphthylene group, and a phenylene group is particularly preferable.

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

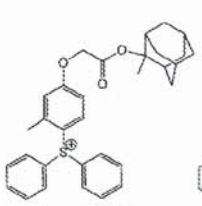
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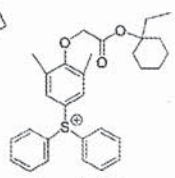
Specific examples of the suitable cation represented by General Formula (ca-1) include cations respectively represented by Chemical Formulae (ca-1-1) and (ca-1-70) shown below.

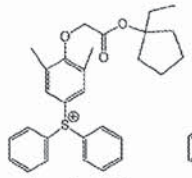
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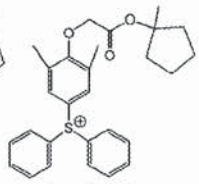


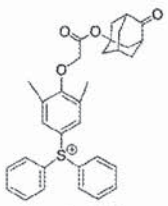
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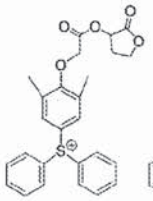

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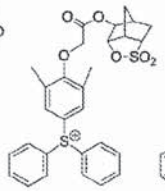

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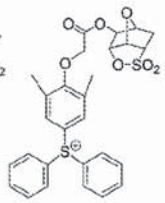

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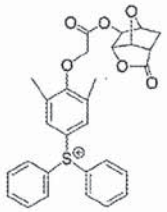

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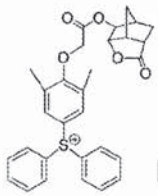

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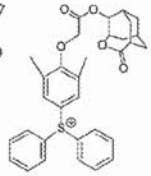

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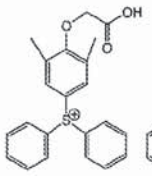

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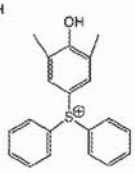

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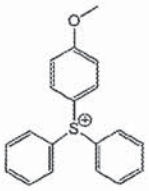

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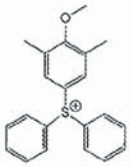

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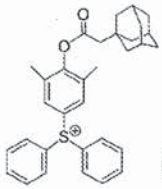

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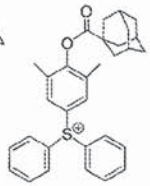

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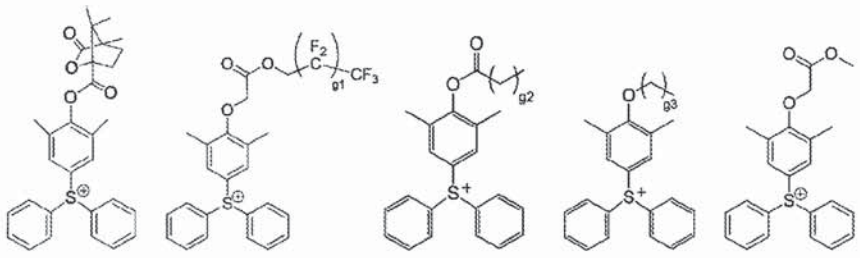

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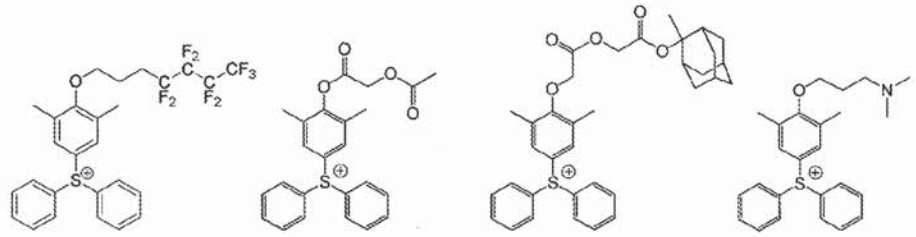

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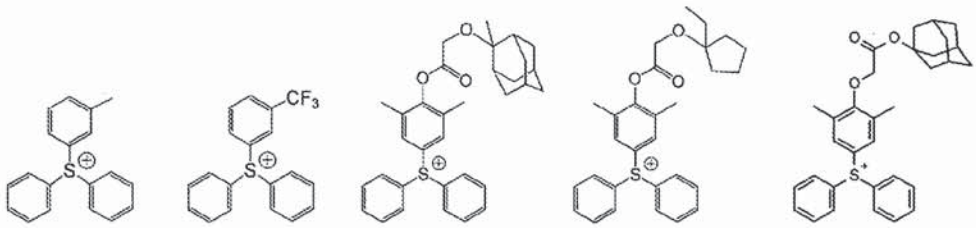
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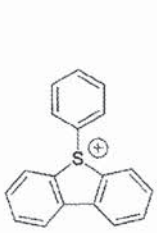
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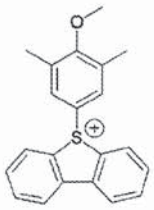


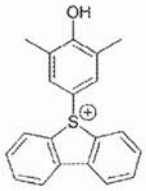
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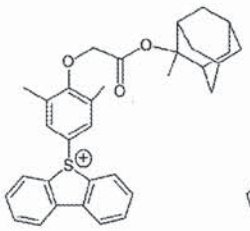
[In the formula, g1, g2, and g3 represent the numbers of repetitions, g1 is an integer in a range of 1 to 5, g2 is an integer in a range of 0 to 20, and g3 is an integer in a range of 0 to 20.]

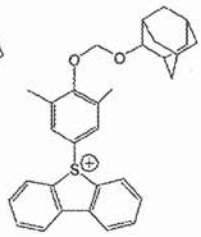
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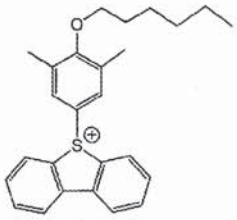

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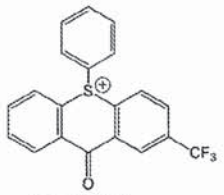

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(ca-1-50)

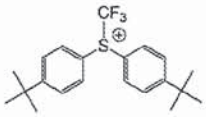

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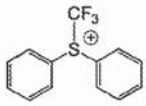

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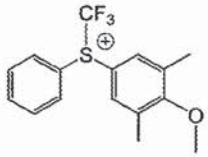

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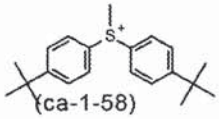

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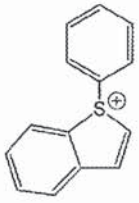

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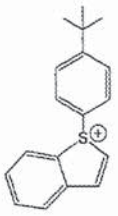

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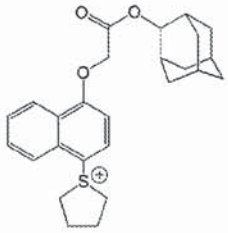

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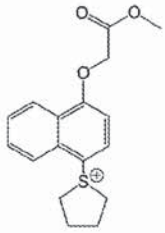

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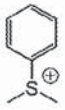
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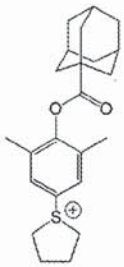

(ca-1-59)

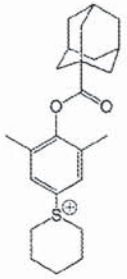

(ca-1-60)

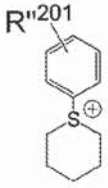

(ca-1-61)

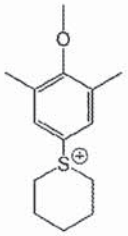

(ca-1-62)

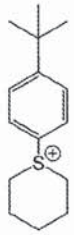

(ca-1-63)


(ca-1-64)


(ca-1-65)


(ca-1-66)


(ca-1-67)


(ca-1-68)

[In the formula, R"^{201} represents a hydrogen atom or a substituent, and examples

of the substituent include the same substituent as that exemplified as the substituent which R^{201} to R^{207} and R^{210} to R^{212} may have.]

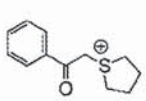
[0310]

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

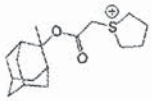
[0311]

Specific examples of the suitable cation represented by General Formula (ca-3) include cations respectively represented by General Formulae (ca-3-1) to (ca-3-6) shown below.

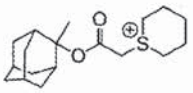
[0312]



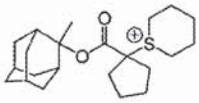
(ca-3-1)



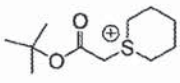
(ca-3-2)



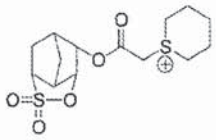
(ca-3-3)



(ca-3-4)



(ca-3-5)

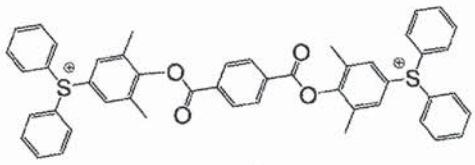


(ca-3-6)

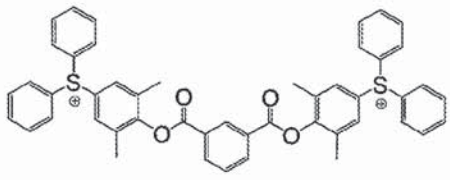
[0313]

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

[0314]



(ca-4-1)



(ca-4-2)

[0315]

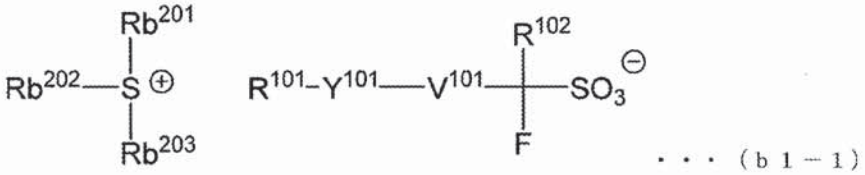
Among the above, the cation moiety ($(M'^{m+})_{1/m}$) is preferably a cation represented by General Formula (ca-1). From the viewpoint that the transparency is maintained in a thick resist film, in General Formula (ca-1), it is preferable that at least

one of R^{202} and R^{203} preferably be an alkyl or alkenyl group, more preferable that two or more of R^{202} and R^{203} be alkyl groups or alkenyl groups, and still more preferable that two or more of R^{202} and R^{203} be alkyl groups. In a case where two or more of R^{202} and R^{203} are an alkyl group or an alkenyl group, two of them may be bonded to each other to form a ring together with the sulfur atom in the formula. The cation represented by General Formula (ca-1) is preferably a cation represented by General Formulae (ca-1-55) to (ca-1-68) and more preferably a cation represented by General Formulae (ca-1-63) to (ca-1-68).

[0316]

Among them, the component (B1) is particularly preferably a compound represented by General Formula (b1-1).

[0317]



... (b1-1)

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

[0318]

In General Formula (b1-1), the aryl group which may have a substituent, as Rb^{201}, is the same as the aryl group which may have a substituent, as R^{201} in General Formula (ca-1). Among them, Rb^{201} is preferably a phenyl group or a naphthyl group and more preferably a phenyl group.

In General Formula (b1-1), the alkyl group which may have a substituent or the

alkenyl group which may have a substituent, as Rb^{202} and Rb^{203} is the same the alkyl group which may have a substituent or the alkenyl group which may have a substituent, as R^{202} and R^{203} in General Formula (ca-1). Among them, Rb^{202} and Rb^{203} is preferably a linear alkyl group having 1 to 5 carbon atoms, and it is more preferable that Rb^{202} and Rb^{203} be bonded to each other to form a 5-membered ring or a 6-membered ring together with the sulfur atom in the formula.

In General Formula (b1-1), R^{101}, R^{102}, Y^{101}, and V^{101} are respectively the same as R^{101}, R^{102}, Y^{101}, and V^{101} in General Formula (b-1).

[0319]

· In regard to component (B2)

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

[0320]

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

In a case where the resist composition contains the component (B), the content of the component (B) in the resist composition is preferably less than 50 parts by mass, more preferably in a range of 0.1 to 40 parts by mass, and still more preferably in a range of 0.3 to 25 parts by mass with respect to 100 parts by mass of the component (A).

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

[0321]

<Base component (D)>>

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

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

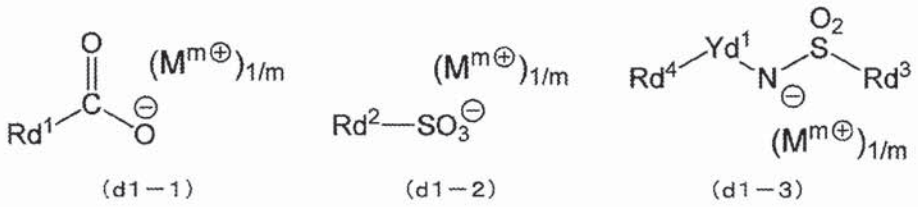
[0322]

· In regard to component (D1)

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

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

[0323]



(d1-1)　　(d1-2)　　(d1-3)

[In the formulae, Rd^1 to Rd^4 represent cyclic groups which may have a substituent, chain-like alkyl groups which may have a substituent, or chain-like alkenyl groups which may have a substituent. Here, the carbon atom adjacent to the S atom as Rd^2 in General Formula (d1-2) has no fluorine atom bonded thereto. Yd^1 represents a single bond or a divalent linking group. m represents an integer of 1 or greater, and each M^{m+} independently represents an m-valent organic cation.]

[0324]

{Component (d1-1)}

·· Anion moiety

In Formula (d1-1), Rd^1 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, which is the same as that described above as R'^{201}.

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

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

The aliphatic cyclic group is preferably a group 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 group, or a decyl group, and a branched alkyl group such as a 1-methylethyl group, a 1-methylpropyl group, a 2-methylpropyl group, a 1-methylbutyl group, a 2-methylbutyl group, a 3-methylbutyl group, a 1-ethylbutyl group, a 2-ethylbutyl group, a 1-methylpentyl group, a 2-methylpentyl group, a 3-methylpentyl group, or a 4-methylpentyl group.

[0325]

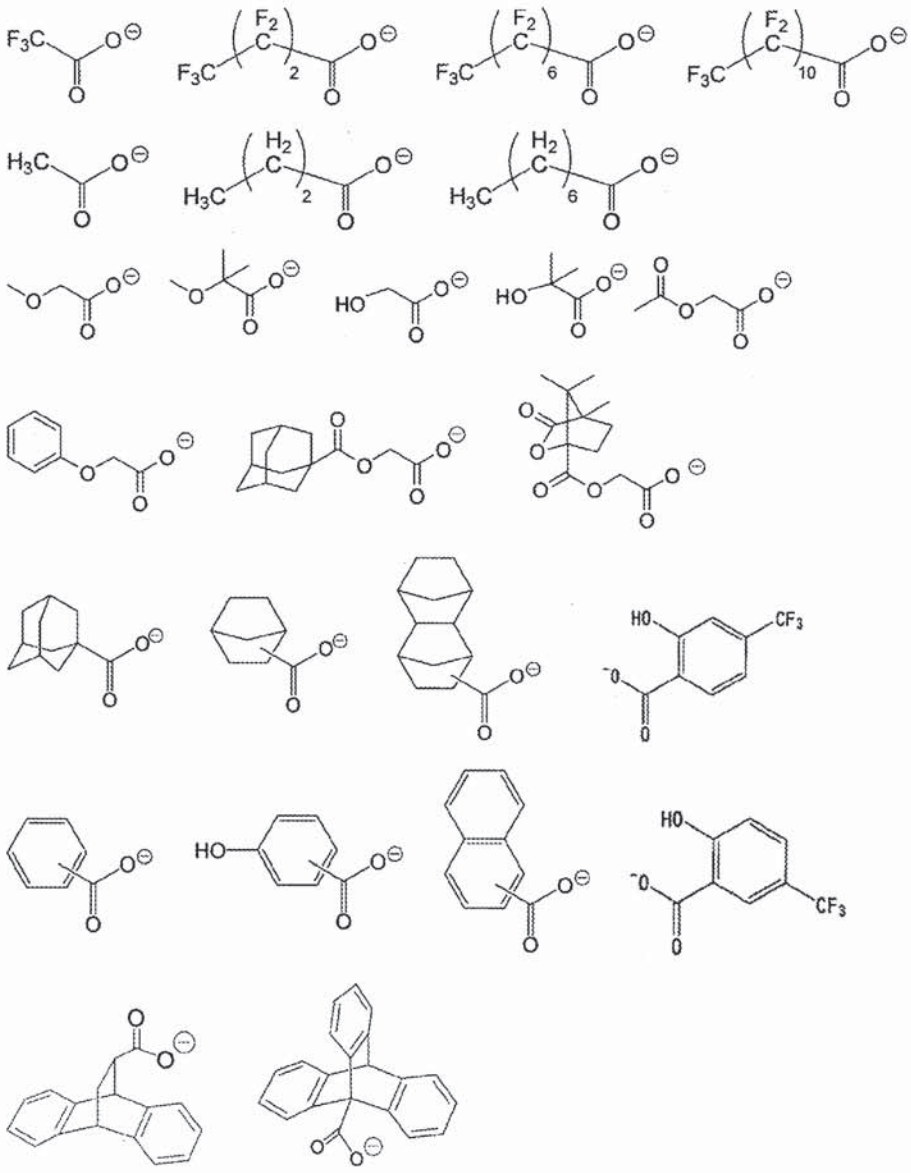
In a case where the chain-like alkyl group is a fluorinated alkyl group having a fluorine atom or a fluorinated alkyl group as a substituent, the fluorinated alkyl group preferably has 1 to 11 carbon atoms, more preferably 1 to 8 carbon atoms, and still more preferably 1 to 4 carbon atoms. The fluorinated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

Rd^1 is preferably a fluorinated alkyl group in which part or all of hydrogen atoms constituting a linear alkyl group have been substituted with a fluorine atom and particularly preferably a fluorinated alkyl group in which all of the hydrogen atoms constituting a linear alkyl group have been substituted with a fluorine atom (a linear perfluoroalkyl group).

[0326]

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

[0327]



[0328]

·· Cation moiety

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

Suitable examples of the organic cation of M^{m+} include the same cations as those respectively represented by General Formulae (ca-1) to (ca-4), and the cation represented by General Formula (ca-1) is preferable, and cations respectively represented by General Formulae (ca-1-1) to (ca-1-70) are more preferable.

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

[0329]

{Component (d1-2)}

·· Anion moiety

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

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

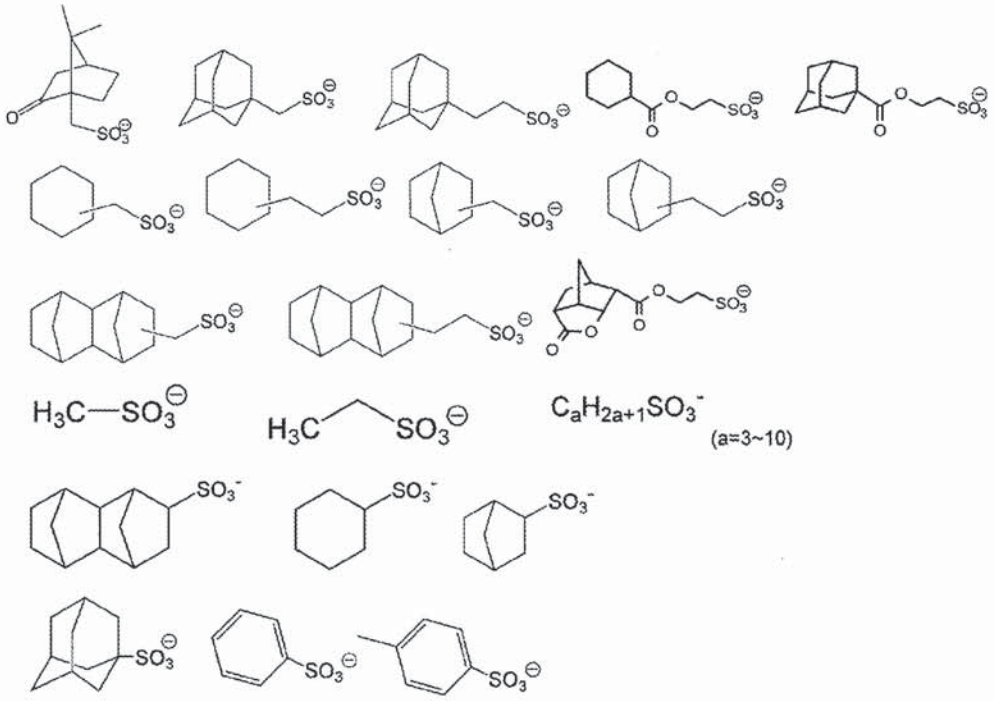
Rd^2 is preferably a chain-like alkyl group which may have a substituent or an aliphatic cyclic group which may have a substituent. The chain-like alkyl group preferably has 1 to 10 carbon atoms and more preferably 3 to 10 carbon atoms. The aliphatic cyclic group is more preferably a group (which may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

The hydrocarbon group as Rd^2 may have a substituent. Examples of the substituent include the same substituent as that which the hydrocarbon group (an aromatic hydrocarbon group, an aliphatic cyclic group, or a chain-like alkyl group) as Rd^1 In General Formula (d1-1) may have.

[0330]

Specific examples of the preferred anion moiety for the component (d1-2) are shown below.

[0331]



[0332]

·· Cation moiety

In General Formula (d1-2), M^{m+} represents an m-valent organic cation and has the same definition as that for M^{m+} In General Formula (d1-1).

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

[0333]

{Component (d1-3)}

·· Anion moiety

In General 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, examples thereof include the same group as that described above as R'^{201}, and a cyclic group containing a fluorine atom, a chain-like alkyl group, or a chain-like alkenyl group is preferable. Among them, a fluorinated alkyl group is preferable, and the same fluorinated alkyl group as that described above as Rd^1 is more preferable.

[0334]

In Formula (d1-3), Rd^4 represents a cyclic group which may have a substituent,

a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent, and examples thereof include the same group as that described above as R'^{201}.

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

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

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

[0335]

Examples of the alkenyl group as Rd^4 include the same group as the alkenyl group described above as 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 further have an alkyl group having 1 to 5 carbon atoms or a halogenated alkyl group having 1 to 5 carbon atoms as a substituent.

[0336]

Examples of the cyclic group as Rd^4 include the same group as the cyclic group described above as R'^{201} and an alicyclic 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 such as a phenyl group or a naphthyl group is preferable. In a case where Rd^4 represents an alicyclic group, the resist composition can be satisfactorily dissolved in an organic solvent, thereby improving lithography characteristics. In a case where Rd^4 is an aromatic group, the resist composition is excellent in light absorption efficiency and thus has good sensitivity and lithography characteristics in lithography using EUV or the

like as a light source for exposure.

[0337]

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

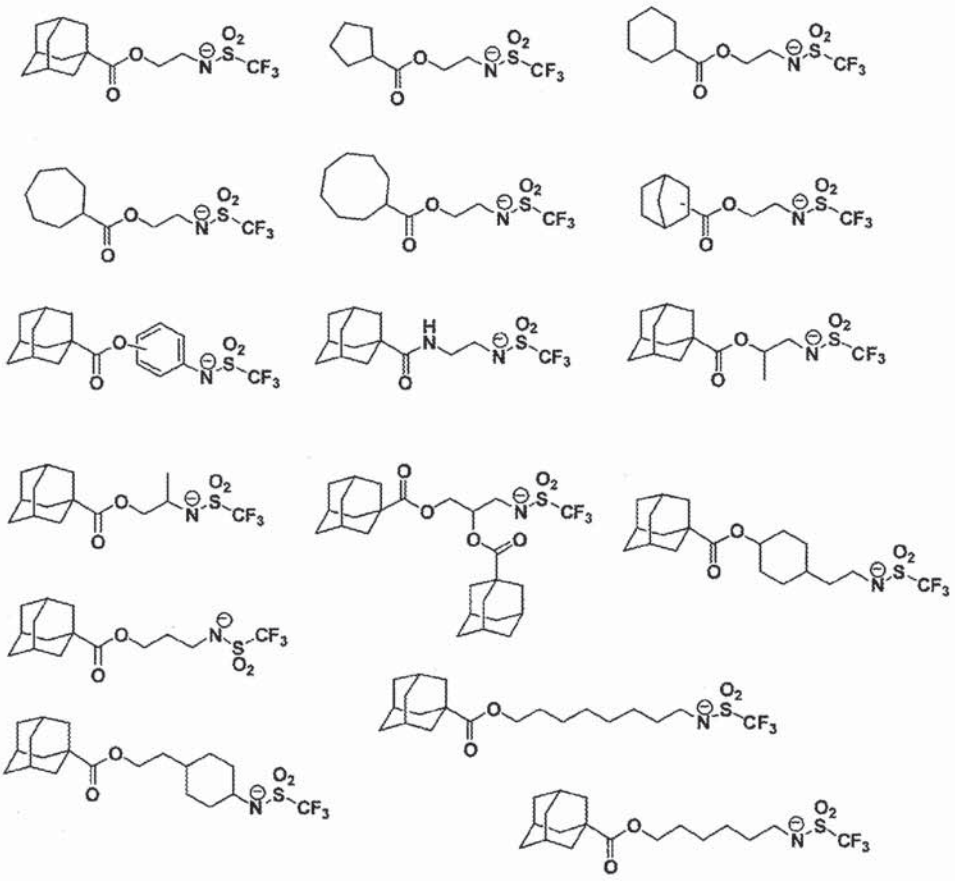
The divalent linking group as Yd^1 is not particularly limited, and examples thereof include a divalent hydrocarbon group (an aliphatic hydrocarbon group or an aromatic hydrocarbon group) which may have a substituent and a divalent linking group containing a hetero atom. The divalent linking groups are the same as those described above as the divalent hydrocarbon group which may have a substituent and the divalent linking group containing a hetero atom described above as the divalent linking group as Ya^{21} In General Formula (a2-1).

Yd^1 is preferably a carbonyl group, an ester bond, an amide bond, an alkylene group, or a combination thereof. The alkylene group is preferably a linear or branched alkylene group and more preferably a methylene group or an ethylene group.

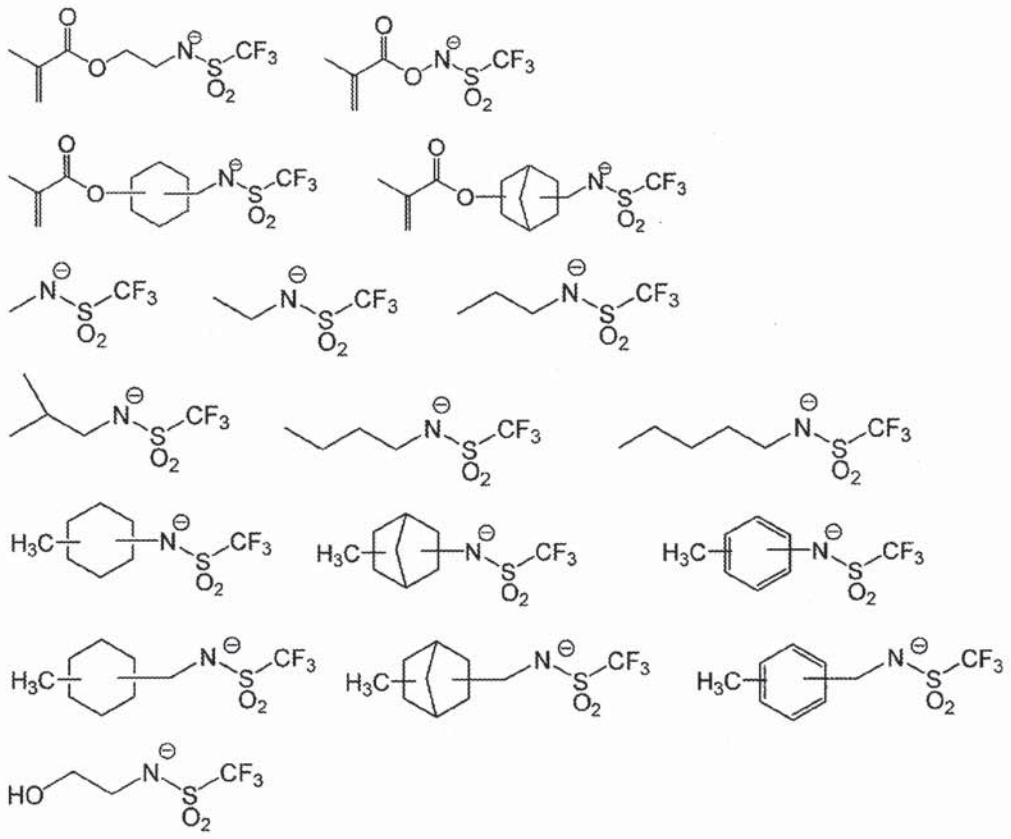
[0338]

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

[0339]



[0340]



[0341]

·· Cation moiety

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

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

[0342]

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

In a case where the resist composition contains the component (D1), the content of the component (D1) in the resist composition is preferably in a range of 0.5 to 20 parts by mass, more preferably in a range of 1 to 15 parts by mass, and still more preferably in a range of 5 to 10 parts by mass with respect to 100 parts by mass of the component (A).

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

component (D1) is equal to or lower than the upper limit, the sensitivity can be maintained satisfactorily and the throughput is also excellent.

[0343]

Method of producing component (D1):

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

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

[0344]

· In regard to component (D2)

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

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

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

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

Specific examples of alkyl amines and alkyl alcohol amines include monoalkyl amines such as n-hexyl amine, n-heptyl amine, n-octyl amine, n-nonyl amine, and n-decyl amine; dialkyl amines such as diethyl amine, di-n-propyl amine, di-n-heptyl amine, di-n-octyl amine, and dicyclohexyl amine; trialkyl amines such as trimethyl amine, triethyl amine, tri-n-propyl amine, tri-n-butyl amine, tri-n-hexyl amine, tri-n-pentyl amine, tri-n-heptyl amine, tri-n-octyl amine, tri-n-nonyl amine, tri-n-decyl amine, and tri-n-dodecyl amine; and alkyl alcohol amines such as diethanol amine, triethanol amine,

diisopropanol amine, triisopropanol amine, di-n-octanol amine, and tri-n-octanol amine. Among these, trialkyl amines of 5 to 10 carbon atoms are preferable, and tri-n-pentyl amine and tri-n-octyl amine are particularly preferable.

[0345]

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

Specific examples of the aliphatic monocyclic amine include piperidine and piperazine. The aliphatic polycyclic amine preferably has 6 to 10 carbon atoms, and specific examples thereof include 1, 5-diazabicyclo[4.3.0]-5-nonene, 1,8-diazabicyclo[5.4.0]-7-undecene, hexamethylenetetramine, and 1,4-diazabicyclo[2.2.2]octane.

[0346]

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 triethanol amine triacetate, and triethanol amine triacetate is preferable.

[0347]

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

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

[0348]

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

[0349]

The component (D2) may be used alone or in a combination of two or more

kinds thereof. In a case where the resist composition contains the component (D2), the content of the component (D2) in the resist composition is typically used in a range of 0.005 to 5 parts by mass with respect to 100 parts by mass of the component (A). By setting the content within the above range, the resist pattern shape, the post-exposure temporal stability, and the like are improved.

[0350]

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

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

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

Examples of phosphorus oxo acid include phosphoric acid, phosphonic acid, and phosphinic acid.

Among these, phosphonic acid is particularly preferable.

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

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

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

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 according to the present embodiment, the component (E) may be used alone or in a combination of two or more kinds thereof.

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

parts by mass of the component (A).

[0351]

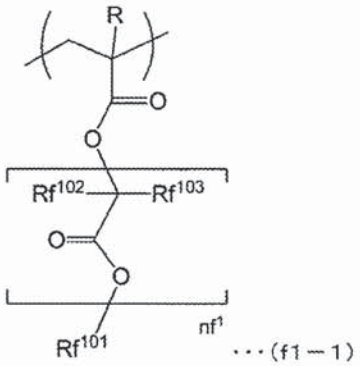
<<Fluorine additive component (F)>>

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

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

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

[0352]



・・・(f1－1)

[In the formula, R has the same definition as described above. Rf^{102} and Rf^{103} each independently represent a hydrogen atom, a halogen atom, an alkyl group having 1

to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms, and Rf^{102} and Rf^{103} may be the same as or different from each other. nf^1 represents an integer in a range of 1 to 5 and Rf^{101} represents an organic group containing a fluorine atom.]

[0353]

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

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

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

[0354]

In General 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 particularly preferably 1 to 10 carbon atoms.

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

Among them, Rf^{101} is more preferably a fluorinated hydrocarbon group having 1 to 6 carbon atoms, still more preferably a trifluoromethyl group, and particularly preferably $-CH_2-CF_3$, $-CH_2-CF_2-CF_3$, $-CH(CF_3)_2$, $-CH_2-CH_2-CF_3$, or $-CH_2-CH_2-CF_2-CF_2-$

CF_2-CF_3.

[0355]

The weight-average molecular weight (Mw) (based on the polystyrene-equivalent value determined by gel permeation chromatography) of the component (F) is preferably in a range of 1,000 to 50,000, more preferably in a range of 5,000 to 40,000, and most preferably in a range of 10,000 to 30,000. In a case where the weight-average molecular weight is equal to or lower than the upper limit of this range, the resist composition exhibits sufficiently satisfactory solubility in a solvent for a resist to be used as a resist composition. On the other hand, in a case where the weight-average molecular weight is equal to or greater than the lower limit of this range, water repellency of the resist film is excellent.

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

[0356]

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

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

[0357]

<<Organic solvent component (S)>>

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

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

Examples of the component (S) 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 monoalkyl ether (such as monomethyl ether, monoethyl ether, monopropyl ether or monobutyl ether) or monophenyl ether 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, ethylbenzyl ether, cresylmethyl ether, diphenyl ether, dibenzyl ether, phenetole, butylphenyl ether, ethyl benzene, diethyl benzene, pentyl benzene, isopropyl benzene, toluene, xylene, cymene and mesitylene; and dimethylsulfoxide (DMSO).

In the resist composition according to the present embodiment, the component (S) may be used alone or as a mixed solvent of two or more kinds thereof. Among them, the component (S) is preferably at least one selected from the group consisting of PGMEA, PGME, γ-butyrolactone, EL, butyl acetate, and cyclohexanone, and more preferably at least one selected from the group consisting of PGMEA, PGME, and butyl acetate.

[0358]

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

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

Further, the component (S) is also preferably a mixed solvent of at least one

selected from PGMEA and EL and γ-butyrolactone. In this case, as the mixing ratio, the mass ratio of the former to the latter is preferably in a range of 70:30 to 95:5.

[0359]

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

Solid content concentration (% by mass) = total mass of components other than component (S) / total mass of resist composition × 100

[0360]

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

[0361]

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

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

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

[0362]

As desired, other miscible additives can also be added to the resist composition according to the present embodiment. For example, for improving the performance of the resist film, an additive resin, a dissolution inhibitor, a plasticizer, a stabilizer, a colorant, a halation prevention agent, and a dye can be suitably contained therein.

[0363]

After dissolving the resist material in the component (S), the resist composition according to the present embodiment may be subjected to removal of impurities and the like by using a porous polyimide film, a porous polyamideimide film, or the like. For example, the resist composition may be filtered using a filter made of a porous polyimide film, a filter made of a porous polyamideimide film, or a filter made of a porous polyimide film and a porous polyamideimide film. Examples of the porous polyimide film and the porous polyamideimide film include those described in Japanese Unexamined Patent Application, First Publication No. 2016-155121.

[0364]

The resist composition according to the present embodiment described above has a solid content concentration of 25% by mass or more and contains the plasticizer component (Z).

In the resist composition according to the present embodiment, since the solid content concentration of the resist composition is 25% by mass or more, a thick resist film (for example, a film having a thickness of 5 μm or more) is formed in a case where the resist composition is applied onto a substrate to form a resist film. In a case of such a thick resist film, in conventional resist composition, cracking easily occurs in the resist pattern. Further, since it is difficult for light to reach the bottom of the film in the conventional resist composition, it is difficult to maintain sensitivity during exposure, and it is difficult to form a resist pattern having a good shape.

Since the resist composition according to the present embodiment contains the plasticizer component (Z), both cracking resistance and suppression of surface roughness during etching can be achieved at the same time. It is speculated that this is because the presence of the plasticizer component (Z) in the resist film formed using the resist composition alleviates the stress of the resist film. Here, the plasticizer component (Z) does not contain an acid-dissociable group. Therefore, it is presumed that the plasticizer component (Z) present in the resist film does not undergo a deprotection reaction during

etching, and the deprotected product of the plasticizer component (Z) does not volatilize from the resist film. As a result, it is presumed that the occurrence of surface roughness during etching is suppressed.

Further, since the base material component (A) in the resist composition according to the present embodiment has the constitutional unit (a1) and the constitutional unit (a10), sensitivity and resolution can be improved in addition to the effects of cracking resistance and suppression of surface roughness during etching.

[0365]

(Method of forming resist pattern)

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

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

[0366]

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

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

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

[0367]

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

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

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

In this manner, a resist pattern can be formed.

[0368]

The support is not specifically limited and a conventionally known support can be used. For example, substrates for electronic components and such substrates having predetermined 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. As a material for the wiring pattern. copper, aluminum, nickel, gold, or the like can be used.

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

Here, the multilayer resist method is a 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-layer resist film) are provided on a substrate, and a resist pattern formed on the upper-layer resist film is used as a mask to conduct patterning of the lower-layer organic film.

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

The multilayer resist method is classified into a method in which a double-layer structure consisting of an upper-layer resist film and a lower-layer organic film is formed

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

[0369]

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

[0370]

The wavelength to be used for exposure is not particularly limited and the exposure can be performed using radiation such as an ArF excimer laser, a KrF excimer laser, an F_2 excimer laser, extreme ultraviolet (EUV) rays, vacuum ultraviolet (VUV) rays, electron beams (EB), X-rays, or soft X-rays. The resist composition is highly useful for KrF excimer laser, ArF excimer laser, EB, or EUV, more useful for KrF excimer laser or ArF excimer laser, and particularly useful for KrF excimer laser. That is, the method of forming a resist pattern according to the present embodiment is a particularly useful method in a case where the step of exposing the resist film includes an operation of exposing the resist film to KrF excimer laser light.

[0371]

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

In liquid immersion lithography is an exposure method in which the region between the resist film and the lens at the lowermost position of the lithography apparatus is pre-filled with a solvent (liquid immersion medium) that has a larger

refractive index than the refractive index of air, and the exposure (dipping exposure) is performed in this state.

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

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

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

The fluorine-based inert liquid is particularly preferably a perfluoroalkyl compound in which all of the hydrogen atoms of the alkyl group are substituted with a fluorine atom. Examples of these perfluoroalkyl compounds include perfluoroalkyl ether compounds and perfluoroalkyl amine compounds.

Specific examples of the perfluoroalkyl ether compound include perfluoro(2-butyl-tetrahydrofuran) (boiling point of 102°C), and specific examples of the perfluoroalkyl amine compound include perfluorotributyl amine (boiling point of 174°C).

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

[0372]

Examples of the alkali developing solution used for a developing treatment in an alkali developing process include a 0.1 to 10% by mass aqueous solution of tetramethylammonium hydroxide (TMAH).

As the organic solvent contained in the organic developing solution, which is used for a developing treatment in a solvent developing process, any one of the conventionally known organic solvents capable of dissolving the component (A) (component (A) prior to exposure) can be suitably selected from the conventionally

known organic solvents. Specific examples of the organic solvent include polar solvents such as a ketone-based solvent, an ester-based solvent, an alcohol-based solvent, a nitrile-based solvent, an amide-based solvent, and an ether-based solvent, and hydrocarbon-based solvents.

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

Some organic solvents have a plurality of the functional groups which characterize the above-described solvents in the structure thereof.

In such a case, the organic solvent can be classified as any type of solvent having a characteristic functional group. For example, diethylene glycol monomethyl ether can be classified as an alcohol-based solvent or an ether-based solvent.

A hydrocarbon-based 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.

Among the above, the organic solvent contained in the organic developing solution is preferably a polar solvent and more preferably a ketone-based solvent, an ester-based solvent, or a nitrile-based solvent.

[0373]

Examples of ketone-based solvent 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, diacetonyl alcohol, acetylcarbinol, acetophenone, methyl naphthyl ketone, isophorone, propylenecarbonate, γ-butyrolactone and methylamyl ketone (2-heptanone). Among these, the ketone-based solvent is preferably methylamyl ketone (2-heptanone).

[0374]

Examples of the ester-based solvent include methyl acetate, butyl acetate, ethyl acetate, isopropyl acetate, amyl acetate, isoamyl acetate, ethyl methoxyacetate, ethyl ethoxyacetate, ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene glycol monobutyl ether acetate, ethylene glycol monophenyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monopropyl ether acetate, diethylene glycol monophenyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, 2-methoxybutyl acetate, 3-methoxybutyl acetate, 4-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, 3-ethyl-3-methoxybutyl acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, 2-ethoxybutyl acetate, 4-ethoxybutyl acetate, 4-propoxybutyl acetate, 2-methoxypentyl acetate, 3-methoxypentyl acetate, 4-methoxypentyl acetate, 2-methyl-3-methoxypentyl acetate, 3-methyl-3-methoxypentyl acetate, 3-methyl-4-methoxypentyl acetate, 4-methyl-4-methoxypentyl acetate, propylene glycol diacetate, methyl formate, ethyl formate, butyl formate, propyl formate, ethyl lactate, butyl lactate, propyl lactate, ethyl carbonate, propyl carbonate, butyl carbonate, methyl pyruvate, ethyl pyruvate, propyl pyruvate, butyl pyruvate, methyl acetoacetate, ethyl acetoacetate, methyl propionate, ethyl propionate, propyl propionate, isopropyl propionate, methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, methyl-3-methoxypropionate, ethyl-3-methoxypropionate, ethyl-3-ethoxypropionate, and propyl-3-methoxypropionate. Among these, the ester-based solvent is preferably butyl acetate.

[0375]

Examples of the nitrile-based solvent include acetonitrile, propionitrile, valeronitrile, and butyronitrile.

[0376]

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

In a case where a surfactant is blended, the amount of the surfactant to be

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

[0377]

The developing treatment can be performed by a conventionally known developing method. Examples thereof include a method in which the support is immersed in the developing solution for a predetermined time (a dip method), a method in which the developing solution is cast upon the surface of the support 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 support (spray method), and a method in which a developing solution is continuously ejected from a developing solution-ejecting nozzle and applied to a support which is scanned at a constant rate while being rotated at a constant rate (dynamic dispense method).

[0378]

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

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

As the organic solvent, one kind of solvent may be used alone, or two or more

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

A conventionally known additive can be blended with the rinse liquid as necessary. Examples of the additive include surfactants. Examples of the surfactant include the same surfactants as those described above, the surfactant is preferably a non-ionic surfactant and more preferably a non-ionic fluorine surfactant or a non-ionic silicone-based surfactant.

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

[0379]

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

[0380]

According to the method of forming a resist pattern according to the present embodiment described above, since the resist composition according to the first aspect described above is used, it is possible to form a resist pattern which has few cracks and in which the occurrence of surface roughness is suppressed during etching.

[0381]

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

Examples

[0382]

Hereinafter, the present invention will be described in more detail based on

Examples, but the present invention is not limited to these Examples.

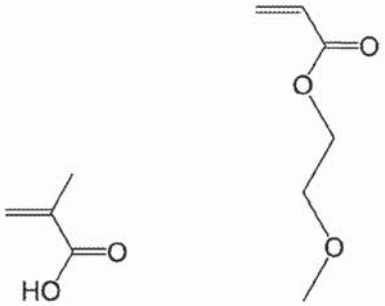
[0383]

<Production Example of plasticizer component (Z)>

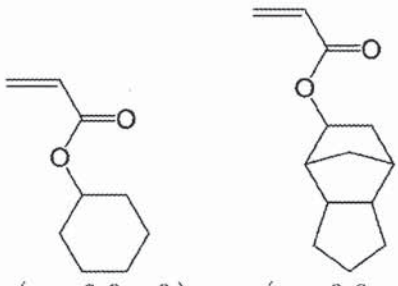
Compounds shown in Table 1 were used at the molar ratio shown in Table 1 and subjected to radical polymerization to synthesize polymers Z-1 to Z-10, Z-101, and Z-102.

With respect to the obtained polymers Z-1 to Z-10, Z-101, and Z-102, the copolymerization compositional ratio (the ratio (molar ratio) between constitutional units of the high-molecular-weight compound) in the high-molecular-weight compound, which was determined by ^{13}C-NMR, the standard polystyrene-equivalent mass-average molecular weight (Mw), which was determined by GPC measurement, and the molecular weight polydispersity (Mw/Mn) are shown in Table 1.

[0384]



(mz1-1) (mz21-1) (mz22-1)



(mz22-2) (mz22-3) (m1-1)

[0385]

[Table 1]

Polymer	Compositional ratio						Molecular weight	Polydispersity
	Constitutional unit (z1-1-1)	Constitutional unit (z1-1-21)	Constitutional unit (z1-1-22)			Constitutional unit (a1)		
	Monomer (mz1-1)	Monomer (mz21-1)	Monomer (mz22-1)	Monomer (mz22-2)	Monomer (mz22-3)	Monomer (m1-1)		
	Ratio (% by mole)							
Z-1	15	40	15	30	0	0	80,000	5.1
Z-2	15	40	15	0	30	0	80,000	5.1
Z-3	15	40	45	0	0	0	80,000	5.1
Z-4	15	55	0	30	0	0	80,000	5.1
Z-5	15	25	30	30	0	0	80,000	5.1
Z-6	10	90	0	0	0	0	80,000	5.1
Z-7	10	65	25	0	0	0	80,000	5.1
Z-8	15	40	45	0	0	0	40000	4.6
Z-9	15	40	45	0	0	0	20000	3.4
Z-10	10	60	0	0	30	0	80,000	5.1
Z-101	15	40	15	0	0	30	80,000	5.1
Z-102	15	25	10	0	30	20	40000	4.6

[0386]

<Preparation of resist composition>

(Examples 1 to 21 and Comparative Examples 1 to 6)

Each of the components shown in Tables 2 to 4 was mixed and dissolved to prepare a resist composition of each Example.

[0387]

[Table 2]

	Component (A)	Component (B)	Component (D)	Component (Z)	Component (S)		Solid content concentration (% by mass)
Example 1	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-1 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Example 2	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-2 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Example 3	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-3 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Example 4	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-4 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Example 5	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-5 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Example 6	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-6 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Example 7	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-7 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Example 8	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-8 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Example 9	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-9 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Example 10	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-10 [10.0]	(S)-1 [87]	(S)-2 [87]	40

[0388]

[Table 3]

	Component (A)	Component (B)	Component (D)	Component (Z)	Component (S)			Solid content concentration (% by mass)
Example 11	(A)-2 [100]	(B)-2 [1.0]	(D)-1 [0.01]	(Z)-2 [10.0]	(S)-1 [70]	(S)-2 [70]	(S)-3 [35]	40
Example 12	(A)-2 [100]	(B)-3 [1.0]	(D)-1 [0.01]	(Z)-2 [10.0]	(S)-1 [70]	(S)-2 [70]	(S)-3 [35]	40
Example 13	(A)-2 [100]	(B)-4 [1.0]	(D)-1 [0.01]	(Z)-2 [10.0]	(S)-1 [70]	(S)-2 [70]	(S)-3 [35]	40
Example 14	(A)-2 [100]	(B)-5 [1.0]	(D)-1 [0.01]	(Z)-2 [10.0]	(S)-1 [70]	(S)-2 [70]	(S)-3 [35]	40
Example 15	(A)-2 [100]	(B)-6 [1.0]	(D)-1 [0.01]	(Z)-2 [10.0]	(S)-1 [70]	(S)-2 [70]	(S)-3 [35]	40
Example 16	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-1 [5.0]	(S)-1 [87]	(S)-2 [87]	-	40
Example 17	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-1 [15.0]	(S)-1 [87]	(S)-2 [87]	-	40
Example 18	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-1 [25.0]	(S)-1 [87]	(S)-2 [87]	-	40
Example 19	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-1 [10.0]	(S)-1 [174]	(S)-2 [174]	-	25
Example 20	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-1 [10.0]	(S)-1 [135]	(S)-2 [135]	-	30
Example 21	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-1 [10.0]	(S)-1 [58]	(S)-2 [58]	-	50

[0389]

[Table 4]

	Component (A)	Component (B)	Component (D)	Component (Z)	Component (S)		Solid content concentration (% by mass)
Comparative Example 1	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-101 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Comparative Example 2	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-102 [10.0]	(S)-1 [87]	(S)-2 [87]	40
Comparative Example 3	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	-	(S)-1 [87]	(S)-2 [87]	40
Comparative Example 4	(A)-11 [100]	(B)-1 [1.0]	(D)-1 [0.01]	-	(S)-1 [87]	(S)-2 [87]	40
Comparative Example 5	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	(Z)-1 [100.0]	(S)-1 [87]	(S)-2 [87]	40
Comparative Example 6	(A)-1 [100]	(B)-1 [1.0]	(D)-1 [0.01]	-	(S)-1 [174]	(S)-2 [174]	25

[0390]

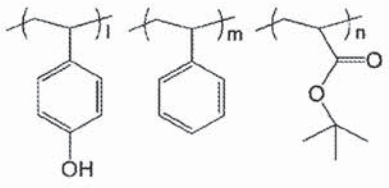
In Tables 2 to 4, each abbreviation has the following meaning. The numerical values in the brackets are blending amounts (parts by mass). The solid content concentration was calculated according to the following expression, the solid content concentration (% by mass) = [(the component (A) + the component (B) + the component (D) + the component (Z))/(the component (A) + the component (B) + the component (D)+ the component (Z) + the component (S))] × 100.

[0391]

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

(A)-2: a high-molecular-weight compound represented by Chemical Formula (A-1). The standard polystyrene-equivalent weight-average molecular weight (Mw) determined by GPC measurement and the molecular weight polydispersity (Mw/Mn) are respectively 10,000 and 1.4. The copolymerization compositional ratio (the ratio (molar ratio) among constitutional units in the structural formula) determined by ^{13}C-NMR is l/m/n = 60/25/15.

[0392]



···(A－1)

[0393]

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

(B)-2: an acid generator constituted of a compound represented by Chemical Formula (B-2).

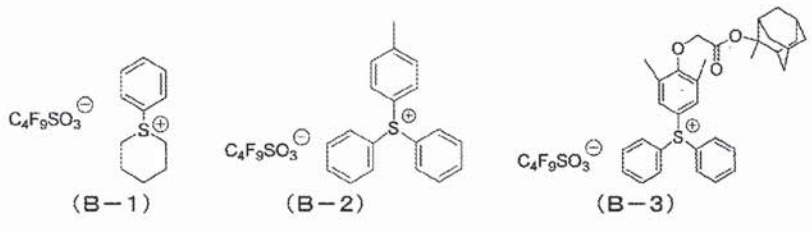
(B)-3: an acid generator constituted of a compound represented by Chemical Formula (B-3).

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

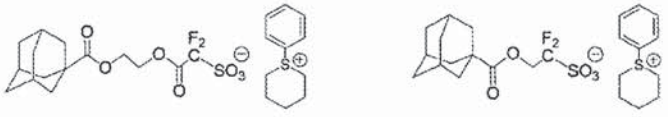
(B)-5: an acid generator constituted of a compound represented by Chemical Formula (B-5).

(B)-6: an acid generator constituted of a compound represented by Chemical Formula (B-6).

[0394]

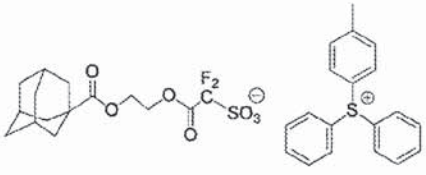


(B－1)　(B－2)　(B－3)



(B－4)

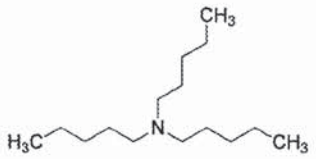
(B－5)



(B－6)

(D)-1: a nitrogen-containing organic compound constituted of a compound represented by Chemical Formula (D-1).

[0395]



(D－1)

[0396]

(Z)-1 to (Z)-10: the polymers Z-1 to Z-10.

(Z)-101: the polymer Z-101.

(Z)-102: the polymer Z-102.

(S)-1: propylene glycol monomethyl ether

(S)-2: propylene glycol monomethyl ether acetate

(S)-3: Butyl acetate

[0397]

<Formation of resist pattern>

Step (i):

The resist composition of each example was applied using a spinner onto an 8-inch silicon wafer that had been treated with hexamethyldisilazane (HMDS) at 110°C for 60 seconds. The coated wafer was subjected to a post-apply baking (PAB) treatment on a hot plate at a temperature of 150°C for 90 seconds so that the coated wafer was dried to form a resist film having a film thickness of 15 μm.

Step (ii):

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

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

Step (iii):

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

developing solution.

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

As a result, an isolated space pattern having a space width of 5 μm was formed.

[0398]

[Evaluation of resolution]

In <Formation of resist pattern> described above, an optimum exposure amount Eop ($\mu C/cm^2$) for forming an isolated space pattern of 5 μm was determined. Then, using the optimum exposure amount Eop as the exposure amount, an isolated space pattern of 3 μm was formed in the same manner as in <Formation of resist pattern>. The pattern shape of the isolated space pattern of 3 μm was observed using a scanning electron microscope S-9380 (manufactured by Hitachi High-Tech Corporation) and evaluated based on the following evaluation criteria. This is shown in Tables 5 to 7 as "Resolution".

Evaluation criteria

A: The pattern is definitely formed up to the substrate.

B: Trailing shape is slightly observed.

C: Pattern cannot be formed.

[0399]

[Evaluation of cracking resistance]

The silicon wafer on which the isolated space pattern was formed according to <Formation of resist pattern> described above was placed in the chamber of a scanning electron microscope S-9380 (manufactured by Hitachi High-Tech Corporation), and vacuum-treated for 60 seconds under a pressure of 0.0001 Pa. The silicon wafer after the vacuum treatment was observed using an optical microscope, and the number of cracks was counted. The number of cracks was evaluated based on the following evaluation criteria. The results are shown in Tables 5 to 7 as "Cracks". Evaluation criteria

A: 0 cracks

B: 1 to 5 cracks

C: 6 or more cracks

[0400]

[Evaluation of surface roughness after etching]

The isolated space pattern formed by the method of forming a resist pattern described above was subjected to dry etching under the following conditions using an etching apparatus manufactured by Tokyo Ohka Kogyo Co., Ltd.

Conditions:

Kind of etching gas and flow rate; a mixed gas of tetrafluoromethane 30 cc/min, trifluoromethane 30 cc/min, and helium 100 cc/min

Pressure; 300 mm Torr

Output: 600 W

Time; 120 seconds

After dry etching, the cross section of the isolated space pattern was observed with a scanning electron microscope (product name: S4500; Hitachi High-Tech Corporation), and the presence or absence of surface roughness in the pattern cross section was visually evaluated. The results are shown in Tables 5 to 7.

[0401]

[Table 5]

	Resolution	Cracking	Surface roughness after etching
Example 1	A	A	Absent
Example 2	A	B	Absent
Example 3	A	A	Absent
Example 4	A	B	Absent
Example 5	A	A	Absent
Example 6	B	A	Absent
Example 7	B	A	Absent
Example 8	A	A	Absent
Example 9	A	B	Absent
Example 10	A	B	Absent

[0402]

[Table 6]

	Resolution	Cracking	Surface roughness after etching
Example 11	B	A	Absent
Example 12	B	A	Absent
Example 13	A	A	Absent
Example 14	A	A	Absent
Example 15	B	A	Absent
Example 16	A	B	Absent
Example 17	A	A	Absent
Example 18	B	A	Absent
Example 19	A	A	Absent
Example 20	A	A	Absent
Example 21	A	B	Absent

[0403]

[Table 7]

	Resolution	Cracking	Surface roughness after etching
Comparative Example 1	A	A	Present
Comparative Example 2	A	A	Present
Comparative Example 3	A	C	Present
Comparative Example 4	B	C	Present
Comparative Example 5	C	A	Absent
Comparative Example 6	A	C	Present

[0404]

From the results shown in Tables 5 to 7, it has been confirmed that in a case where the resist compositions of Examples 1 to 21 are used, the resolution is good, the occurrence of cracking is suppressed, and the occurrence of surface roughness is suppressed during etching.

[0405]

While preferred embodiments of the invention have been described and illustrated above, it should be understood that these are exemplary of the invention and are not to be considered as limiting. Additions, omissions, substitutions, and other modifications can be made without departing from the spirit or scope of the present invention. Accordingly, the invention is not to be considered as being limited by the foregoing description and is only limited by the scope of the appended claims.

What is claimed is:

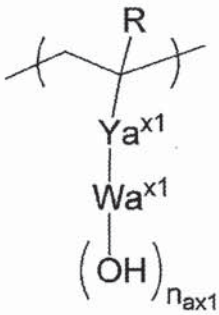
1. A resist composition generating an acid upon exposure and having solubility in a developing solution, which is changed by action of an acid, the resist composition comprising:

a resin component (A1) that has a constitutional unit (a1) containing an acid-decomposable group having a polarity which is increased by action of an acid and a constitutional unit (a10) represented by General Formula (a10-1); and

a plasticizer component (Z) that has a constitutional unit (z1) represented by General Formula (z1-1) and does not contain an acid-dissociable group,

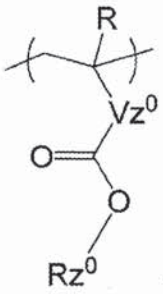
wherein a content of the plasticizer component (Z) is 50 parts by mass or less with respect to 100 parts by mass of the resin component (A1), and

a solid content concentration is 25% by mass or more,



... (a10-1)

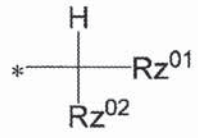
wherein R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms, Ya^{x1} represents a single bond or a divalent linking group, Wa^{x1} represents an aromatic hydrocarbon group which may have a substituent, and n_{ax1} represents an integer of 1 or greater;



... (z1-1)

wherein R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms, Vz^0 represents a single bond or a

divalent hydrocarbon group which may contain a hetero atom, provided that in a case where Vz^0 represents a divalent hydrocarbon group which may contain a hetero atom, Vz^0 does not contain an acid-dissociable group, and Rz^0 represents a hydrogen atom or a group represented by General Formula (z1-r-1):



$\cdots (z1-r-1)$

wherein Rz^{01} represents a hydrocarbon group which may have a substituent, Rz^{02} represents a hydrogen atom or a hydrocarbon group which may have a substituent, Rz^{01} and Rz^{02} may be bonded to each other to form a ring structure, provided that Rz^{01} and Rz^{02} do not contain an acid-dissociable group, and * represents a bond.

2. The resist composition according to Claim 1, wherein the content of the plasticizer component (Z) is 1 to 30 parts by mass with respect to 100 parts by mass of the resin component (A1).

3. A method of forming a resist pattern, comprising:

a step of forming a resist film on a support using the resist composition according to Claim 1 or 2;

a step of exposing the resist film; and

a step of developing the exposed resist film to form a resist pattern.