RESIST COMPOSITION AND METHOD OF FORMING RESIST PATTERN

TECHNICAL FIELD

[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. 2018-217631, filed November 20, 2018, and Japanese Patent Application No. 2019-188955, filed October 15, 2019, the contents of which are incorporated herein by reference.

DESCRIPTION OF RELATED ART

[0002]

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

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

Furthermore, research is also being conducted into lithography techniques that use an exposure light source having a wavelength shorter (energy higher) than these excimer lasers, such as electron beam (EB), extreme ultraviolet radiation (EUV), and X ray.

[0003]

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

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

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

On the other hand, when such a base resin is applied to a solvent developing process using a developing solution containing an organic solvent (organic developing solution), the solubility of the exposed portions in an organic developing solution is

decreased. As a result, the unexposed portions of the resist film are dissolved and removed by the organic developing solution, and a negative resist pattern in which the exposed portions of the resist film are remaining is formed. Such a solvent developing process for forming a negative-tone resist composition is sometimes referred to as "negative-tone developing process".

[0004]

In a chemically amplified resist composition, for suppressing film thickness loss during the formation of a resist pattern, and improve the difference in the solubility of the resist film between exposed portions and unexposed portions (dissolution contrast), it is known to add a dissolution inhibitor to suppress the solubility in a developing solution (see, for example, Patent Literatures 1 to 3).

[0005]

In recent years, photofabrication has become the mainstream of precision micromachining technology. Photofabrication refers to a processing technique for producing various precision parts, and includes applying the chemically amplified resist composition to the surface of a workpiece to form a resist film, forming a resist pattern having a predetermined shape on the resist film, and, using the formed pattern as a mask, conducting chemical etching, electrolytic etching or electroforming mainly involving electroplating.

DOCUMENTS OF RELATED ART

[Patent Literature]

[0006]

[Patent Literature 1] Japanese Unexamined Patent Application, First Publication No. 2006–328241

[Patent Literature 2] Japanese Unexamined Patent Application, First Publication No. 2007–206425

[Patent Document 3] Japanese Unexamined Patent Application, First Publication No. 2008–122932

SUMMARY OF THE INVENTION

[0007]

In such photofabrication, there is a case where a thick resist film having a film thickness of, for example, a micron order is formed on the surface of the workpiece depending on the application, etc., and etching is performed by forming a resist pattern. For example, in the development of a three-dimensional structure device (three-dimensional NAND), the capacity of a memory is increased by stacking several tens of layers of cells manufactured using a thick film resist pattern in the vertical direction.

As a result of the studies of the present inventors, in the case where a thick resist film of micron order is formed using a chemically amplified resist composition containing a conventional dissolution inhibitor, followed by forming a resist pattern and etching the pattern, in some cases, the etching resistance was insufficient. On the other hand, in the case where a thick film resist film is formed using a chemically amplified resist composition containing no dissolution inhibitor, and a resist pattern is formed, in some cases, film thickness loss of the resist film occurs during the formation of the resist pattern, and a pattern having a desired shape could not be formed.

[0008]

The present invention takes the above circumstances into consideration, with an object of providing a resist composition which exhibits satisfactory etching resistance,

and which is capable of forming a resist pattern having a good shape; and a method of forming a resist pattern using the resist composition.

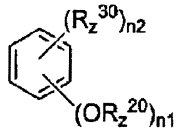
[0009]

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

A first aspect of the present invention is a resist composition which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid, and which includes a base component (A) which exhibits changed solubility in a developing solution under action of acid and a dissolution inhibitor (Z) which suppresses dissolution in a developing solution, the dissolution inhibitor (Z) including a compound (Z1) having a weight average molecular weight of 3,000 or less and containing a phenolic hydroxy group or a carboxy group in a molecule thereof, and a compound (Z2) having a weight average molecular weight of 3,000 or less and being represented by general formula (z2) shown below.

[0010]

[Chemical Formula 1]



. . . (z2)

In the formula, R_z^{20} represents an acid dissociable group; R_z^{30} represents a hydrogen atom or an organic group; n1 represents an integer of 1 to 6, and n2 represents an integer of 0 to 5, provided that n1+n2=6.

[0011]

A second aspect of the present invention is a method of forming a resist pattern, including: step (i) of using the aforementioned resist composition to form a resist film,

step (ii) of exposing the resist film, and step (iii) of developing the exposed resist film to form a resist pattern.

[0012]

According to the present invention, there are provided a resist composition which exhibits satisfactory etching resistance, and which is capable of forming a resist pattern having a good shape; and a method of forming a resist pattern using the resist composition.

DETAILED DESCRIPTION OF THE INVENTION

[0013]

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

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

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

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

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

The term "structural unit" refers to a monomer unit that contributes to the

formation of a polymeric compound (resin, polymer, copolymer).

The case of describing "may have a substituent" includes both of the case where the hydrogen atom (-H) is substituted with a monovalent group and the case where the methylene group ($-CH_2-$) is substituted with a divalent group.

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

[0014]

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

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

The acrylate ester may have the hydrogen atom bonded to the carbon atom on the α-position substituted with a substituent. The substituent ($R^{\alpha 0}$) that substitutes the hydrogen atom bonded to the carbon atom on the α-position is an atom other than hydrogen or a group, and examples thereof include an alkyl group of 1 to 5 carbon atoms and a halogenated alkyl group of 1 to 5 carbon atoms. Further, an acrylate ester having the hydrogen atom bonded to the carbon atom on the α-position substituted with a substituent ($R^{\alpha 0}$) in which the substituent has been substituted with a substituent containing an ester bond (e.g., an itaconic acid diester), or an acrylic acid having the hydrogen atom bonded to the carbon atom on the α-position substituted with a substituent ($R^{\alpha 0}$) in which the substituent has been substituted with a hydroxyalkyl group or a group in which the hydroxy group within a hydroxyalkyl group has been modified (e.g., α-hydroxyalkyl acrylate ester) can be mentioned as an acrylate ester having the hydrogen atom bonded to the carbon atom on the α-position substituted with a substituent. A

carbon atom on the α-position of an acrylate ester refers to the carbon atom bonded to the carbonyl group, unless specified otherwise.

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

[0015]

A "structural unit derived from acrylamide" refers to a structural unit that is formed by the cleavage of the ethylenic double bond of acrylamide.

The acrylamide may have the hydrogen atom bonded to the carbon atom on the α-position substituted with a substituent, and may have either or both terminal hydrogen atoms on the amino group of acrylamide substituted with a substituent. A carbon atom on the α-position of an acrylamide refers to the carbon atom bonded to the carbonyl group, unless specified otherwise.

As the substituent which substitutes the hydrogen atom on the α-position of acrylamide, the same substituents as those described above for the substituent ($R^{\alpha 0}$) on the α-position of the aforementioned α-position of the aforementioned α-substituted acrylate ester can be mentioned.

[0016]

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

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

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

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

[0017]

A "structural unit derived from vinylbenzoic acid or a vinylbenzoic acid derivative" refers to a structural unit that is formed by the cleavage of the ethylenic double bond of vinylbenzoic acid or a vinylbenzoic acid derivative.

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

[0018]

The term "styrene derivative" includes compounds in which the hydrogen atom at the α-position of styrene 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 which has a substituent other than a hydroxy group bonded to the benzene ring and may have the hydrogen atom on the α-position substituted with a substituent. Here, the α-position (carbon atom on the α-position) refers to the carbon atom having the benzene ring bonded thereto, unless specified otherwise.

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

[0019]

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

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

Specific examples of the hydroxyalkyl group as the substituent on the α-position include groups in which part or all of the hydrogen atoms of the aforementioned "alkyl group as the substituent on the α-position" are substituted with a hydroxy group. The

number of hydroxy groups within the hydroxyalkyl group is preferably 1 to 5, and most preferably 1.

[0020]

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

[0021]

(Resist composition)

The resist composition according to a first aspect of the present invention is a resist composition which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid.

As one embodiment of such resist composition, for example, a resist composition including a base component (A) (hereafter, sometimes referred to as "component (A)") which exhibits changed solubility in a developing solution under action of acid, a dissolution inhibitor (Z) (hereafter, sometimes referred to as "component (Z)") which suppresses dissolution in a developing solution, and an organic solvent (S) (hereafter, sometimes referred to as "component (S)").

[0022]

The resist composition according to the present embodiment may be preferably used in the formation of a resist pattern in which exposure is conducted using an exposure light source such as an ultraviolet ray (e.g., g-line or i-line), and KrF excimer laser.

Further, the resist composition of the present embodiment may be preferably used in forming a resist film having a film thickness of 1 to 10 μm, and in particular, in

forming a resist pattern using a resist film having a large film thickness. Here, a film having large film thickness refers to a film having a thickness of 3μm or more. The resist composition of the present embodiment may be used in forming a resist film preferably having a thickness of 3μm or more, more preferably a thickness of 3.5μm or more, and still more preferably 4μm or more.

[0023]

When a resist film is formed using the resist composition and the formed resist film is subjected to a selective exposure, acid is generated at exposed portions 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 unexposed portions of the resist film, thereby generating difference in solubility in a developing solution between exposed portions and unexposed portions. Therefore, by subjecting the resist film to development, the exposed portions of the resist film are dissolved and removed to form a positive-tone resist pattern in the case of a positive resist, whereas the unexposed portions of the resist film are dissolved and removed to form a negative-tone resist pattern in the case of a negative resist.

In the present specification, a resist composition which forms a positive resist pattern by dissolving and removing the exposed portions of the resist film is called a positive resist composition, and a resist composition which forms a negative resist pattern by dissolving and removing the unexposed portions of the resist film is called a negative resist composition.

The resist composition of the present invention may be either a positive resist composition or a negative resist composition.

Further, in the formation of a resist pattern, the resist composition of the present

invention 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.

[0024]

The resist composition of the present embodiment has a function of generating acid upon exposure, and in the resist composition, the component (A) may generate acid upon exposure, or an additive component other than the component (A) may generate acid upon exposure.

In the present embodiment, the resist composition may be a resist composition (1) containing an acid generator component (B) which generates acid upon exposure (hereafter, referred to as "component (B)"; a resist composition (2) in which the component (A) is a component which generates acid upon exposure; or a resist composition (3) in which the component (A) is a component which generates acid upon exposure, and further containing an acid generator component (B).

That is, when the resist composition of the present invention is the aforementioned resist composition (2) or (3), the component (A) is a "base component which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid". In the case where the component (A) is a base component which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid, the component (A1) described later is preferably a polymeric compound which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid. As the polymeric compound, a resin having a structural unit which generates acid upon exposure can be used. As the structural unit which generates acid upon exposure, a conventional structural unit can be

used.

[0025]

The resist composition of the present embodiment is preferably the aforementioned resist composition (1), i.e., a resist composition containing components (A) and (Z), and also component (B).

[0026]

<Component (A)>

In the resist composition of the present embodiment, the component (A) is a base component which exhibits changed solubility in a developing solution under action of acid.

In the present invention, the term "base component" refers to an organic compound capable of forming a film, and is preferably an organic compound having a molecular weight of 500 or more. When the organic compound has a molecular weight of 500 or more, the film-forming ability is improved, and a resist pattern of nano level can be easily formed.

The organic compound used as the base component is broadly classified into non-polymers and polymers.

In general, as a non-polymer, any of those which have a molecular weight in the range of 500 to less than 4,000 is used. Hereafter, a "low molecular weight compound" refers to a non-polymer having a molecular weight in the range of 500 to less than 4,000.

As a polymer, any of those which have a molecular weight of 1,000 or more is generally used. Hereafter, a "resin" or a "polymer" refers to a polymer having a molecular weight of 1,000 or more.

As the molecular weight of the polymer, the weight average molecular weight in terms of the polystyrene equivalent value determined by gel permeation chromatography

(GPC) is used.

[0027]

In the case where the resist composition of the present embodiment is a "negative resist composition for alkali developing process" which forms a negative resist pattern in an alkali developing process, or a "positive resist composition for solvent developing process", as the component (A), a base component (A-2) which is soluble in an alkali developing solution (hereafter, referred to as "component (A-2)") may be preferably used, and a cross-linking agent is blended. In such a resist composition, for example, when acid is generated from the component (B) upon exposure, the action of the acid causes cross-linking between the component (A-2) and the cross-linking component. As a result, the solubility of the resist composition in an alkali developing solution is decreased (the solubility of the resist composition in an organic developing solution is increased).

Therefore, in the formation of a resist pattern, by conducting selective exposure of a resist film formed by applying the resist composition to a substrate, the exposed portions of the resist film become insoluble in an alkali developing solution (soluble in an organic developing solution), whereas the unexposed portions of the resist film remain soluble in an alkali developing solution (insoluble in an organic developing solution), and hence, a negative resist pattern is formed by conducting development using an alkali developing solution. Alternatively, in such a case, by developing using an organic developing solution, a positive resist pattern is formed.

As the component (A-2), a resin that is soluble in an alkali developing solution (hereafter, referred to as “alkali-soluble resin”) is preferably used.

Examples of the alkali soluble resin include a resin having a structural unit derived from at least one of α-(hydroxyalkyl)acrylic acid and an alkyl ester of

α-(hydroxyalkyl)acrylic acid (preferably an alkyl ester having 1 to 5 carbon atoms), as disclosed in Japanese Unexamined Patent Application, First Publication No. 2000-206694; an acrylic resin which has a sulfonamide group and may have the hydrogen atom bonded to the carbon atom on the α-position substituted with a substituent or polycycloolefin resin having a sulfoneamide group, as disclosed in U.S. Patent No. 6,949,325; an acrylic resin which may have the hydrogen atom bonded to the carbon atom on the α-position substituted with a substituent and having a fluorinated alcohol, as disclosed in U.S. Patent No. 6,949,325, Japanese Unexamined Patent Application, First Publication No. 2005-336452 or Japanese Unexamined Patent Application, First Publication No. 2006-317803; and a polycyclolefin resin having a fluorinated alcohol, as disclosed in Japanese Unexamined Patent Application, First Publication No. 2006-259582. These resins are preferable in that a resist pattern can be formed with minimal swelling.

Here, the term "α-(hydroxyalkyl)acrylic acid" refers to one or both of acrylic acid in which a hydrogen atom is bonded to the carbon atom on the α-position having the carboxyl group bonded thereto, and α-hydroxyalkylacrylic acid in which a hydroxyalkyl group (preferably a hydroxyalkyl group of 1 to 5 carbon atoms) is bonded to the carbon atom on the α-position.

As the cross-linking agent, typically, an amino-based cross-linking agent such as a glycoluril having a methylol group or alkoxymethyl group, or a melamine-based cross-linking agent is preferable, as it enables formation of a resist pattern with minimal swelling. The amount of the cross-linker added is preferably within a range from 1 to 50 parts by weight, relative to 100 parts by weight of the alkali-soluble resin.

[0028]

In the case where the resist composition of the present embodiment is a

"positive resist composition for alkali developing process" which forms a positive resist pattern in an alkali developing process, or a "negative resist composition for solvent developing process", as the component (A), a base component (A-1) which exhibits increased polarity by the action of acid (hereafter, referred to as "component (A-1)") may be preferably used. By using the component (A-1), since the polarity of the base component changes prior to and after exposure, an excellent development contrast can be obtained not only in an alkali developing process, but also in a solvent developing process.

More specifically, in the case of applying an alkali developing process, the component (A-1) is substantially insoluble in an alkali developing solution prior to exposure, but when acid is generated from the component (B) upon exposure, the action of this acid causes an increase in the polarity of the base component, thereby increasing the solubility of the component (A-1) in an alkali developing solution. Therefore, in the formation of a resist pattern, by conducting selective exposure of a resist film formed by applying the resist composition to a substrate, the exposed portions of the resist film change from an insoluble state to a soluble state in an alkali developing solution, whereas the unexposed portions of the resist film remain insoluble in an alkali developing solution, and hence, a positive resist pattern is formed by alkali developing.

On the other hand, in the case of a solvent developing process, the component (A-1) exhibits high solubility in an organic developing solution prior to exposure, and when acid is generated from the component (B) upon exposure, the polarity of the component (A-1) is increased by the action of the generated acid, thereby decreasing the solubility of the component (A-1) in an organic developing solution. Therefore, in the formation of a resist pattern, by conducting selective exposure of a resist film formed by applying the resist composition to a substrate, the exposed portions of the resist film

changes from an soluble state to an insoluble state in an organic developing solution, whereas the unexposed portions of the resist film remain soluble in an organic developing solution. As a result, by conducting development using an organic developing solution, a contrast can be made between the exposed portions and unexposed portions, thereby forming a negative resist pattern.

[0029]

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

In the resist composition of the present embodiment, the component (A) is preferably a component (A-1). That is, the resist composition of the present embodiment is preferably a resist composition which forms a positive pattern in an alkali developing process (i.e, a positive resist compound for alkali developing process) or a resist composition which forms a negative pattern in a solvent developing process (i.e., a negative type resist composition for solvent developing process). As the component (A), at least one of a polymeric compound and a low molecular weight compound may be used.

In the case where the component (A) is a component (A-1), the component (A-1) preferably contains a resin component (A1) (hereafter, referred to as "component (A1)").

[0030]

- Component (A1)

The component (A1) is a resin component preferably containing a polymeric compound having a structural unit (a1) containing an acid decomposable group that exhibits increased polarity by the action of acid.

The component (A1) preferably has, in addition to the structural unit (a1), a structural unit (a10) containing a hydroxystyrene skeleton.

The component (A1) preferably has, in addition to the structural unit (a1), a structural unit (st) derived from styrene or a derivative thereof.

The component (A1) may further include a structural unit other than the structural units (a1), (a10) and (st).

[0031]

<<Structural unit (a1)>>

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

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

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

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

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

[0032]

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

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

[0033]

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

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

[0034]

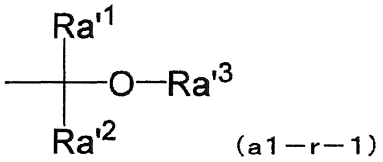
- Acetal-type acid dissociable group

Examples of the acid dissociable group for protecting the carboxy group or

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

[0035]

[Chemical Formula 2]



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

[0036]

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

In the case where Ra'^{1} or Ra'^{2} is an alkyl group, as the alkyl group, the same alkyl groups as those described above the for the substituent which may be bonded to the carbon atom on the α-position of the aforementioned α-substituted acrylate ester can be mentioned, and an alkyl group of 1 to 5 carbon atoms is preferable. Specific examples include linear or branched alkyl groups. Specific examples of the alkyl group include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group and a neopentyl group. Of these, a methyl group or an ethyl group is preferable, and a methyl group is particularly preferable.

[0037]

In formula (a1–r–1), examples of the hydrocarbon group for Ra'^{3} include a linear or branched alkyl group and a cyclic hydrocarbon group.

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

[0038]

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

[0039]

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

As the monocyclic aliphatic hydrocarbon group, a group in which 1 hydrogen atom has been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

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

[0040]

When the monovalent hydrocarbon group for Ra'^3 is an aromatic hydrocarbon group, the aromatic hydrocarbon group is a hydrocarbon group having at least one aromatic ring.

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

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

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

[0041]

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

Here, R^{P1} is a monovalent chain saturated hydrocarbon group having 1 to 10 carbon atoms, a monovalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms, or a monovalent aromatic hydrocarbon group having 6 to 30 carbon atoms. Further, R^{P2} is a single bond, a divalent chain saturated hydrocarbon group having 1 to 10 carbon atoms, a divalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms, or a divalent aromatic hydrocarbon group having 6 to 30 carbon atoms.

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

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

Examples of the monovalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms include a monocyclic aliphatic saturated hydrocarbon group such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclodecyl group, and a cyclododecyl group; and a polycyclic aliphatic saturated hydrocarbon group such as a bicyclo[2.2.2]octanyl group, a tricyclo[5.2.1.02,6]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 obtained by removing one hydrogen atom from the aromatic hydrocarbon ring such as benzene, biphenyl, fluorene, naphthalene, anthracene, and phenanthrene.

[0042]

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

[0043]

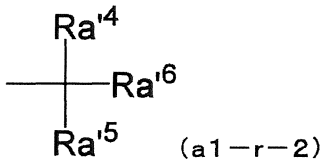
- Tertiary alkyl ester-type acid dissociable group

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

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

[0044]

[Chemical Formula 3]



(a1−r−2)

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

[0045]

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

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

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

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

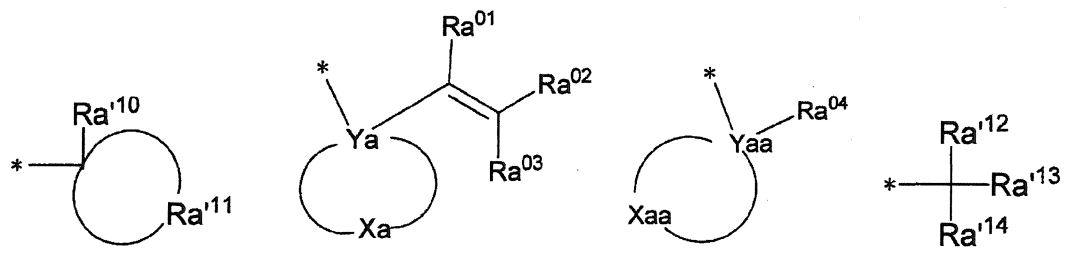
[0046]

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

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

[0047]

[Chemical Formula 4]



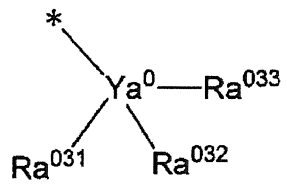
(a1−r2−1) (a1−r2−2) (a1−r2−3) (a1−r2−4)

In formula (a1–r2–1), Ra'^{10} represents an alkyl group of 1 to 10 carbon atoms, or a group

represented by general formula (a1−r2−r1) shown below; Ra'^{11} is a group which forms an aliphatic cyclic group together with a carbon atom having Ra'^{10} bonded thereto. In formula (a1−r2−2), Ya represents a carbon atom; Xa represents a group which forms a cyclic hydrocarbon group together with Ya, provided that part or all of the hydrogen atoms of the cyclic hydrocarbon group may be substituted; Ra^{01} to Ra^{03} each independently represents a hydrogen atom, a monovalent saturated chain hydrocarbon group of 1 to 10 carbon atoms or a monovalent saturated aliphatic cyclic hydrocarbon group of 3 to 20 carbon atoms, provided that part or all of the hydrogen atoms of the saturated chain hydrocarbon or the saturated aliphatic cyclic hydrocarbon may be substituted; two or more of Ra^{01} to Ra^{03} may be mutually bonded to form a cyclic structure. In formula (a1−r2−3), Yaa represents a carbon atom; Xaa represents a group which forms an aliphatic cyclic group together with Yaa; Ra^{04} represents an aromatic hydrocarbon group which may have a substituent. In formula (a1−r2−4), Ra'^{12} and Ra'^{13} each independently represents a hydrogen atom or a monovalent saturated hydrocarbon group of 1 to 10 carbon atoms, provided that part or all of the hydrogen atoms of the saturated hydrocarbon group may be substituted; Ra'^{14} represents a hydrocarbon group which may have a substituent; and * represents a bonding site (the same definition hereafter).

[0048]

[Chemical Formula 5]



... (a1−r2−r1)

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

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

[0049]

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

[0050]

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

[0051]

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

[0052]

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

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

The chain or cyclic alkenyl group for Ra^{031}, Ra^{032} and Ra^{033} is preferably an

alkenyl group having 2 to 10 carbon atoms.

[0053]

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

As the monocyclic aliphatic hydrocarbon group, a group in which 1 hydrogen atom has been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

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

[0054]

The aromatic hydrocarbon group for Ra^{031}, Ra^{032} and Ra^{033} is a hydrocarbon group having at least one aromatic ring. The aromatic ring is not particularly limited, as long as it is a cyclic conjugated compound having $(4n + 2)$ π electrons, and may be either monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20, still more preferably 6 to 15, and most preferably 6 to 12. Examples of the aromatic ring include aromatic hydrocarbon rings, such as benzene, naphthalene, anthracene and phenanthrene; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic hydrocarbon rings has been substituted with a hetero atom. Examples of the hetero atom within the aromatic hetero rings include an oxygen atom, a sulfur atom and a nitrogen atom. Specific examples of the aromatic hetero ring include a pyridine ring and a thiophene ring. Specific examples of the

aromatic hydrocarbon group include a group in which one hydrogen atom has been removed from the aforementioned aromatic hydrocarbon ring or aromatic hetero ring (aryl group or heteroaryl group); a group in which one hydrogen atom has been removed from an aromatic compound having two or more aromatic rings (biphenyl, fluorene or the like); and a group in which one hydrogen atom of the aforementioned aromatic hydrocarbon ring or aromatic hetero ring has been substituted with an alkylene group (an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group). The alkylene group bonded to the aforementioned aromatic hydrocarbon ring or the aromatic hetero ring preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and most preferably 1 carbon atom.

[0055]

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

[0056]

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

[0057]

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

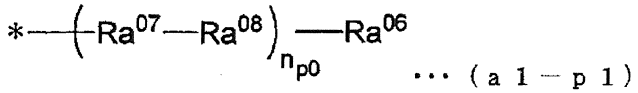
The "hydrocarbon group having a polar group" includes a group in which a

methylene group (–CH_2–)constituting the hydrocarbon group is substituted with a polar group, and a group in which at least one hydrogen atom constituting the hydrocarbon group has been substituted with a polar group.

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

[0058]

[Chemical Formula 6]



$$*-\left(-Ra^{07}-Ra^{08}\right)_{n_{p0}}-Ra^{06} \quad \cdots (a1-p1)$$

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

and n_{p0} represents an integer of1 to 6.

[0059]

In formula (a1–p1), Ra^{07} represents a divalent hydrocarbon group having 2 to 12 carbon atoms.

Ra^{07} has 2 to 12 carbon atoms, preferably 2 to 8 carbon atoms, more preferably 2 to 6 carbon atoms, still more preferably 2 to 4 carbon atoms, and most preferably 2 carbon atoms.

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

Examples of Ra^{07} include a linear alkanediyl group, such as an ethylene group, a propane-1,3-diyl group, butane-1,4-diyl group, a pentane-1,5-diyl group, a hexane-1,6-diyl group, a heptane-1,7-diyl group, an octane-1,8-diyl group, a nonane-1,9-diyl group, a decane-1,10-diyl group, an undecane-1,11-diyl group, and a

dodecane-1,12-diyl group; a branched alkanediyl group, such as a propane-1,2-diyl group, a 1-methylbutane-1,3-diyl group, a 2-methylpropane-1,3-diyl group, a pentane-1,4-diyl group, and a 2-methylbutane-1,4-diyl group; a cycloalkanediyl group, such as a cyclobutane-1,3-diyl group, a cyclopentane-1,3-diyl group, a cyclohexane-1,4-diyl group, and a cyclooctane-1,5-diyl group; and a polycyclic divalent alicyclic hydrocarbon group, such as a norbornane-1,4-diyl group, a norbornane-2,5-diyl group, an adamantane-1,5-diyl group, and an adamantane-2,6-diyl group.

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

[0060]

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

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

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

[0061]

In formula (a1–p1), Ra^{06} represents a monovalent hydrocarbon group having 1 to 12 carbon atoms.

Ra^{06} has 1 to 12 carbon atoms. In terms of solubility in a developing solution, Ra^{06} preferably has 1 to 8 carbon atoms, more preferably 1 to 5 carbon atoms, still more preferably 1 to 3 carbon atoms, still more preferably 1 or 2 carbon atoms, and most preferably 1 carbon atoms.

[0062]

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

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

[0063]

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

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

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

[0064]

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

[0065]

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

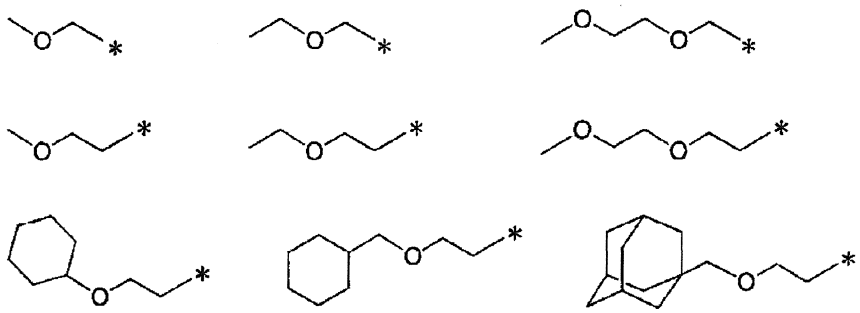
[0066]

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

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

[0067]

[Chemical Formula 7]



[0068]

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

two of Ra^{031}, Ra^{032} and Ra^{033} is a hydrocarbon group having a polar group, and it is more preferable that one of Ra^{031}, Ra^{032} and Ra^{033} is hydrocarbon group having a polar group.

[0069]

The hydrocarbon group having a polar group may have a substituent other than a polar group.

Examples of such substituent include a halogen atom (such as a fluorine atom, a chlorine atom or a bromine atom), and a halogenated alkyl group having 1 to 5 carbon atoms.

[0070]

In formula(a1–r2–1), the aliphatic cyclic group which is formed by Ra'^{11} together with the carbon atom bonded to Ra'^{10}, the same groups as those described above for the monocyclic or polycyclic aliphatic hydrocarbon group for Ra'^{3} in formula (a1-r-1) are preferable.

[0071]

In formula (a1–r2–2), as the cyclic hydrocarbon group formed by Xa together with Ya, a group in which 1 or more hydrogen atoms have been removed from the monovalent cyclic hydrocarbon group (aliphatic hydrocarbon group) for Ra'^{3} in the aforementioned formula (a1–r–1) may be mentioned.

The cyclic hydrocarbon group which Xa forms with Ya may have a substituent. Examples of substituents include the same substituents as those which the cyclic hydrocarbon group for Ra'^{3} may have.

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

Examples of the monovalent aliphatic cyclic saturated hydrocarbon group having 3 to 20 carbon atoms for Ra^{01} to Ra^{03} include a monocyclic aliphatic saturated hydrocarbon group such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclodecyl group, and a cyclododecyl group; and a polycyclic aliphatic saturated hydrocarbon group such as a bicyclo[2.2.2]octanyl group, a tricyclo[5.2.1.02,6]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 these examples, as Ra^{01} to Ra^{03}, in terms of ease in synthesis of the monomeric compound which derives the structural unit (a1), a hydrogen atom or a saturated chain hydrocarbon group having 1 to 10 carbon atoms is preferable, a hydrogen atom, a methyl group or an ethyl group is more preferable, and a hydrogen atom is most preferable.

[0072]

As the substituent for the saturated chain hydrocarbon group or saturated cyclic aliphatic hydrocarbon group represented by Ra^{01} to Ra^{03}, for example, the same substituents as those described above for Ra^{05} may be mentioned.

[0073]

Examples of the group containing a carbon-carbon double bond which is 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 methyl cyclopentenyl group, a methyl cyclohexenyl group, a cyclopentylideneethenyl group, and a cyclohexylidenethenyl group. Among these examples, from the viewpoint of the ease of synthesis of the monomer compound which derives the structural unit (a1), a cyclopentenyl group, a cyclohexenyl group, and a cyclopentylidenethenyl group are

preferable.

[0074]

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

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

[0075]

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

[0076]

In general formula (a1-r2-4), Ra'^{12} and Ra'^{13} each independently represent a monovalent chain saturated hydrocarbon group having 1 to 10 carbon atoms or a

hydrogen atom. With respect to Ra'^{12} and Ra'^{13}, examples of the monovalent chain saturated hydrocarbon group having 1 to 10 carbon atoms include the same monovalent chain saturated hydrocarbon group having 1 to 10 carbon atoms as that for Ra^{01} to Ra^{03}, provided that part or all of the hydrogen atoms of the saturated hydrocarbon group may be substituted;

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

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

[0077]

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

[0078]

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

[0079]

The branched alkyl group for Ra'^{14} preferably has 3 to 10 carbon atoms, and more preferably 3 to 5 carbon atoms. Specific examples include an isopropyl group, an

isobutyl group, a tert-butyl group, an isopentyl group, a neopentyl group a 1,1-diethylpropyl group and a 2,2-dimethylbutyl group. Among these, an isopropyl group is preferable.

[0080]

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

As the monocyclic aliphatic hydrocarbon group, a group in which 1 hydrogen atom has been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

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

[0081]

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

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

[0082]

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

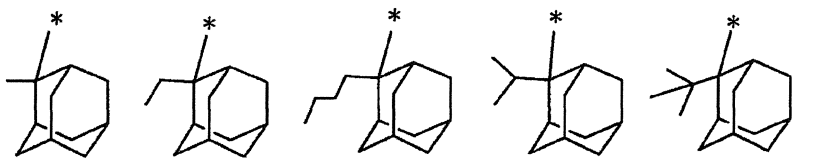
In the case where Ra'^{14} in general formula (a1-r2-4) is an anthryl group, a position which is bonded to a tertiary carbon atom in general formula (a1-r2-4) may be any one of 1-position, 2-position, and 9-position of the anthryl group.

[0083]

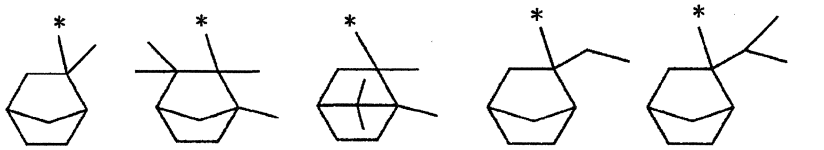
Specific examples of the group represented by the aforementioned formula (a1−r2−1) are shown below.

[0084]

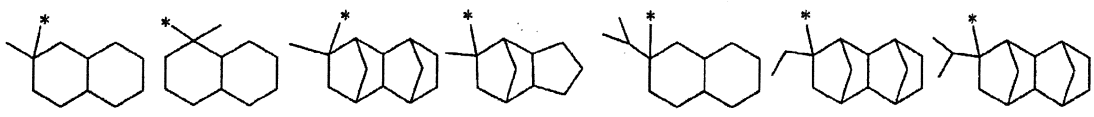
[Chemical Formula 8]



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



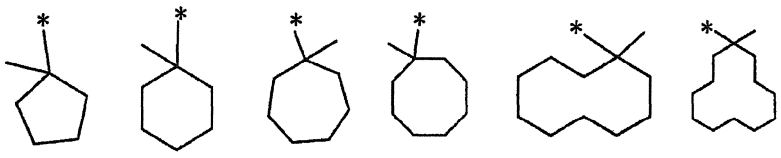
(r-pr-m6) (r-pr-m7) (r-pr-m8) (r-pr-m9) (r-pr-m10)



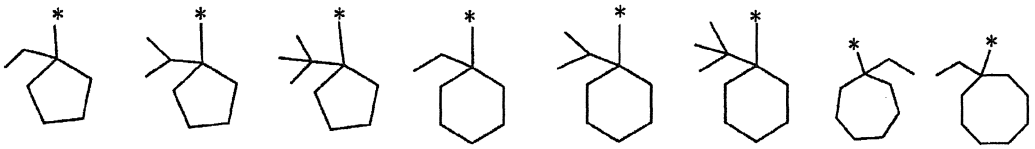
(r-pr-m11) (r-pr-m12) (r-pr-m13) (r-pr-m14) (r-pr-m15) (r-pr-m16) (r-pr-m17)

[0085]

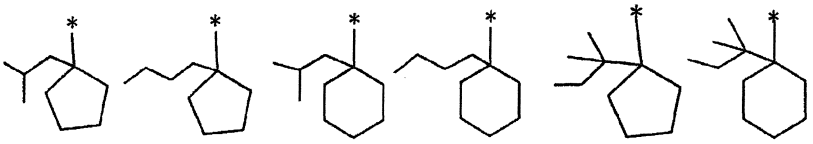
[Chemical Formula 9]



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



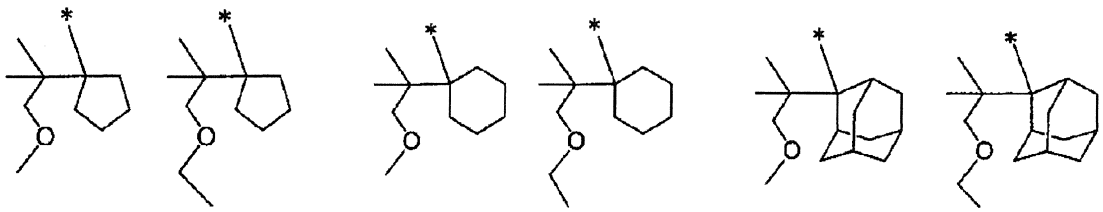
(r-pr-s7) (r-pr-s8) (r-pr-s9) (r-pr-s10) (r-pr-s11) (r-pr-s12) (r-pr-s13) (r-pr-s14)



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

[0086]

[Chemical Formula 10]



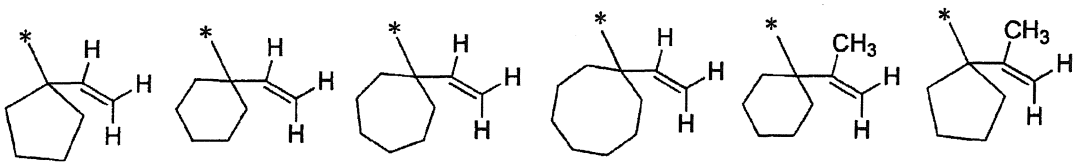
(r-pr-sp1) (r-pr-sp2) (r-pr-sp3) (r-pr-sp4) (r-pr-mp1) (r-pr-mp2)

[0087]

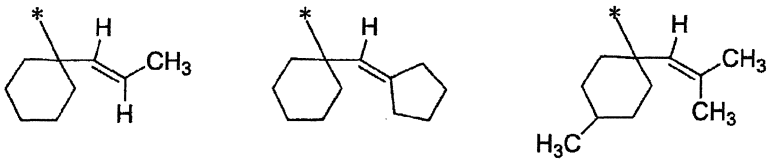
Specific examples of the group represented by the aforementioned formula (a1–r2–2) are shown below.

[0088]

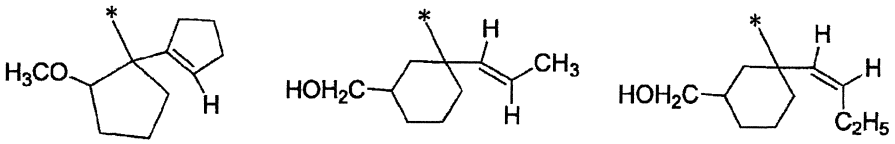
[Chemical Formula 11]



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



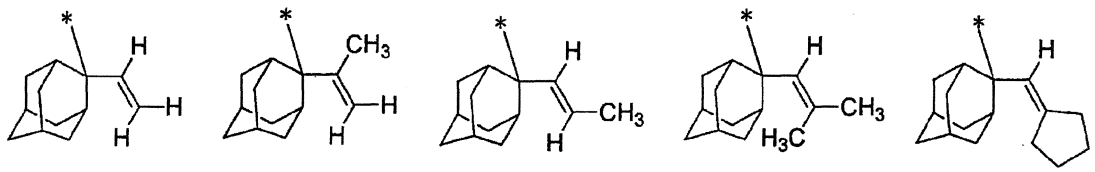
(r-pr-sv7) (r-pr-sv8) (r-pr-sv9)



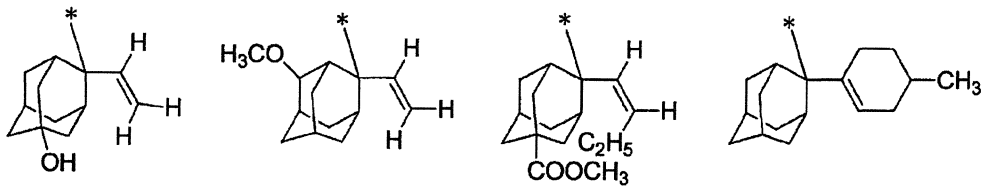
(r-pr-sv10) (r-pr-sv11) (r-pr-sv12)

[0089]

[Chemical Formula 12]



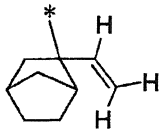
(r-pr-mv1) (r-pr-mv2) (r-pr-mv3) (r-pr-mv4) (r-pr-mv5)



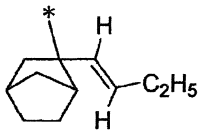
(r-pr-mv6) (r-pr-mv7) (r-pr-mv8) (r-pr-mv9)

[0090]

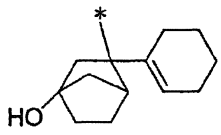
[Chemical Formula 13]



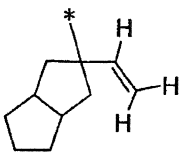
(r-pr-mv10)



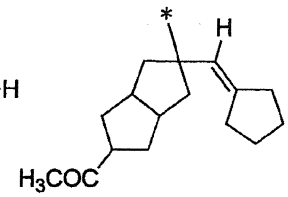
(r-pr-mv11)



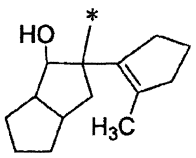
(r-pr-mv12)



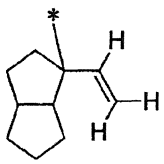
(r-pr-mv13)



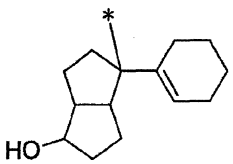
(r-pr-mv14)



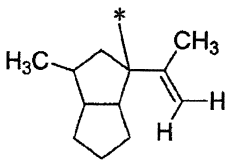
(r-pr-mv15)



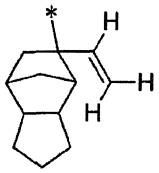
(r-pr-mv16)



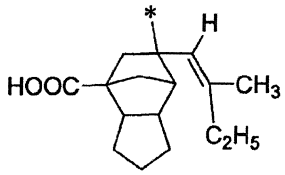
(r-pr-mv17)



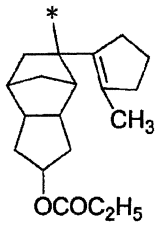
(r-pr-mv18)



(r-pr-mv19)



(r-pr-mv20)



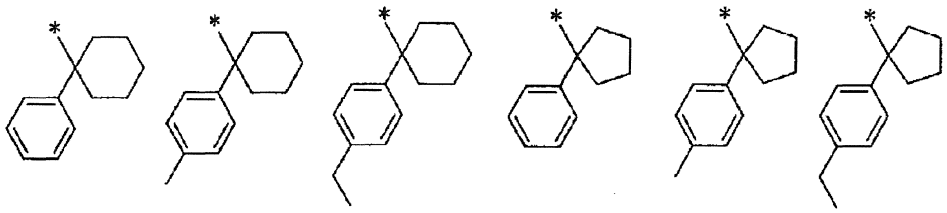
(r-pr-mv21)

[0091]

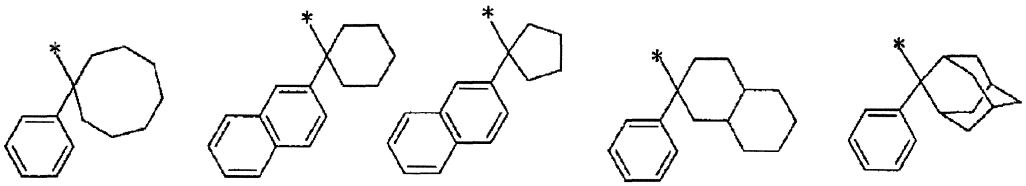
Specific examples of the group represented by the aforementioned formula (a1–r2–3) are shown below.

[0092]

[Chemical Formula 14]



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



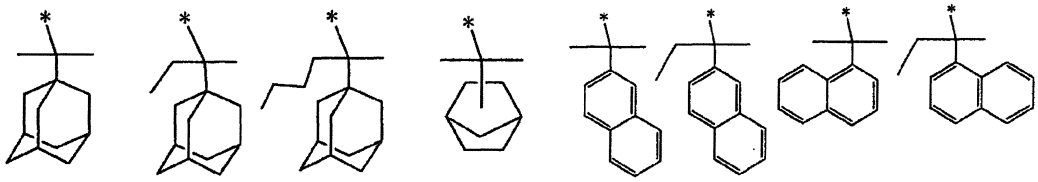
(r-pr-sa7) (r-pr-sa8) (r-pr-sa9) (r-pr-ma1) (r-pr-ma2)

[0093]

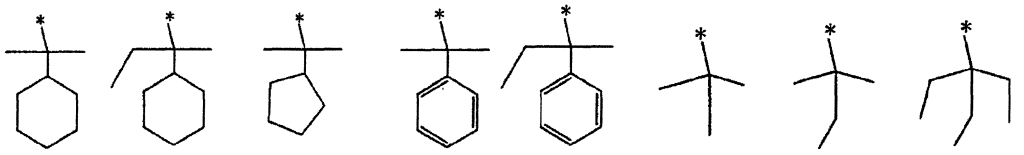
Specific examples of the group represented by the aforementioned formula (a1–r2–4) are shown below.

[0094]

[Chemical Formula 15]



(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)

[0095]

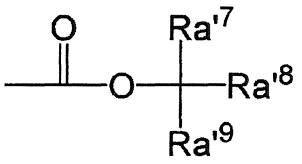
- Tertiary alkyloxycarbonyl acid dissociable group

Examples of the acid dissociable group for protecting a hydroxy group as a polar

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

[0096]

[Chemical Formula 16]



(a1−r−3)

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

[0097]

In formula (a1−r−3), each of Ra'^{7} to Ra'^{9} is preferably an alkyl group having 1 to 5 carbon atoms, and more preferably an alkyl group having 1 to 3 carbon atoms.

Further, the total number of carbon atoms in the alkyl groups is preferably 3 to 7, more preferably 3 to 5, and still more preferably 3 or 4.

[0098]

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

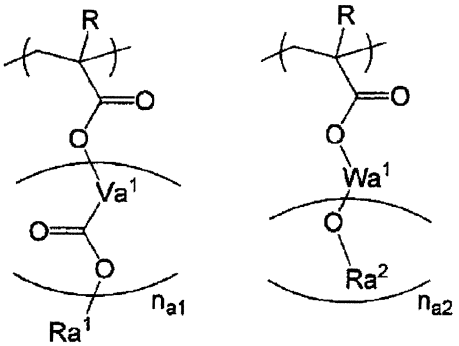
[0099]

As the structural unit (a1), a structural unit derived from an acrylate ester which may have the hydrogen atom bonded to the carbon atom on the α-position substituted with a substituent is preferable.

Specific examples of preferable structural units for the structural unit (a1) include structural units represented by general formula (a1-1) or (a1-2) shown below.

[0100]

[Chemical Formula 17]



(a 1 − 1) (a 1 − 2)

In the formula, R represents a hydrogen atom, an alkyl group of 1 to 5 carbon atoms or a halogenated alkyl group of 1 to 5 carbon atoms; Va^1 represents a divalent hydrocarbon group optionally having an ether bond; n_{a1} represents an integer of 0 to 2; Ra^1 represents an acid dissociable group represented by the aforementioned formula(a1−r−1) or (a1−r−2); Wa^1represents a hydrocarbon group having a valency of n_{a2} + 1; n_{a2} represents an integer of 1 to 3; and Ra^2 represents an acid dissociable group represented by the aforementioned general formula (a1-r-1) or (a1-r-3).

[0101]

In the aforementioned formula (a1-1), as the alkyl group of 1 to 5 carbon atoms for R, a linear or branched alkyl group of 1 to 5 carbon atoms is preferable, and specific examples thereof include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an

isopentyl group and a neopentyl group. The halogenated alkyl group of 1 to 5 carbon atoms represented by R is a group in which part or all of the hydrogen atoms of the aforementioned alkyl group of 1 to 5 carbon atoms have been substituted with halogen atoms. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom and an iodine atom, and a fluorine atom is particularly desirable.

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

[0102]

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

[0103]

The aliphatic hydrocarbon group as the divalent hydrocarbon group for Va^1 may be either saturated or unsaturated. In general, the aliphatic hydrocarbon group is preferably saturated.

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

[0104]

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

As the linear aliphatic hydrocarbon group, a linear alkylene group is preferable. Specific examples thereof include a methylene group [$-CH_2-$], an ethylene group [$-(CH_2)_2-$], a trimethylene group [$-(CH_2)_3-$], a tetramethylene group [$-(CH_2)_4-$] and a

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

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

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

[0105]

As examples of the hydrocarbon group containing a ring in the structure thereof, an alicyclic hydrocarbon group (a group in which two hydrogen atoms have been removed from an aliphatic hydrocarbon ring), a group in which the alicyclic hydrocarbon group is bonded to the terminal of the aforementioned chain-like aliphatic hydrocarbon group, and a group in which the alicyclic group is interposed within the aforementioned linear or branched aliphatic hydrocarbon group, can be given. The linear or branched aliphatic hydrocarbon group is the same as defined for the aforementioned linear aliphatic hydrocarbon group or the aforementioned branched aliphatic hydrocarbon group.

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

The alicyclic hydrocarbon group may be either a monocyclic group or a

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

[0106]

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

The aromatic hydrocarbon group preferably has 3 to 30 carbon atoms, more preferably 5 to 30, still more preferably 5 to 20, still more preferably 6 to 15, and most preferably 6 to 12. Here, the number of carbon atoms within a substituent(s) is not included in the number of carbon atoms of the aromatic hydrocarbon group.

Examples of the aromatic ring contained in the aromatic hydrocarbon group include aromatic hydrocarbon rings, such as benzene, biphenyl, fluorene, naphthalene, anthracene and phenanthrene; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic hydrocarbon rings has been substituted with a hetero atom. Examples of the hetero atom within the aromatic hetero rings include an oxygen atom, a sulfur atom and a nitrogen atom.

Specific examples of the aromatic hydrocarbon group include a group in which two hydrogen atoms have been removed from the aforementioned aromatic hydrocarbon ring (arylene group); and a group in which one hydrogen atom has been removed from the aforementioned aromatic hydrocarbon ring (aryl group) and one hydrogen atom has been substituted with an alkylene group (such as a benzyl group, a phenethyl group, a

1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group). The alkylene group (alkyl chain within the arylalkyl group) preferably has 1 to 4 carbon atom, more preferably 1 or 2, and most preferably 1.

[0107]

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

[0108]

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

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

[0109]

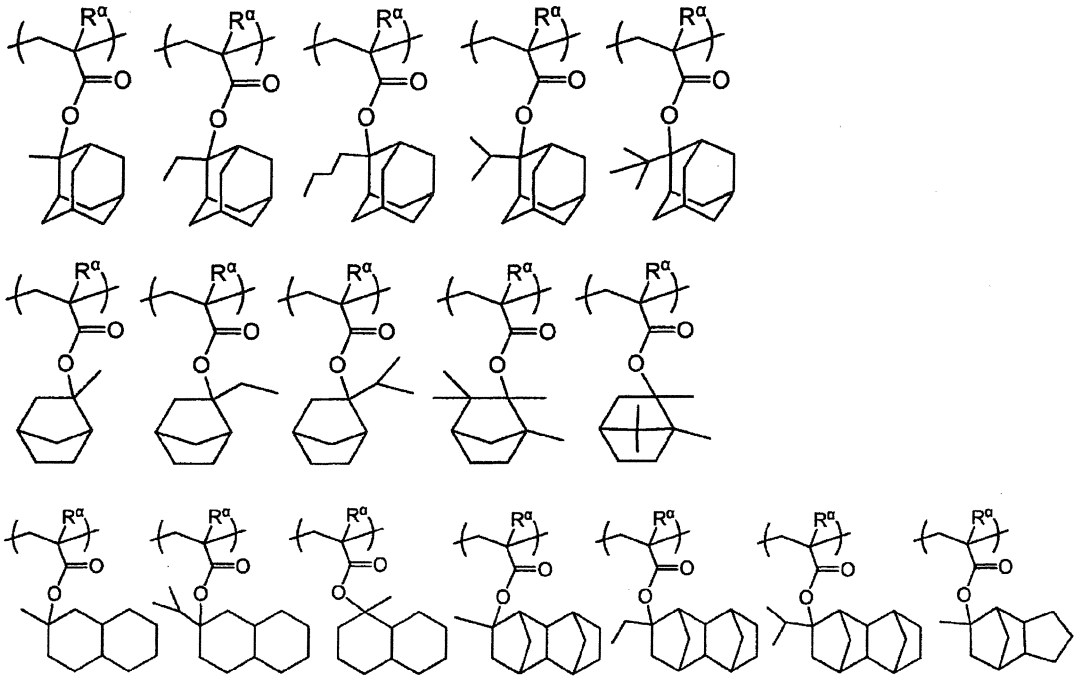
In formula (a1−2), Ra^2 represents an acid dissociable group represented by the aforementioned formula (a1−r−1) or (a1−r−3).

[0110]

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

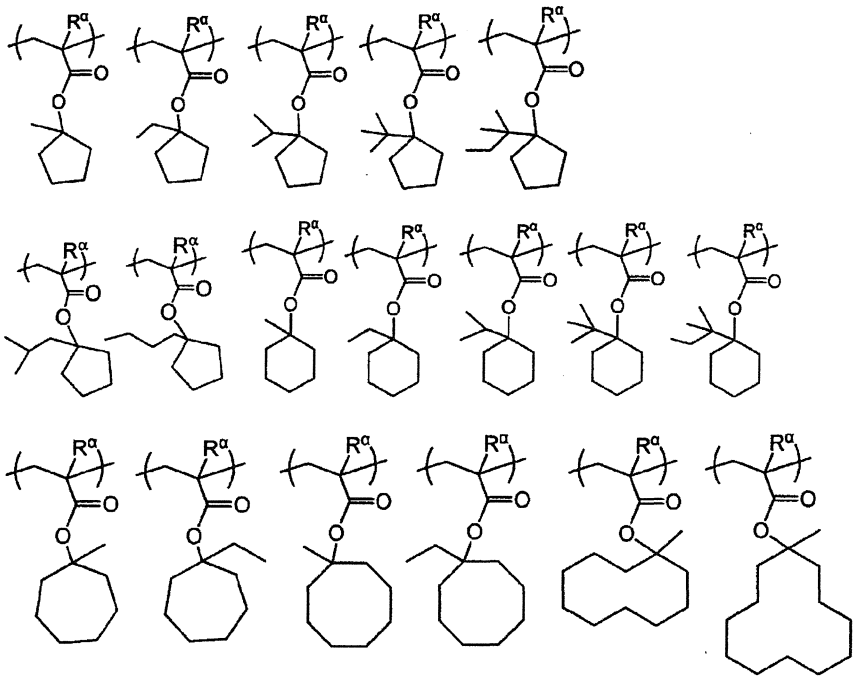
[0111]

[Chemical Formula 18]



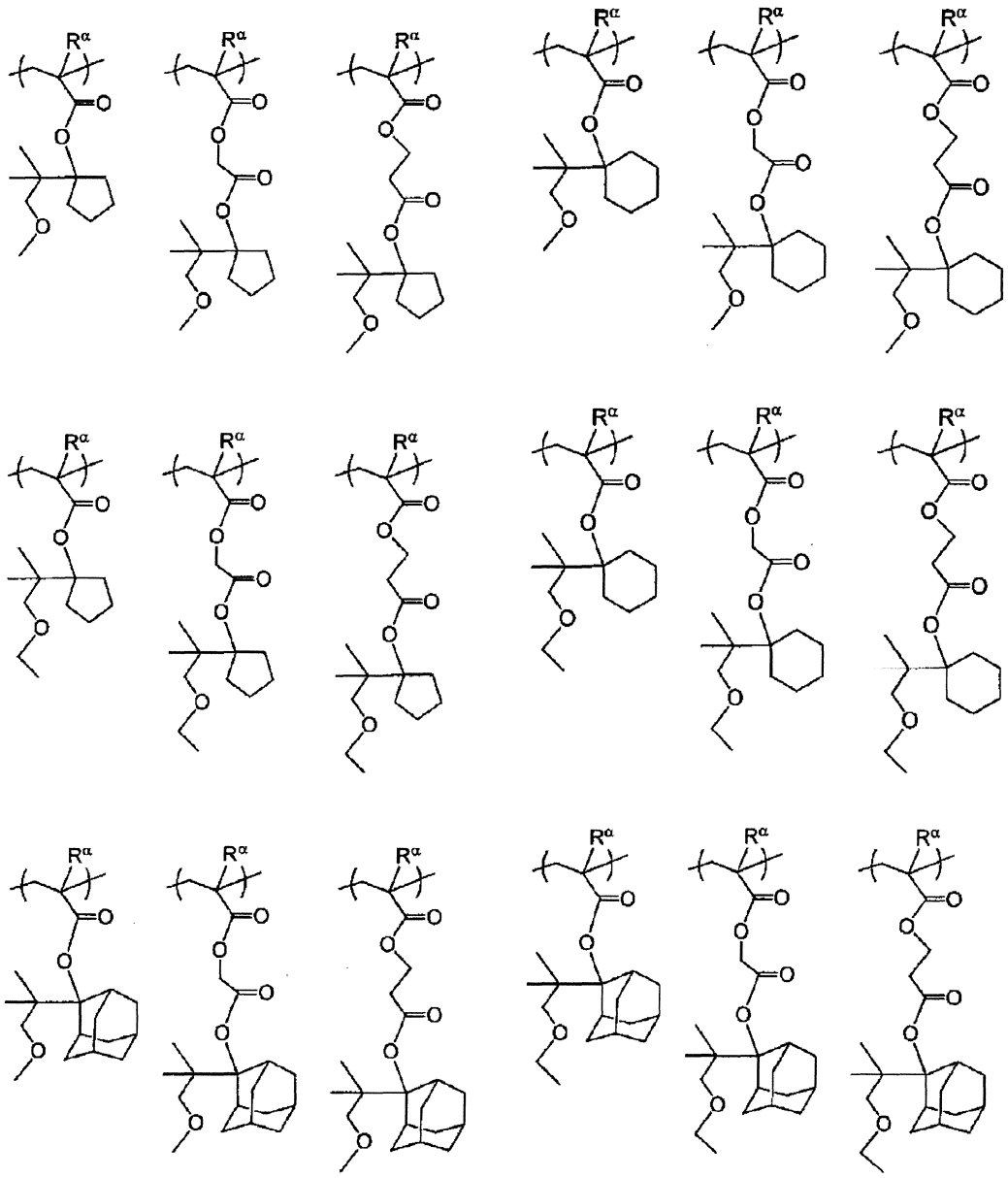
[0112]

[Chemical Formula 19]



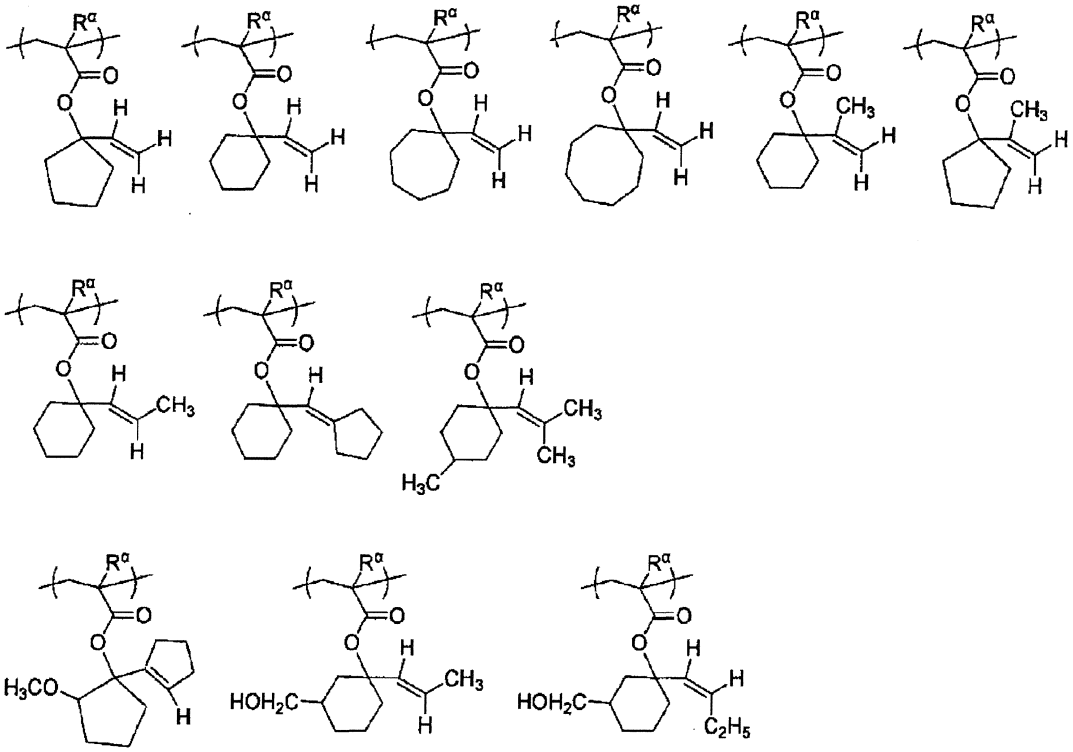
[0113]

[Chemical Formula 20]



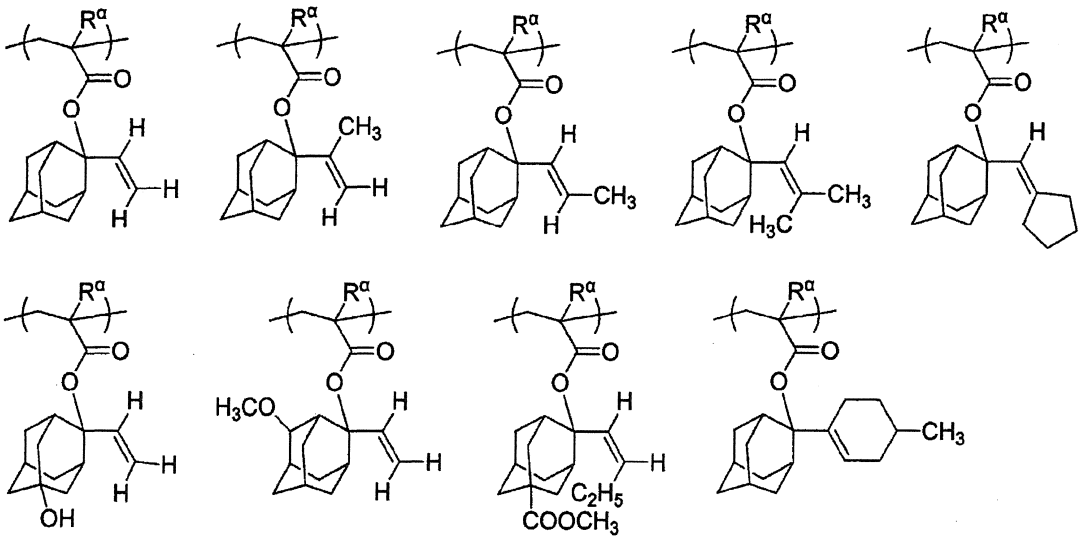
[0114]

[Chemical Formula 21]



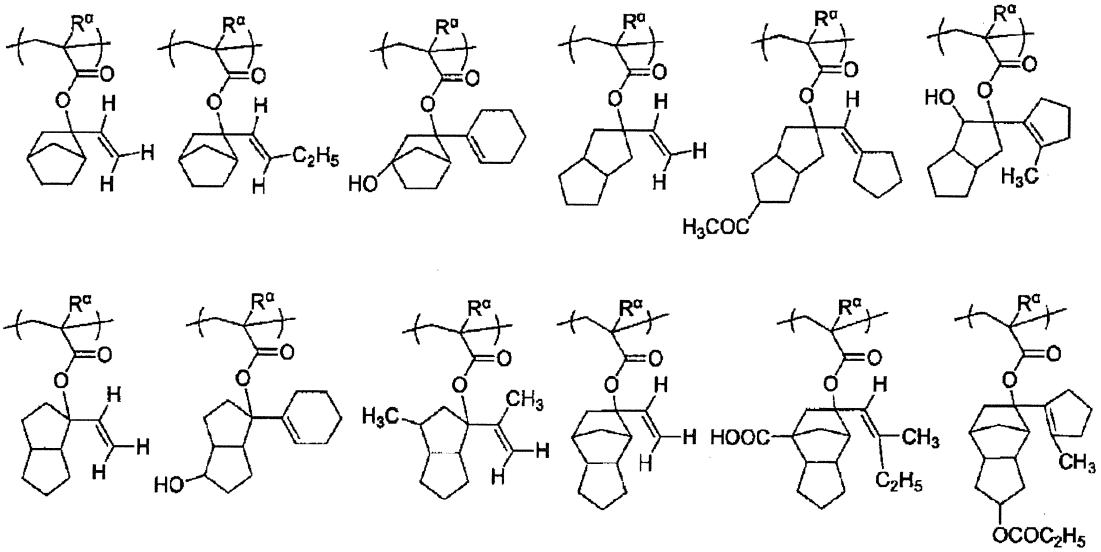
[0115]

[Chemical Formula 22]



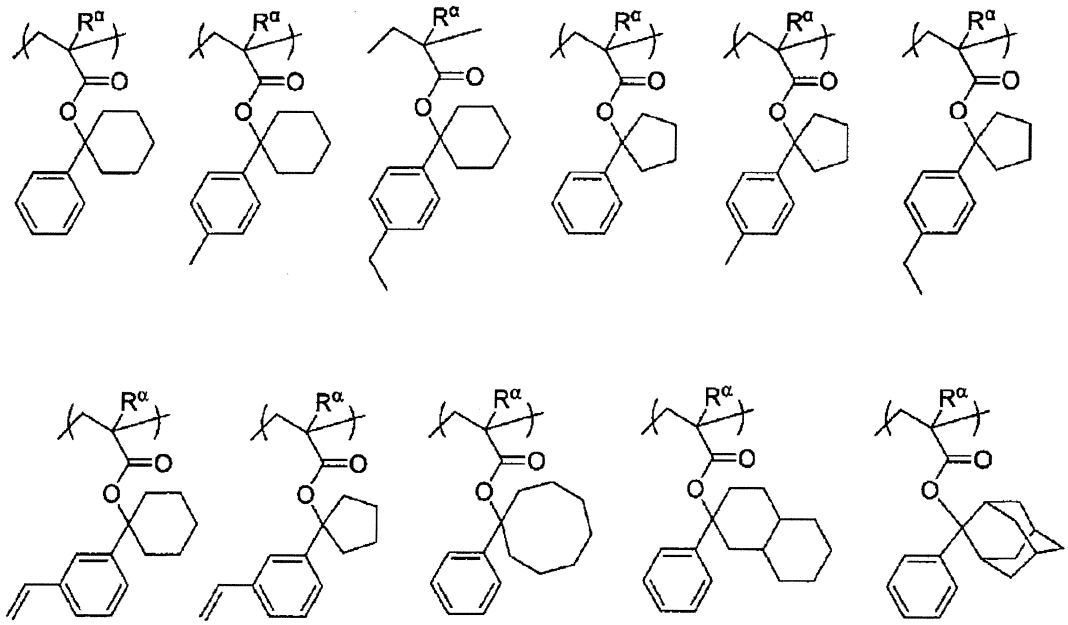
[0116]

[Chemical Formula 23]



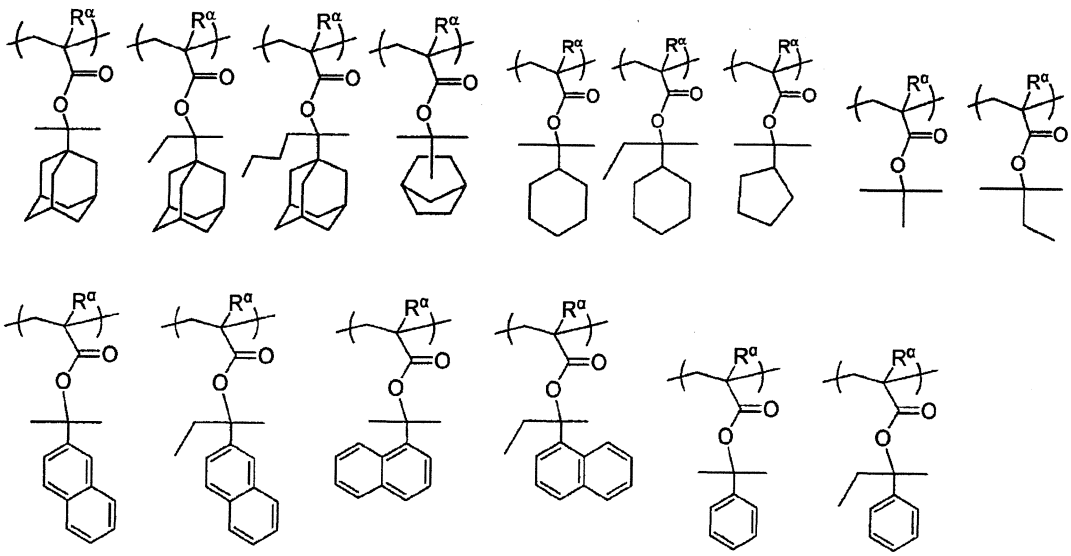
[0117]

[Chemical Formula 24]



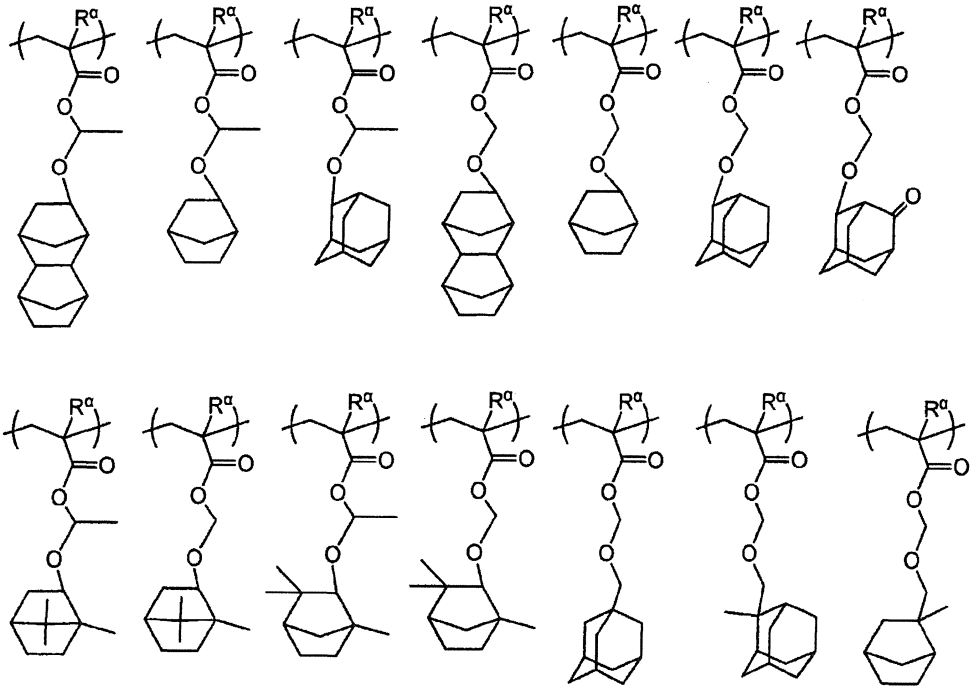
[0118]

[Chemical Formula 25]



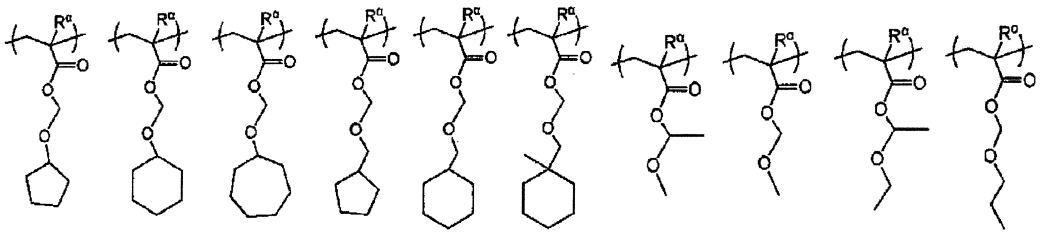
[0119]

[Chemical Formula 26]



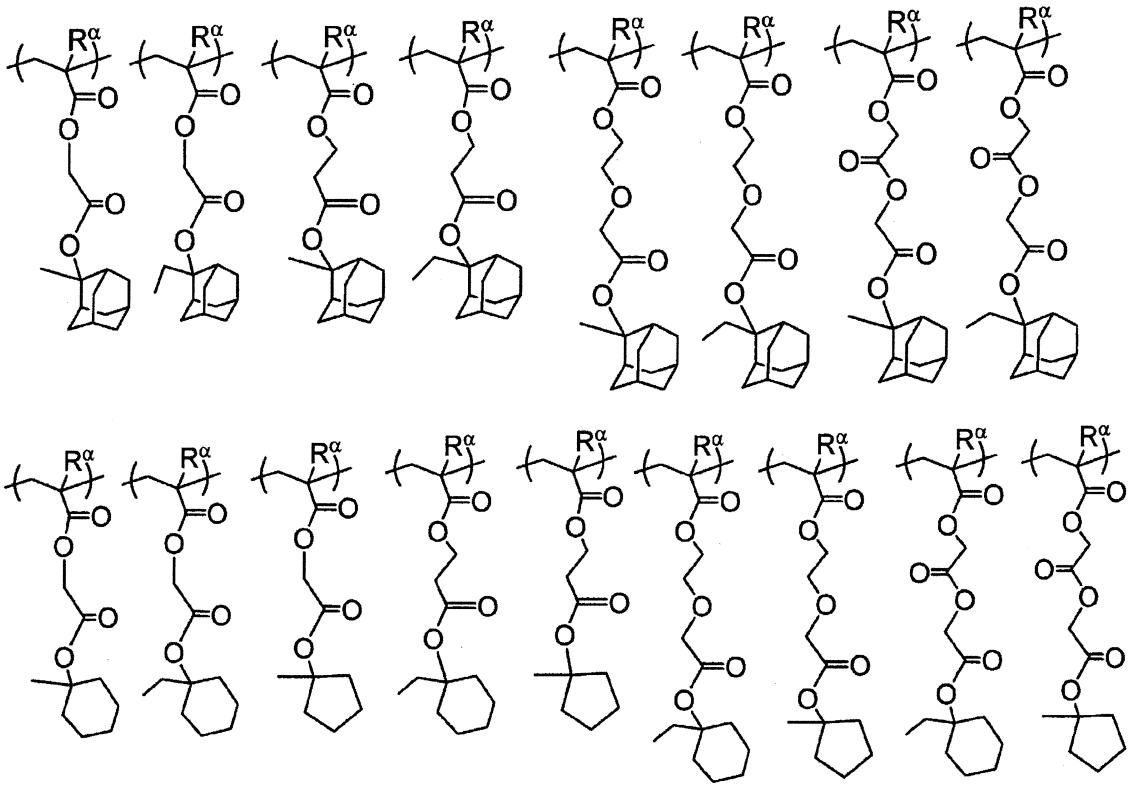
[0120]

[Chemical Formula 27]



[0121]

[Chemical Formula 28]

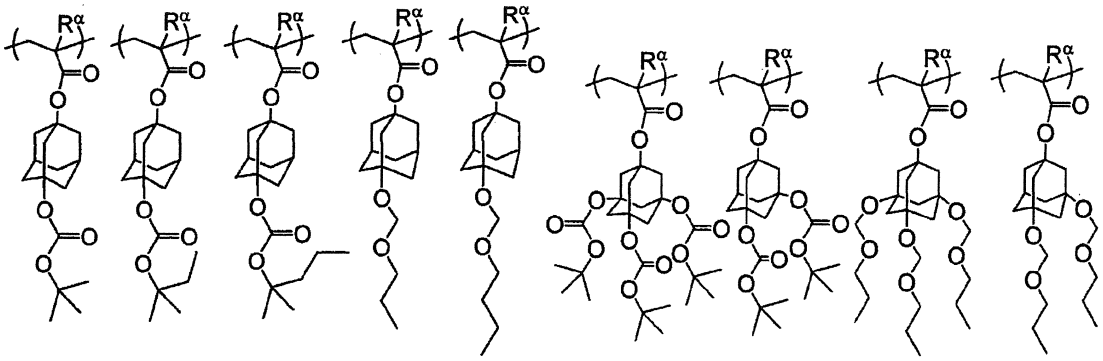


[0122]

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

[0123]

[Chemical Formula 29]



[0124]

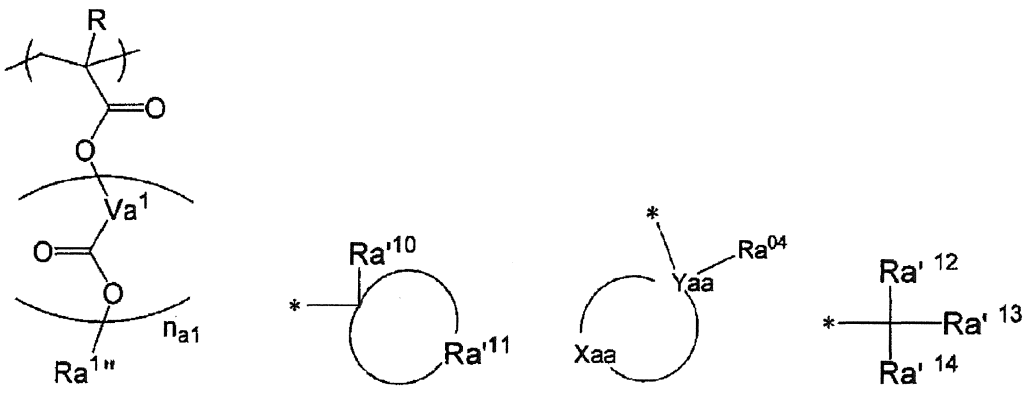
As the structural unit (a1) contained in the component (A1), 1 type of structural unit may be used, or 2 or more types may be used.

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

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

[0125]

[Chemical Formula 30]



(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).

[0126]

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

The description of the acid dissociable group represented by general formula (a1-r2-1), (a1-r2-3), or (a1-r2-4) is the same as described above.

[0127]

In the component (A1), the amount of the structural unit (a1) based on the combined total (100 mol%) of all structural units constituting the component (A1) is preferably 1 to 80 mol%, more preferably 5 to 70 mol%, and still more preferably 10 to 60 mol%.

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

[0128]

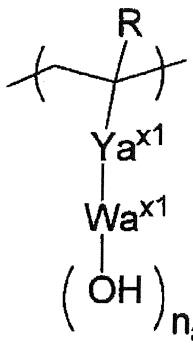
<<Structural unit (a10) containing hydroxystyrene skeleton>>

The component (A1) preferably has, in addition to the structural unit (a1), a structural unit (a10) containing a hydroxystyrene skeleton.

Preferable examples of the structural unit (a10) include a structural unit represented by general formula (a10-1) shown below.

[0129]

[Chemical Formula 31]



... (a10-1)

In the formula, R represents a hydrogen atom, an alkyl group of 1 to 5 carbon atoms or a halogenated alkyl group of 1 to 5 carbon atoms; Ya^{x1} represents a single bond or a divalent linking group; Wa^{x1} represents an aromatic hydrocarbon group having a valency of $(n_{ax1}+1)$; and n_{ax1} represents an integer of 1 to 3.

[0130]

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

As the alkyl group of 1 to 5 carbon atoms for R, a linear or branched alkyl group of 1 to 5 carbon atoms is preferable, and specific examples thereof include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group and a neopentyl group. The halogenated alkyl group of 1 to 5 carbon atoms represented by R is a group in which part or all of the hydrogen atoms of the aforementioned alkyl group of 1 to 5 carbon atoms have been substituted with halogen atoms. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom and an iodine atom, and a fluorine atom is particularly desirable.

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

[0131]

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

Preferable examples of the divalent linking group for Ya^{x1} include a divalent hydrocarbon group which may have a substituent, and a divalent linking group containing a hetero atom.

[0132]

- Divalent hydrocarbon group which may have a substituent:

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

[0133]

- Aliphatic hydrocarbon group for Ya^{x1}

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

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

[0134]

- Linear or branched aliphatic hydrocarbon group

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

As the linear aliphatic hydrocarbon group, a linear alkylene group is preferable. Specific examples thereof include a methylene group [$-CH_2-$], an ethylene group [$-(CH_2)_2-$], a trimethylene group [$-(CH_2)_3-$], a tetramethylene group [$-(CH_2)_4-$] and a

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

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

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

[0135]

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

[0136]

- Aliphatic hydrocarbon group containing a ring in the structure thereof

As examples of the hydrocarbon group containing a ring in the structure thereof, a cyclic aliphatic hydrocarbon group containing a hetero atom in the ring structure thereof and may have a substituent (a group in which two hydrogen atoms have been removed from an aliphatic hydrocarbon ring), a group in which the cyclic aliphatic hydrocarbon group is bonded to the terminal of the aforementioned chain-like aliphatic hydrocarbon group, and a group in which the cyclic aliphatic group is interposed within the aforementioned linear or branched aliphatic hydrocarbon group, can be given. As the

linear or branched aliphatic hydrocarbon group, the same groups as those described above can be used.

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

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

[0137]

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

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

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

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

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

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

[0138]

- Aromatic hydrocarbon group for 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 compound having $(4n + 2)\pi$ electrons, and may be either monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, and still more preferably 6 to 15 carbon atoms, and most preferably 6 to 12 carbon atoms. Here, the number of carbon atoms within a substituent(s) is not included in the number of carbon atoms of the aromatic hydrocarbon group. Examples of the aromatic ring include aromatic hydrocarbon rings, such as benzene, naphthalene, anthracene and phenanthrene; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic hydrocarbon rings has been substituted with a hetero atom. Examples of the hetero atom within the aromatic hetero rings include an oxygen atom, a sulfur atom and a nitrogen atom. Specific examples of the aromatic hetero ring include a pyridine ring and a thiophene ring.

Specific examples of the aromatic hydrocarbon group include a group in which two hydrogen atoms have been removed from the aforementioned aromatic hydrocarbon

ring or aromatic hetero ring (arylene group or heteroarylene group); a group in which two hydrogen atoms have been removed from an aromatic compound having two or more aromatic rings (biphenyl, fluorene or the like); and a group in which one hydrogen atom of the aforementioned aromatic hydrocarbon ring or aromatic hetero ring has been substituted with an alkylene group (a group in which one hydrogen atom has been removed from the aryl group within the aforementioned arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, or a 2-naphthylethyl group, or a heteroarylalkyl group). The alkylene group which is bonded to the aforementioned aryl group or heteroaryl group preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and most preferably 1 carbon atom.

[0139]

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

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

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

[0140]

- Divalent linking group containing a hetero atom

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

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

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

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

As Y^{22}, a linear or branched aliphatic hydrocarbon group is preferable, and a

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

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

[0141]

Ya^{x1} preferably represents an ester bond [-C(=O)-O-], an ether bond (-O-), –C(=O)–NH–, a linear or branched alkylene group, a combination of these, or a single bond, and more preferably a single bond.

[0142]

In formula (a10–1), Wa^{x1} represents an aromatic hydrocarbon group having a valency of $(n_{ax1}+1)$.

Examples of the aromatic hydrocarbon group for Wa^{x1}include a group obtained by removing $(n_{ax1}+1)$hydrogen atoms from an aromatic ring. The aromatic ring is not particularly limited, as long as it is a cyclic conjugated compound having $(4n + 2)\pi$ electrons, and may be either monocyclic or polycyclic. The aromatic ring preferably has 5 to 30 carbon atoms, more preferably 5 to 20 carbon atoms, and still more preferably 6

to 15 carbon atoms, and most preferably 6 to 12 carbon atoms. Examples of the aromatic ring include aromatic hydrocarbon rings, such as benzene, naphthalene, anthracene and phenanthrene; and aromatic hetero rings in which part of the carbon atoms constituting the aforementioned aromatic hydrocarbon rings has been substituted with a hetero atom. Examples of the hetero atom within the aromatic hetero rings include an oxygen atom, a sulfur atom and a nitrogen atom. Specific examples of the aromatic hetero ring include a pyridine ring and a thiophene ring.

[0143]

In formula (a10–1), n_{ax1} is an integer of 1 to 3, preferably 1 or 2, and more preferably 1.

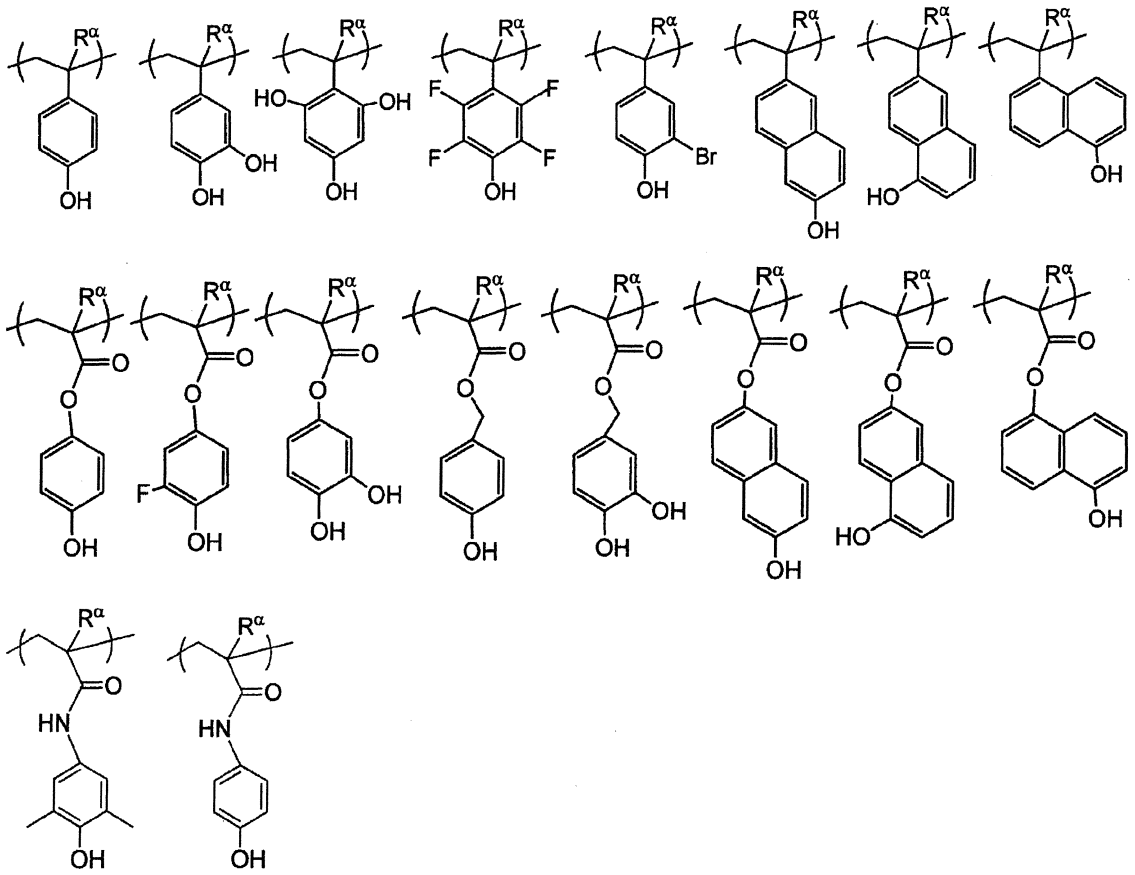
[0144]

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

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

[0145]

[Chemical Formula 32]



[0146]

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

In the component (A1), the amount of the structural unit (a10) based on the combined total (100 mol%) of all structural units constituting the component (A1) is, for example, 1 to 90 mol%, preferably 10 to 85 mol%, more preferably 20 to 80 mol%, and still more preferably 30 to 75 mol%.

When the amount of the structural unit (a10) is at least as large as the lower limit of the above-mentioned preferable range, various lithography properties such as sensitivity, resolution and roughness may be improved. On the other hand, when the amount of the structural unit (a10) is no more than the upper limit of the

above-mentioned range, a good balance may be achieved with the other structural units, and the lithography properties may be improved.

[0147]

<<Structural unit (a2)>>

The component (A1) may have, in addition to the structural unit (a1), a structural unit (a2) containing a lactone-containing cyclic group, an $-SO_2-$ containing cyclic group or a carbonate-containing cyclic group (provided that structural units which fall under the definition of the structural unit (a1) are excluded).

When the component (A1) is used for forming a resist film, the lactone-containing cyclic group, the $-SO_2-$ containing cyclic group or the carbonate-containing cyclic group within the structural unit (a2) is effective in improving the adhesion between the resist film and the substrate. In addition, by virtue of containing the structural unit (a2), for example, the acid diffusion length is appropriately adjusted, the adhesion of the resist film to the substrate is enhanced, or the solubility during development is appropriately adjusted. As a result, the lithography properties are enhanced.

[0148]

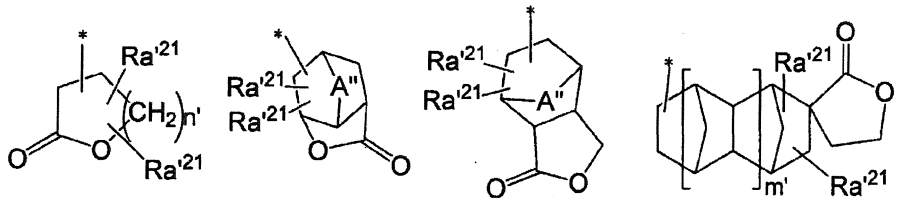
The term "lactone-containing cyclic group" refers to a cyclic group including a ring containing a -O-C(=O)- structure (lactone ring). The term "lactone ring" refers to a single ring containing a -O-C(O)- structure, and this ring is counted as the first ring. A lactone-containing cyclic group in which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

The lactone-containing cyclic group for the structural unit (a2) is not particularly

limited, and an arbitrary structural unit may be used. Specific examples include groups represented by general formulae (a2-r-1) to (a2-r-7) shown below.

[0149]

[Chemical Formula 33]

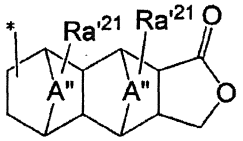


(a2-r-1)

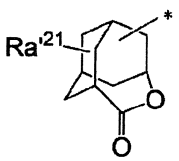
(a2-r-2)

(a2-r-3)

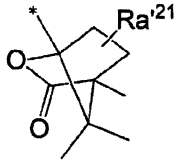
(a2-r-4)



(a2-r-5)



(a2-r-6)



(a2-r-7)

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

[0150]

In formulae (a2–r–1) to (a2–r–7), the alkyl group for Ra'^{21} is preferably an alkyl group of 1 to 6 carbon atoms. Further, the alkyl group is preferably a linear alkyl group or a branched alkyl group. Specific examples include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, a neopentyl group and a hexyl group.

Among these, a methyl group or ethyl group is preferable, and a methyl group is particularly desirable.

The alkoxy group for Ra'^{21} is preferably an alkoxy group of 1 to 6 carbon atoms.

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

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

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

[0151]

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

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

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

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

been removed from a monocycloalkane or a polycycloalkane such as a bicycloalkane, tricycloalkane or tetracycloalkane which may or may not be substituted with a fluorine atom or a fluorinated alkyl group. Specific examples include groups in which one or more hydrogen atoms have been removed from a monocycloalkane such as cyclopentane or cyclohexane; and groups in which one or more hydrogen atoms have been removed from a polycycloalkane such as adamantane, norbornane, isobornane, tricyclodecane or tetracyclododecane.

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

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

The $-SO_2-$ containing cyclic group for R" is the same as defined for the $-SO_2-$ containing cyclic group described later. Specific examples of the $-SO_2-$ containing cyclic group include groups represented by general formulae (a5–r–1) to (a5–r–4).

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

[0152]

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

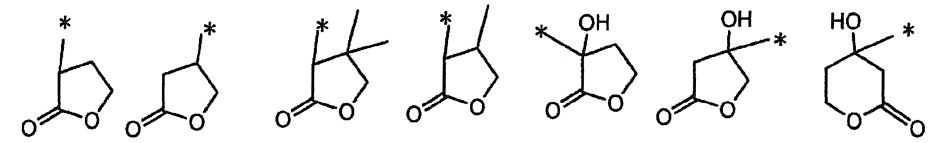
to the terminal of the alkylene group or present between the carbon atoms of the alkylene group. Specific examples of such alkylene groups include -O-CH_2-, -CH_2-O-CH_2-, -S-CH_2- and -CH_2-S-CH_2-. As A", an alkylene group of 1 to 5 carbon atoms or -O- is preferable, more preferably an alkylene group of 1 to 5 carbon atoms, and most preferably a methylene group.

[0153]

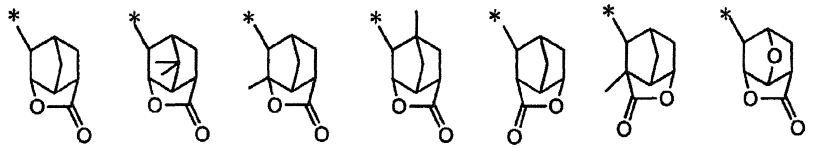
Specific examples of the groups represented by the aforementioned general formulae (a2-r-1) to (a2-r-7) are shown below.

[0154]

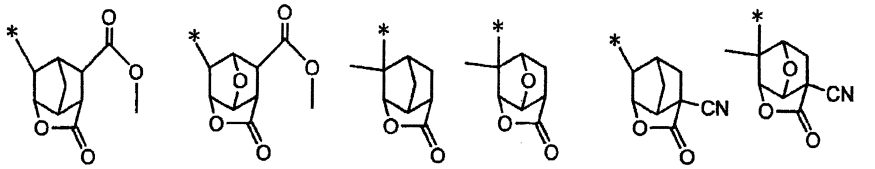
[Chemical Formula 34]



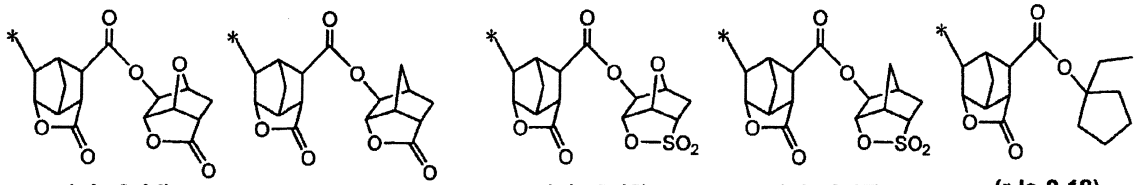
(r-lc-1-1) (r-lc-1-2) (r-lc-1-3) (r-lc-1-4) (r-lc-1-5) (r-lc-1-6) (r-lc-1-7)



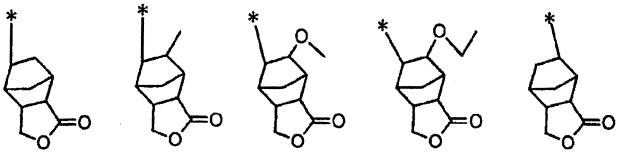
(r-lc-2-1) (r-lc-2-2) (r-lc-2-3) (r-lc-2-4) (r-lc-2-5) (r-lc-2-6) (r-lc-2-7)



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



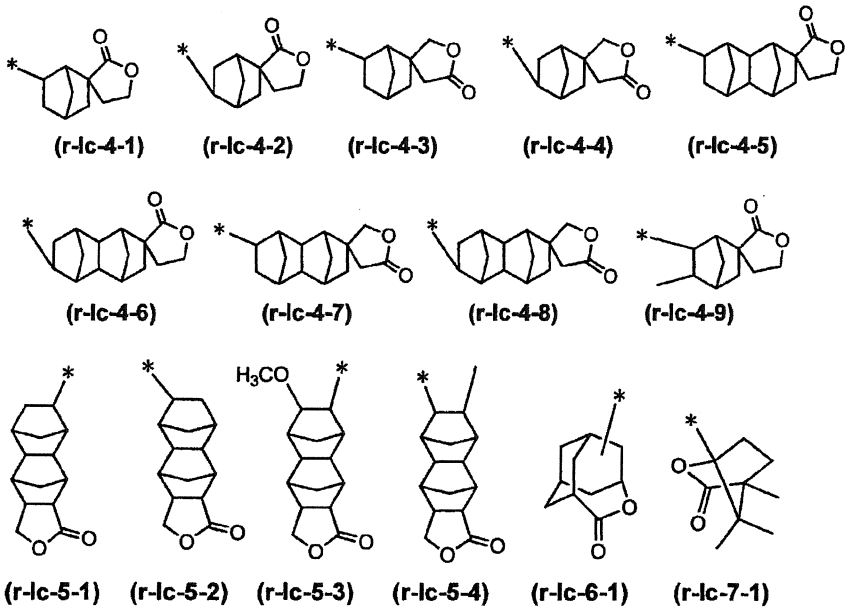
(r-lc-2-14) (r-lc-2-15) (r-lc-2-16) (r-lc-2-17) (r-lc-2-18)



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

[0155]

[Chemical Formula 35]



[0156]

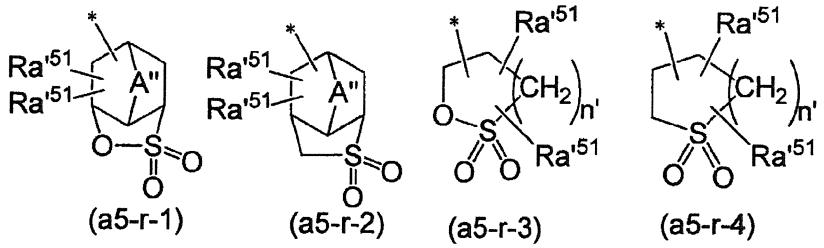
An "$-SO_2-$ containing cyclic group" refers to a cyclic group having a ring containing $-SO_2-$ within the ring structure thereof, i.e., a cyclic group in which the sulfur atom (S) within $-SO_2-$ forms part of the ring skeleton of the cyclic group. The ring containing $-SO_2-$ within the ring skeleton thereof is counted as the first ring. A cyclic group in which the only ring structure is the ring that contains $-SO_2-$ in the ring skeleton thereof is referred to as a monocyclic group, and a group containing other ring structures is described as a polycyclic group regardless of the structure of the other rings. The $-SO_2-$ containing cyclic group may be either a monocyclic group or a polycyclic group.

As the $-SO_2-$ containing cyclic group, a cyclic group containing $-O-SO_2-$ within the ring skeleton thereof, i.e., a cyclic group containing a sultone ring in which -O-S- within the $-O-SO_2-$ group forms part of the ring skeleton thereof is particularly desirable.

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

[0157]

[Chemical Formula 36]



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

[0158]

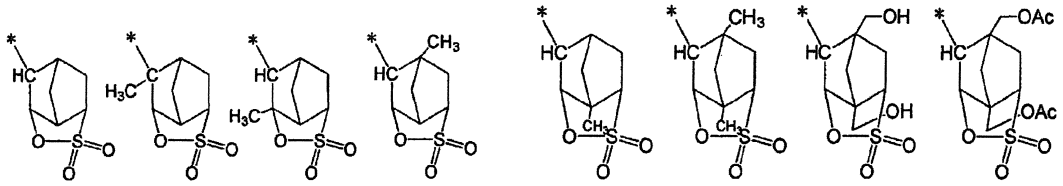
In general formulae (a5-r-1) and (a5-r-2), A" is the same as defined for A" in general formulae (a2–r–2), (a2–r–3) and (a2–r–5).

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

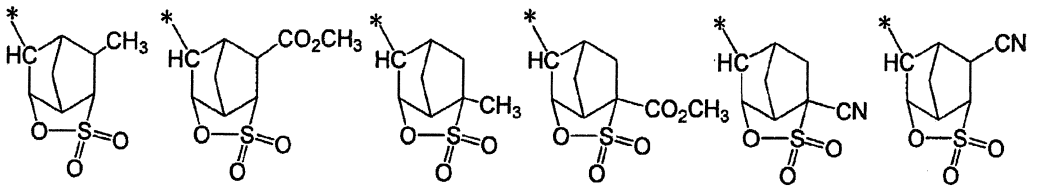
Specific examples of the groups represented by the aforementioned general formulae (a5-r-1) to (a5-r-4) are shown below. In the formulae shown below, "Ac" represents an acetyl group.

[0159]

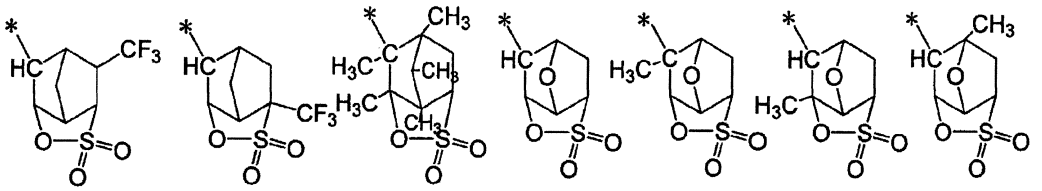
[Chemical Formula 37]



(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)



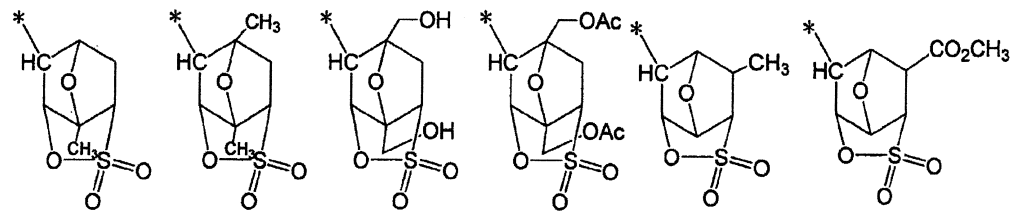
(r-sl-1-9) (r-sl-1-10) (r-sl-1-11) (r-sl-1-12) (r-sl-1-13) (r-sl-1-14)



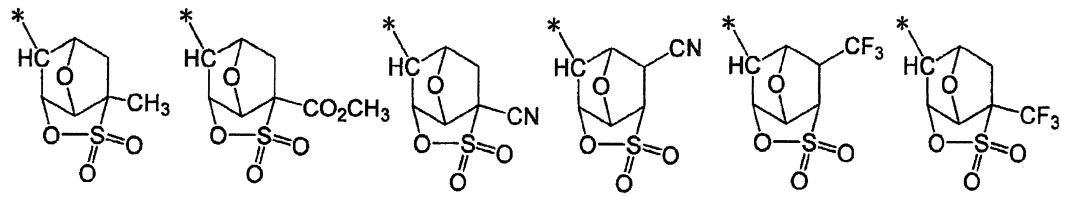
(r-sl-1-15) (r-sl-1-16) (r-sl-1-17) (r-sl-1-18) (r-sl-1-19) (r-sl-1-20) (r-sl-1-21)

[0160]

[Chemical Formula 38]



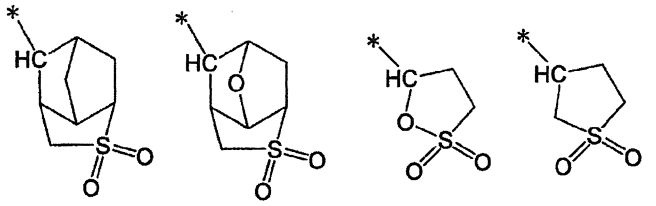
(r-sl-1-22) (r-sl-1-23) (r-sl-1-24) (r-sl-1-25) (r-sl-1-26) (r-sl-1-27)



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

[0161]

[Chemical Formula 39]



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

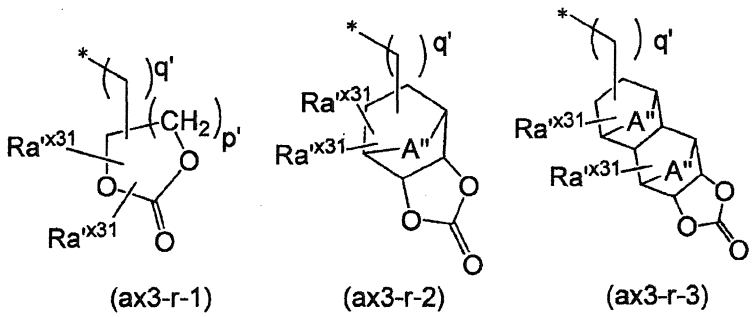
[0162]

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

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

[0163]

[Chemical Formula 40]



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

In the formulae, each Ra'^{x31} independently represents a hydrogen atom, an alkyl group,

an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxy group, -COOR", -OC(=O)R", a hydroxyalkyl group or a cyano group; R" represents a hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group or an $-SO_2-$ containing cyclic group; A" represents an oxygen atom, a sulfur atom or an alkylene group of 1 to 5 carbon atoms which may contain an oxygen atom or a sulfur atom; p' represents an integer of 0 to 3; and q' represents 0 or 1.

[0164]

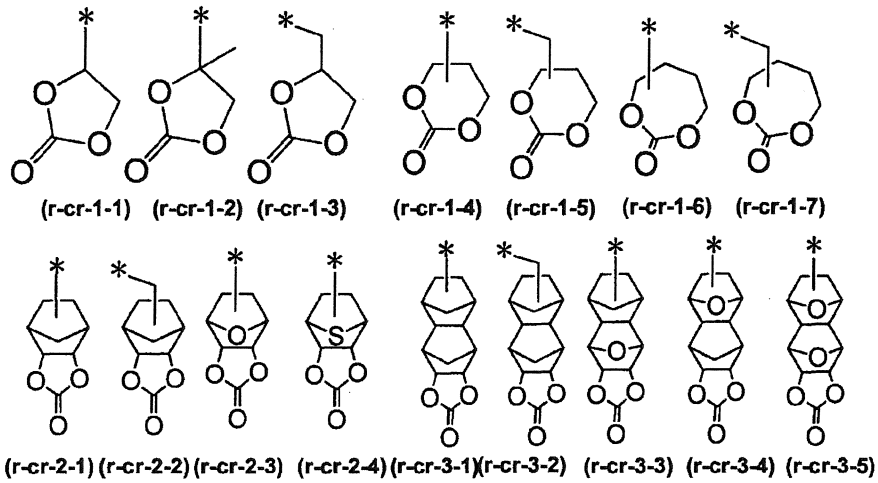
In general formulae (ax3–r–2) and (ax3–r–3), A" is the same as defined for A" in general formulae (a2–r–2), (a2–r–3) and (a2–r–5).

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

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

[0165]

[Chemical Formula 41]



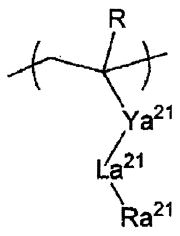
[0166]

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

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

[0167]

[Chemical Formula 42]



・・・ (a 2 − 1)

In the formula, R represents a hydrogen atom, an alkyl group of 1 to 5 carbon atoms or a halogenated alkyl group of 1 to 5 carbon atoms; 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; provided that, when La^{21} represents -O-, Ya^{21} does not represents -CO-; and Ra^{21} represents a lactone-containing cyclic group, a carbonate-containing cyclic group or an $–SO_2–$ containing cyclic group.

[0168]

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

[0169]

In the formula (a2–1), the divalent linking group for Ya^{21} is not particularly limited, and preferable examples thereof include a divalent hydrocarbon group which may have a substituent and a divalent linking group containing a hetero atom. The divalent hydrocarbon group which may have a substituent and the divalent linking group containing a hetero atom for Ya^{21} are the same as defined for the divalent hydrocarbon group which may have a substituent and the divalent linking group containing a hetero atom described above in relation to Ya^{x1} in general formula (a10-1).

Ya^{21} preferably represents an ester bond [-C(=O)-O-], an ether bond (-O-), a linear or branched alkylene group, a combination of these, or a single bond.

[0170]

In the formula (a2-1), Ra^{21} represents a lactone-containing cyclic group, an $-SO_2-$ containing cyclic group or a carbonate-containing cyclic group.

Preferable examples of the lactone-containing cyclic group, the $-SO_2-$ containing cyclic group and the carbonate-containing cyclic group for Ra^{21} include groups represented by general formulae (a2–r–1) to (a2–r–7), groups represented by general formulae (a5–r–1) to (a5–r–4) and groups represented by general formulae (ax3–r–1) to (ax3–r–3).

Among the above examples, a lactone-containing cyclic group or a $-SO_2-$ containing cyclic group is preferable, and a group represented by general formula (a2–r–1), (a2–r–2), (a2–r–6) or (a5–r–1) is more preferable. Specifically, a group represented by any of chemical formulae (r–lc–1–1) to (r–lc–1–7), (r–lc–2–1) to (r–lc–2–18), (r–lc–6–1), (r–sl–1–1) and (r–sl–1–18) is still more preferable.

[0171]

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

When the component (A1) contains the structural unit (a2), the amount of the structural unit (a2) based on the combined total (100 mol%) of all structural units constituting the component (A1) is preferably 0 to 50 mol%, more preferably 5 to 45 mol%, still more preferably 10 to 40 mol%, and most preferably 10 to 30 mol%.

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

[0172]

<<Structural unit (a3)>>

The component (A1) may have, in addition to the structural unit (a1), a structural unit (a3) containing a polar group-containing aliphatic hydrocarbon group (provided that the structural units that fall under the definition of structural units (a1) and (a2) are excluded). By virtue of including the structural unit (a3), various advantages may be obtained, such as appropriate adjustment of acid diffusion length, enhancement of adhesion of a resist film to a substrate, appropriate adjustment of solubility of the resist during developing, and improvement in etching resistance, which may lead to improvement in lithography properties.

[0173]

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

Examples of the aliphatic hydrocarbon group include linear or branched hydrocarbon groups (preferably alkylene groups) of 1 to 10 carbon atoms, and cyclic aliphatic hydrocarbon groups (cyclic groups). These cyclic groups can be selected appropriately from the multitude of groups that have been proposed for the resins of resist compositions designed for use with ArF excimer lasers. The cyclic group is preferably a polycyclic group, more preferably a polycyclic group of 7 to 30 carbon atoms.

Of the various possibilities, structural units derived from an acrylate ester that include an aliphatic polycyclic group that contains a hydroxyl group, cyano group, carboxyl group or a hydroxyalkyl group in which part of the hydrogen atoms of the alkyl group have been substituted with fluorine atoms are particularly desirable. Examples of the polycyclic group include groups in which two or more hydrogen atoms have been removed from a bicycloalkane, tricycloalkane, tetracycloalkane or the like. Specific examples include groups in which two or more hydrogen atoms have been removed from a polycycloalkane such as adamantane, norbornane, isobornane, tricyclodecane or tetracyclododecane. Of these polycyclic groups, groups in which two or more hydrogen atoms have been removed from adamantane, norbornane or tetracyclododecane are preferred industrially.

[0174]

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

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

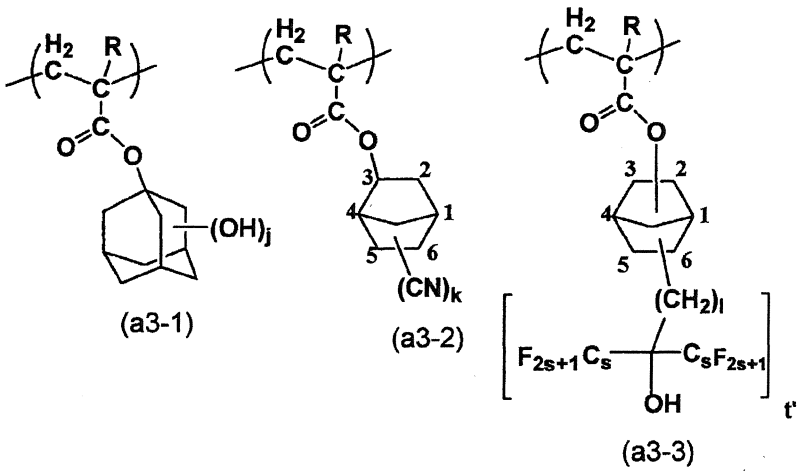
hydrocarbon group.

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

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

[0175]

[Chemical Formula 43]



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

[0176]

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

3rd position of the adamantyl group.

j is preferably 1, and it is particularly desirable that the hydroxyl group be bonded to the 3rd position of the adamantyl group.

[0177]

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

[0178]

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

[0179]

As the structural unit (a3) contained in the component (A1), 1 type of structural unit may be used, or 2 or more types may be used.

When the component (A1) contains the structural unit (a3), the amount of the structural unit (a3) within the component (A1) based on the combined total of all structural units constituting the component (A1) is preferably 1 to 40 mol%, more preferably 2 to 30 mol%, still more preferably 5 to 25 mol%, and still more preferably 5 to 20 mol%.

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

[0180]

<<Structural unit (st)>>

The component (A1) may have, in addition to the structural unit (a1), a structural unit (st) derived from styrene or a derivative thereof. The term “styrene” is a concept including styrene and compounds in which the hydrogen atom at the α-position of styrene is substituted with a substituent such as an alkyl group or a halogenated alkyl group. Examples of the alkyl group as the substituent include an alkyl group having 1 to 5 carbon atoms. Examples of the halogenated alkyl group as the substituent include a halogenated alkyl group having 1 to 5 carbon atoms.

Examples of the "styrene derivative" include styrene which has a substituent other than a hydroxy group bonded to the benzene ring and may have the hydrogen atom on the α-position substituted with a substituent.

Here, the α-position (carbon atom on the α-position) refers to the carbon atom having the benzene ring bonded thereto, unless specified otherwise.

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

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

When the component (A1) includes the structural unit (st), the amount of the structural unit (st) based on the combined total of all structural units constituting the component (A1) (100 mol%) is preferably 1 to 50 mol%, and more preferably 3 to 40 mol%.

[0181]

<<Other structural units>>

The component (A1) may be further include a structural unit other than the structural units (a1), (a10), (a2), (a3) and (st).

Examples of other structural units include a structural unit (a9) represented by general formula (a9-1) described later, a structural unit derived from styrene (provided that the structural units that fall under the definition of structural unit (a10) are excluded).

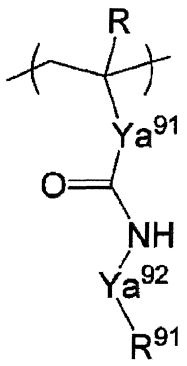
[0182]

(Structural unit (a9)):

The structural unit (a9) is represented by general formula (a9-1) shown below.

[0183]

[Chemical Formula 44]



・・・ (a 9 − 1)

In the formula, R represents a hydrogen atom, an alkyl group of 1 to 5 carbon atoms or a halogenated alkyl group of 1 to 5 carbon atoms; Ya^{91} represents a single bond or a divalent linking group; Ya^{92} represents a divalent linking group; and R^{91} represents a hydrocarbon group which may have a substituent.

[0184]

In the general formula (a9-1), R is the same as defined above.

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

[0185]

In general formula (a9–1), the divalent linking group for Ya^{91} is the same as defined for the divalent linking group for Ya^{x1} in the aforementioned general formula (a10-1). Among these, Ya^{91} is preferably a single bond.

[0186]

In general formula (a9–1), the divalent linking group for Ya^{92} is the same as defined for the divalent linking group for Ya^{x1} in the aforementioned general formula (a10-1).

With respect to the divalent linking group for Ya^{92}, as the divalent hydrocarbon group which may have a substituent, a linear or branched aliphatic hydrocarbon group is preferable.

In the case where Ya^{92} represents a divalent linking group containing a hetero atom, examples of the linking group include –O–, –C(=O)–O–, –C(=O)–, –O–C(=O)–O–, –C(=O)–NH–, –NH–, –NH–C(=NH)– (wherein H may be substituted with a substituent such as an alkyl group or an acyl group), –S–, $-S(=O)_2-$, $-S(=O)_2-O-$, C(=S), a group represented by general formula $-Y^{21}-O-Y^{22}-$, $-Y^{21}-O-$, $-Y^{21}-C(=O)-O-$, $-C(=O)-O--Y^{21}$, $-[Y^{21}-C(=O)-O]_{m'}-Y^{22}-$ or $-Y^{21}-O-C(=O)-Y^{22}-$ [in the formulae, Y^{21} and Y^{22} each independently represents a divalent hydrocarbon group which may have a substituent, and O represents an oxygen atom; and m' represents an integer of 0 to 3. Among these examples, –C(=O)– and –C(=S)– are preferable.

[0187]

In general formula (a9–1), examples of the hydrocarbon group for R^{91} include an alkyl group, a monovalent alicyclic hydrocarbon group, an aryl group and an aralkyl group.

The alkyl group for R^{91} preferably has 1 to 8 carbon atoms, more preferably 1 to

6 carbon atoms, and still more preferably 1 to 4 carbon atoms. The alkyl group may be linear or branched. Specific examples of preferable alkyl groups include a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group and an octyl group.

The monovalent alicyclic hydrocarbon group for R^{91} preferably has 3 to 20 carbon atoms, and more preferably 3 to 12 carbon atoms. The monovalent alicyclic hydrocarbon group may be polycyclic or monocyclic. As the monocyclic alicyclic hydrocarbon group, a group in which one or more hydrogen atoms have been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclobutane, cyclopentane and cyclohexane. As the polycyclic alicyclic hydrocarbon group, a group in which one or more hydrogen atoms have been removed from a polycycloalkane is preferable, and the polycyclic group preferably has 7 to 12 carbon atoms. Examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane and tetracyclododecane.

The aryl group for R^{91} preferably has 6 to 18 carbon atoms, and more preferably 6 to 10 carbon atoms. Specifically, a phenyl group is particularly desirable.

As the aralkyl group for R^{91}, an aralkyl group in which an alkylene group having 1 to 8 carbon atoms has been bonded to the aforementioned "aryl group for R^{91}" is preferable, an aralkyl group in which an alkylene group of 1 to 6 carbon atoms has been bonded to the aforementioned "aryl group for R^{91}" is more preferable, and an aralkyl group in which an alkylene group having 1 to 4 carbon atoms has been bonded to the aforementioned "aryl group for R^{91}" is most preferable.

The hydrocarbon group for R^{91} preferably has part or all of the hydrogen atoms within the hydrocarbon group substituted with fluorine, and the hydrocarbon group more preferably has 30 to 100% of the hydrogen atoms substituted with fluorine. Among these, a perfluoroalkyl group in which all of the hydrogen atoms within the alkyl group have

been substituted with fluorine atoms is particularly desirable.

[0188]

The hydrocarbon group for R^{91} may have a substituent. Examples of the substituent include a halogen atom, an oxo group (=O), a hydroxy group (–OH), an amino group ($–NH_2$) and $–SO_2–NH_2$. Further, part of the carbon atoms constituting the hydrocarbon group may be substituted with a substituent containing a hetero atom. Examples of the substituent containing a hetero atom include –O–, –NH–, –N=, –C(=O)–O–, –S–, $–S(=O)_2–$ and $–S(=O)_2–O–$.

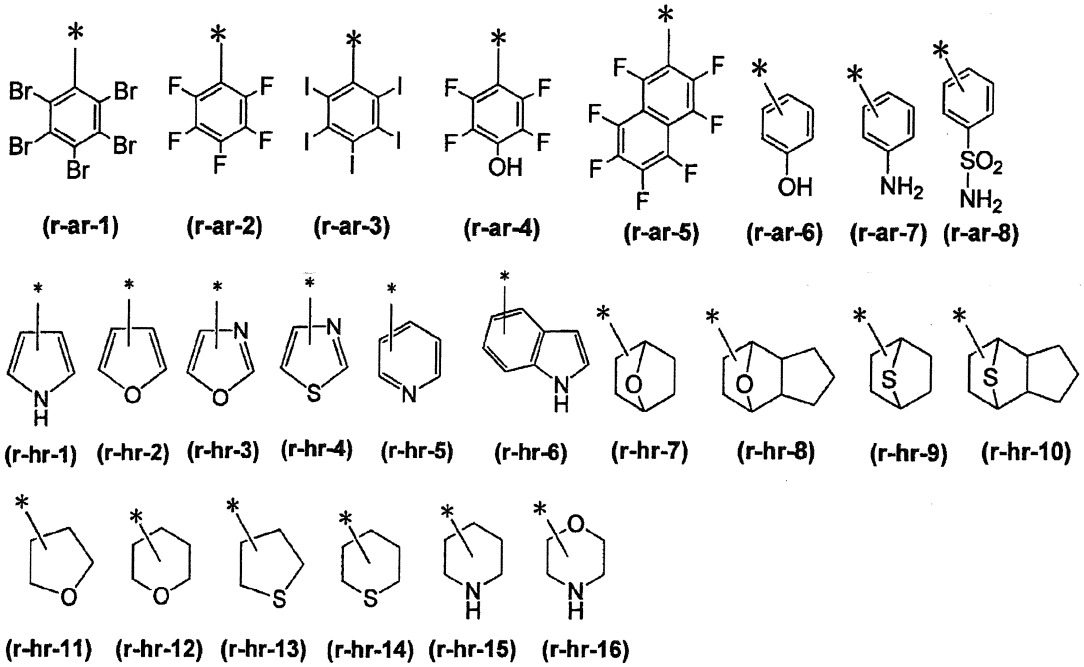
As the hydrocarbon group for R^{91}, examples of the hydrocarbon group having a substituent include lactone-containing cyclic groups represented by the aforementioned general formulae (a2–r–1) to (a2–r–7).

[0189]

Further, as R^{91}, examples of the hydrocarbon group having a substituent include $–SO_2–$ containing cyclic groups represented by general formulae (a5–r–1) to (a5–r–4); and substituted aryl groups and monocyclic heterocyclic groups represented by chemical formulae shown below.

[0190]

[Chemical Formula 45]

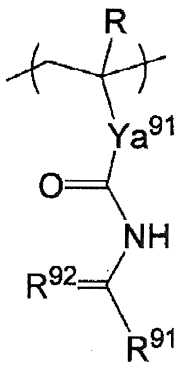


[0191]

As the structural unit (a9), a structural unit represented by general formula (a9-1-1) shown below is preferable.

[0192]

[Chemical Formula 46]



・・・ (a 9 − 1 − 1)

In the formula, R is the same as defined above; Ya^{91} represents a single bond or a divalent linking group; R^{91} represents a hydrocarbon group optionally having a substituent; and Ya^{92} represents an oxygen atom or a sulfur atom.

[0193]

In general formula (a9–1–1), Ya^{91}, R^{91} and R are the same as defined above.

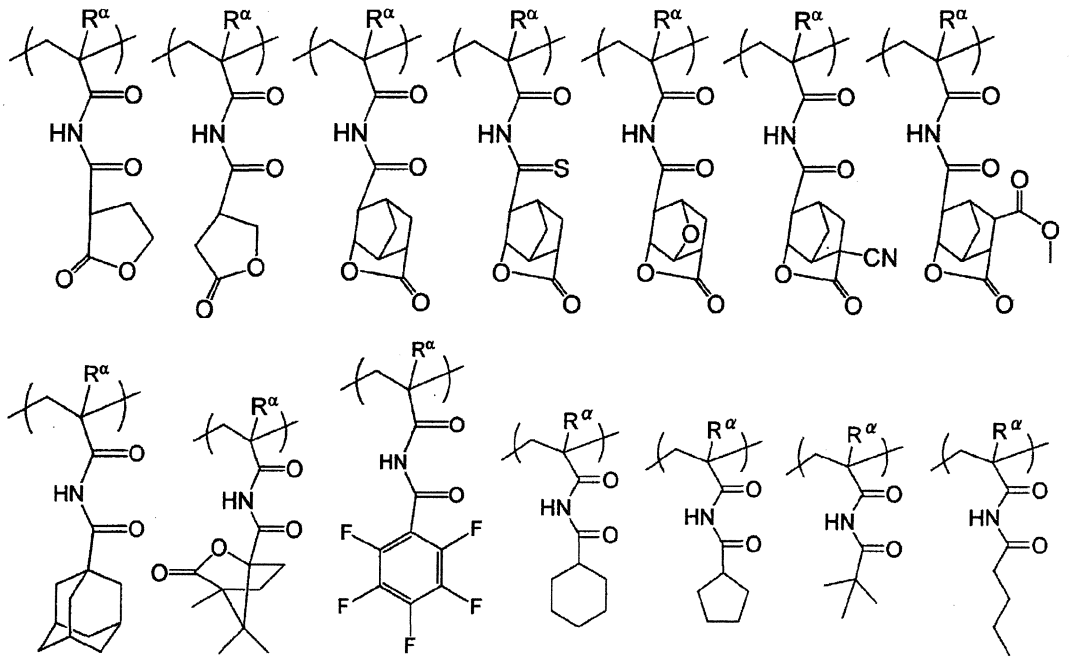
R^{92} represents an oxygen atom or a sulfur atom.

[0194]

Specific examples of structural units represented by general formula (a9–1) or (a9–1–1) are shown below. In the following formulae, R^{α} represents a hydrogen atom, a methyl group or a trifluoromethyl group.

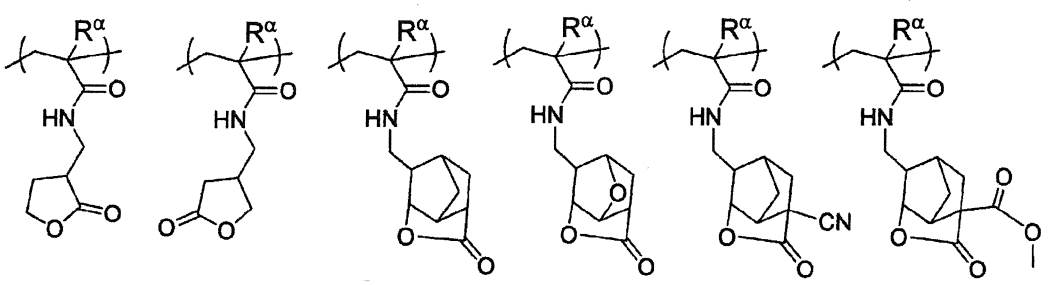
[0195]

[Chemical Formula 47]



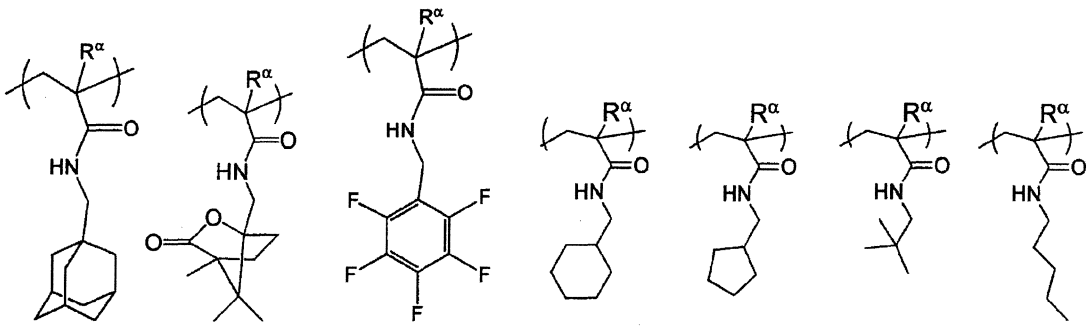
[0196]

[Chemical Formula 48]



[0197]

[Chemical Formula 49]



[0198]

As the structural unit (a9) contained in the component (A1), 1 kind of structural unit may be used, or 2 or more kinds may be used.

When the component (A1) contains the structural unit (a9), the amount of the structural unit (a9) based on the combined total (100 mol%) of all structural units constituting the component (A1) is preferably 1 to 40 mol%, more preferably 3 to 30 mol%, still more preferably 5 to 25 mol%, and most preferably 10 to 20 mol%.

When the amount of the structural unit (a9) is at least as large as the lower limit of the above-mentioned preferable range, for example, the acid diffusion length is appropriately adjusted, the adhesion of the resist film to the substrate is enhanced, the solubility during development is appropriately adjusted, or etching resistance is improved.

On the other hand, when the amount of the structural unit (a9) is no more than the upper limit of the above-mentioned preferable range, a good balance may be achieved with the other structural units, and various lithography properties may be improved.

[0199]

Structural unit (a4):

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

When the component (A1) includes the structural unit (a4), dry etching resistance of the resist pattern to be formed is improved. Further, the hydrophobicity of the component (A) is further improved. Increase in the hydrophobicity contributes to improvement in terms of resolution, shape of the resist pattern and the like, particularly in a solvent developing process.

An "acid non-dissociable, aliphatic cyclic group" in the structural unit (a4) refers to a cyclic group which is not dissociated by the action of the acid (e.g., acid generated from the component (B) described later) upon exposure, and remains in the structural unit.

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

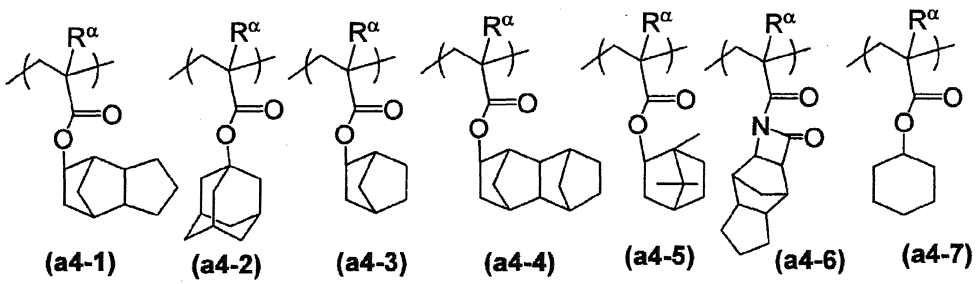
In consideration of industrial availability and the like, at least one polycyclic group selected from amongst a tricyclodecyl group, adamantyl group, tetracyclododecyl group, isobornyl group, and norbornyl group is particularly desirable. These polycyclic

groups may be substituted with a linear or branched alkyl group of 1 to 5 carbon atoms.

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

[0200]

[Chemical Formula 50]



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

[0201]

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

When the component (A1) includes the structural unit (a4), the amount of the structural unit (a4) based on the combined total of all structural units constituting the component (A1) is preferably 1 to 30 mol%, and more preferably 3 to 20 mol%.

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

[0202]

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

The component (A1) preferably includes a polymeric compound (A1-1) having a structural unit (a1) (hereafter, sometimes referred to as "component (A1-1)").

Preferable examples of the component (A1−1) include a polymeric compound having a repeating structure of the structural units (a1) and (a10); and a polymeric compound having a repeating structure of the structural units (a1) and (st).

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

[0203]

The component (A1) may be produced, for example, by dissolving the monomers corresponding with each of the structural units in a polymerization solvent, followed by addition of a radical polymerization initiator such as azobisisobutyronitrile (AIBN) or dimethyl-2,2'-azobisisoutyrate (e.g., V-601). Alternatively, the component (A1) may be prepared by dissolving a monomer from which the structural unit (a1) is derived, and a monomer from which the structural unit other than the structural unit (a1) is derived in a polymerization solvent, polymerizing the dissolved monomers using the radical polymerization initiator described above, followed by performing a deprotection reaction.

In the polymerization, a chain transfer agent such as $HS–CH_2–CH_2–CH_2–C(CF_3)_2–OH$ may be used to introduce a $–C(CF_3)_2–OH$ group at the terminal(s) of the polymer. Such a copolymer having introduced a hydroxyalkyl group in which some of the hydrogen atoms of the alkyl group are substituted with fluorine atoms is effective in reducing developing defects and LER (line edge roughness:

unevenness of the side walls of a line pattern).

[0204]

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

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

The dispersity (Mw/Mn) of the component (A1) is not particularly limited, but is preferably 1.0 to 4.0, more preferably 1.0 to 3.0, and most preferably 1.1 to 2.0. Here, Mn is the number average molecular weight.

[0205]

- Component (A2)

In the resist composition of the present embodiment, as the component (A), "a base component which exhibits changed solubility in a developing solution under action of acid" other than the component (A1) (hereafter, referred to as "component (A2)") may be used in combination.

As the component (A2), there is no particular limitation, and any of the multitude of conventional base resins used within chemically amplified resist compositions may be arbitrarily selected for use.

As the component (A2), one kind of a polymer or a low molecular weight compound may be used, or a combination of two or more kinds may be used.

[0206]

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

[0207]

<Component (Z)>

In the resist composition of the present embodiment, the component (Z) is a dissolution inhibitor which suppresses dissolution in a developing solvent.

The component (Z) includes a compound (Z1) having a weight average molecular weight of 3,000 or less and containing a phenolic hydroxy group or a carboxy group in a molecule thereof (hereafter, sometimes referred to as "component (Z1)"), and a compound (Z2) having a weight average molecular weight of 3,000 or less and being represented by general formula (z2) shown below (hereafter, sometimes referred to as "component (Z2)").

[0208]

- Component (Z1)

The component (Z1) is not particularly limited, as long as it is a compound having a weight average molecular weight of 3,000 or less and containing a phenolic hydroxy group or a carboxy group in a molecule thereof.

The weight average molecular weight of the component (Z1) is preferably 150 to 3,000, more preferably 200 to 2,500, and still more preferably 250 to 2,000.

When the weight average molecular weight of the component (Z1) is at least as

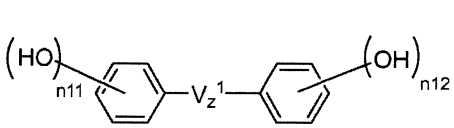
large as the lower limit of the above-mentioned preferable range, the adhesion to a substrate may be improved.

[0209]

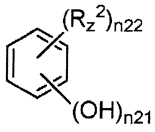
As the component (Z1), a compound represented by general formula (z1-1) shown below is preferable.

[0210]

[Chemical Formula 51]



... (z1-1)



... (z1-2)

In formula (z1-1), V_z^1 represents a divalent linking group; in formula (z1-2), R_z^{10} represents a polycyclic alicyclic hydrocarbon group which may have a substituent or an aromatic hydrocarbon group which may have a substituent; n11 and n12 each independently represents an integer of 1 to 3; in formula (z2-1), Rz^2 represents a hydrocarbon group; n21 represents 1 or 2; n22 represents an integer of 2 to 5; provided that $n21+n22 \leqq 6$.

[0211]

In formula (z1-1), the divalent linking group for V_z^1 is the same as defined for the divalent linking group represented by Ya^{x1} in the aforementioned general formula (a10-1). Further examples of the divalent linking group for V_z^1 include a group in which part of the hydrogen atoms constituting the linear or branched aliphatic hydrocarbon group for Ya^{x1} in general formula (a10-1) has been substituted with an aromatic hydrocarbon group.

[0212]

Examples of the linear or branched aliphatic hydrocarbon group within the

"group in which part of the hydrogen atoms constituting the linear or branched aliphatic hydrocarbon group has been substituted with an aromatic hydrocarbon group" include a methylene group [$-CH_2-$], an ethylene group [$-(CH_2)_2-$], and 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 $-C(CH_2CH_3)_2-$.

Examples of the aromatic hydrocarbon group within the "group in which part of the hydrogen atoms constituting the linear or branched aliphatic hydrocarbon group has been substituted with an aromatic hydrocarbon group" include a group in which 1 hydrogen atom has been removed from benzene, fluorene, naphthalene, anthracene, phenanthrene or biphenyl.

The aromatic hydrocarbon group within the "group in which part of the hydrogen atoms constituting the linear or branched aliphatic hydrocarbon group has been substituted with an aromatic hydrocarbon group" may have a substituent. Examples of the substituent include an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxy group and an arylalkyl group.

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

As the alkoxy group, the halogen atom and the halogenated alkyl group for the substituent, the same groups as the aforementioned substituent groups for substituting a hydrogen atom within the cyclic aliphatic hydrocarbon group as the divalent linking group for Ya^{x1} in the aforementioned general formula (a10-1) may be mentioned.

Examples of the arylalkyl group as the substituent include a benzyl group, a phenethyl group, a phenyl-t-butyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, and a 2-naphthylethyl group. The arylalkyl group may

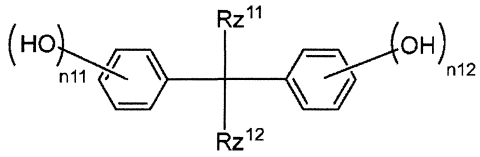
have a substituent, such as an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxy group, or an arylalkyl group.

[0213]

As the compound represented by formula (z1−1), a compound represented by the following general formula (z1−1−1) is preferable.

[0214]

[Chemical Formula 52]



・・・ (z1−1−1)

In the formula, R_z^{11} and R_z^{12} each independently represents a hydrogen atom or a hydrocarbon group which may have a substituent; R_z^{11} and R_z^{12} may be mutually bonded to form a ring; and n11 and n12 each independently represents an integer of 1 to 3.

[0215]

In formula (z1−1−1), examples of the hydrocarbon group for R_z^{11} and R_z^{12} include a linear or branched alkyl group, and an aromatic hydrocarbon group which may have a substituent.

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

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

isobutyl group, a tert-butyl group, an isopentyl group, a neopentyl group a 1,1-diethylpropyl group and a 2,2-dimethylbutyl group. Among these, an isopropyl group is preferable.

[0216]

Examples of the aromatic hydrocarbon group for R_z^{11} and R_z^{12} include a group in which one hydrogen atom has been removed from an aromatic hydrocarbon ring such as benzene, fluorene, naphthalene, anthracene, phenanthrene or biphenyl.

The aromatic hydrocarbon group for R_z^{11} and R_z^{12} may have a substituent. Examples of the substituent include the same substituents as those described above for the aromatic hydrocarbon group within the "group in which part of the hydrogen atoms constituting the linear or branched aliphatic hydrocarbon group has been substituted with an aromatic hydrocarbon group".

[0217]

In formula (z1–1–1), R_z^{11} and R_z^{12} may be mutually bonded to form a ring. Examples of the formed ring include aliphatic rings, such as a cyclopentane ring, a cyclohexane ring and a cycloheptane ring.

[0218]

In formula (z1–1–1), R_z^{11} and R_z^{12} is preferably a linear or branched alkyl group having 1 to 5 carbon atoms, ∅ or an aromatic hydrocarbon group which may have a substituent, or R_z^{11} and R_z^{12} are preferably mutually bonded to form an aliphatic ring, R_z^{11} and R_z^{12} is more preferably a methyl group, a phenyl group or a 4–(4–hydroxyphenyl–t–butyl)phenyl group, or R_z^{11} and R_z^{12} are more preferably mutually bonded to form a cyclohexane ring.

[0219]

In formula (z1–2), the hydrocarbon group for Rz^2 is the same as defined for the

hydrocarbon group represented by R_z^{11} and R_z^{12} in the aforementioned formula (z1−1−1). Among these examples, as Rz^2, an aromatic hydrocarbon group is preferable, a phenyl group or a benzyl group is more preferable, and a phenyl group is still more preferable.

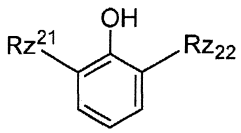
In formula (z1−2), n21 represents 1 or 2, and is preferably 1. n22 represents an integer of 2 to 5, preferably 2 or 3, and more preferably 2.

[0220]

As the compound represented by formula (z1−2), a compound represented by the following general formula (z1−2−1) is preferable.

[0221]

[Chemical Formula 53]



In the formula, Rz^{21} and Rz^{22} each independently represents an aromatic hydrocarbon group.

[0222]

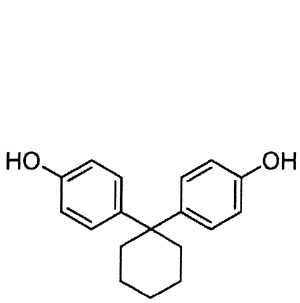
In formula (z1−2-1), the hydrocarbon group for Rz^2 is the same as defined for the hydrocarbon group represented by R_z^{11} and R_z^{12} in the aforementioned formula (z1−1−1). Among these examples, as Rz^2, a phenyl group or a benzyl group is preferable, and a phenyl group is more preferable.

[0223]

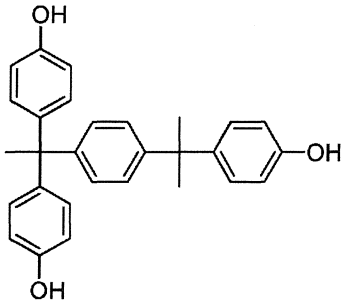
Specific examples of the component (Z1) are shown below.

[0224]

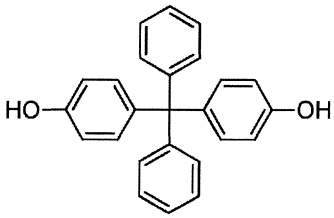
[Chemical Formula 54]



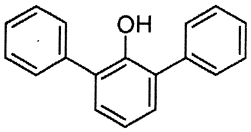
(Z1)-1



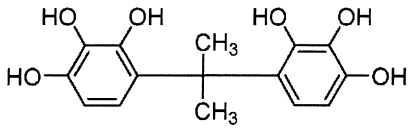
(Z1)-2



(Z1)-3



(Z1)-4



(Z1)-5

[0225]

Other examples of the component (Z1) include compounds described in paragraph [0158] of Japanese Unexamined Patent Application, First Publication No. 2008-122932, and compounds described in paragraphs [0036]-[0055] of Japanese Unexamined Patent Application, First Publication No. Hei 10-097075.

[0226]

In the resist composition, as the component (Z1), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

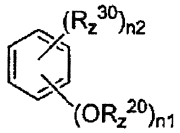
[0227]

- Component (Z2)

The component (Z2) is a compound having a weight average molecular weight of 3,000 or less and being represented by general formula (z2) shown below.

[0228]

[Chemical Formula 55]



. . . (z 2)

In the formula, R_z^{20} represents an acid dissociable group; R_z^{30} represents a hydrogen atom or an organic group; n1 represents an integer of 1 to 6, and n2 represents an integer of 0 to 5, provided that n1+n2=6.

[0229]

The weight average molecular weight of the component (Z2) is preferably 150 to 3,000, more preferably 200 to 2,500, and still more preferably 250 to 2,000.

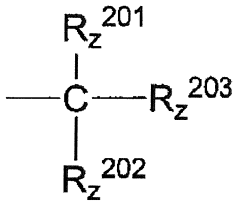
When the weight average molecular weight of the component (Z2) is within the above-mentioned preferable range, the film thickness loss of a resist film formed of a resin composition containing the component (Z2) may be reduced.

[0230]

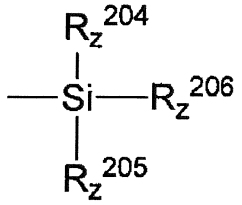
In formula (z2), examples of the acid dissociable group represented by R_z^{20} include groups represented by general formulae (z2–r–1) to (z2–r–4) shown below.

[0231]

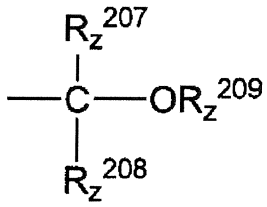
[Chemical Formula 56]



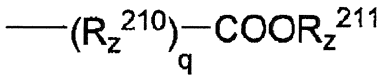
・・・ (z 2－r－1)



・・・ (z 2－r－2)



・・・ (z 2－r－3)



・・・ (z 2－r－4)

In the formula, R_z^{201} to R_z^{206} each independently represents a linear or branched alkyl group, a linear or branched alkoxy group, a linear or branched alkoxyalkyl group, a linear or branched alkenyl group, or an aryl group, wherein these groups may contain a carbonyl group in a chain thereof; R_z^{201} and R_z^{202}, or R_z^{204} and R_z^{205} may be mutually bonded to form a ring; R_z^{207} and R_z^{208} each independently represents a hydrogen atom, a linear or branched alkyl group, a linear or branched alkoxy group, a linear or branched alkoxyalkyl group, a linear or branched alkenyl group, or an aryl group.

R_z^{209} represents a linear or branched alkyl group, a linear or branched alkoxyalkyl group, a linear or branched alkenyl group, or an aryl group, wherein these groups may contain a carbonyl group in a chain thereof; R_z^{209} and R_z^{208} may be mutually bonded to form a ring; R_z^{210} represents a divalent aliphatic group, a divalent alicyclic

group or a divalent aromatic group; R_z^{211} represents an acid dissociable group; and q represents 0 or 1.

[0232]

In formula (z2–r–1) and (z2–r–2), R_z^{201} to R_z^{206} each independently represents a linear or branched alkyl group, a linear or branched alkoxy group, a linear or branched alkoxyalkyl group, a linear or branched alkenyl group, or an aryl group, wherein these groups may contain a carbonyl group in a chain thereof.

Examples of the alkyl group for R_z^{201} to R_z^{206} include alkyl groups having 1 to 10 carbon atoms, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, a sec-butyl group, a tert-butyl group, a hexyl group, a cyclohexyl group, and an adamantyl group. Among these examples, a methyl group, an ethyl group, an isopropyl group or a tert-butyl group is preferable.

Examples of the alkoxy group for R_z^{201} to R_z^{206} include methoxy groups having 1 to 8 carbon atoms, such as a methoxy group, an ethoxy group, a propoxy group, an isopropoxy group, an n-butoxy group, a sec-butoxy group, a tert-butoxy group, a hexyloxy group, and a cyclohexyloxy group. Among these examples, a methoxy group, an ethoxy group, an isopropoxy group or a tert-butoxy group is preferable.

Examples of the alkoxyalkyl group for R_z^{201} to R_z^{206} include alkoxyalkyl groups having 2 to 20 carbon atoms, such as a methoxymethyl group, an ethoxypropyl group, a propoxyethyl group, and a tert-butoxyethyl group. Among these examples, a methoxymethyl group, a methoxyethyl group, an ethoxypropyl group, or a propoxyethyl group is preferable.

Preferable examples of the alkenyl group for R_z^{201} to R_z^{206} include alkenyl groups having 2 to 4 carbon atoms, such as a vinyl group, a propenyl group, an allyl group, and a butenyl group.

Preferable examples of the aryl group for R_z^{201} to R_z^{206} include aryl groups having 6 to 14 carbon atoms, such as a phenyl group, a xylyl group, a toluyl group, and a cumenyl group.

[0233]

In formula (z2–r–1) and (z2–r–2), R_z^{201} and R_z^{202}, or R_z^{204} and R_z^{205} may be mutually bonded to form a ring.

Examples of the ring formed by R_z^{201} and R_z^{202} being mutually bonded include a ring having 4 to 10 carbon atoms, such as a cyclohexylidene group, a cyclopentylidene group, a 3-oxocyclohexylidene group, and a 4-methylcyclohexylidene group.

Examples of the ring formed by R_z^{204} and R_z^{205} being mutually bonded include rings having 3 to 9 carbon atoms, such as a 1-silacyclohexylidene group, a 1-silacyclopentylidene group, a 3-oxo-1-silacyclopentylidene group, and 4-methyl-1-silacyclopentylidene group.

[0234]

In formula (z2–r–3), R_z^{207} and R_z^{208} each independently represents a hydrogen atom, a linear or branched alkyl group, a linear or branched alkoxy group, a linear or branched alkoxyalkyl group, a linear or branched alkenyl group, or an aryl group. R_z^{209} represents a linear or branched alkyl group, a linear or branched alkoxyalkyl group, a linear or branched alkenyl group, or an aryl group, wherein these groups may contain a carbonyl group in a chain thereof.

The alkyl group, the alkoxy group, the alkoxyalkyl group, the alkenyl group and the aryl group for R_z^{207} to R_z^{209} are the same as defined for the alkyl group, the alkoxy group, the alkoxyalkyl group, the alkenyl group and the aryl group for $_z^{201}$ to R_z^{206} in the aforementioned formulae (z2–r–1) and (z2–r–2).

[0235]

In formula (z2–r–3), R_z^{209} and R_z^{208} may be mutually bonded to form a ring.

Examples of the ring formed by R_z^{209} and R_z^{208} being mutually bonded include rings having 4 to 10 carbon atoms, such as a 2-oxacyclohexylidene group, a 2-oxacyclopentylidene group, and a 2-oxa-4-methylcyclohexylidene group.

[0236]

In formula (z2–r–4), R_z^{210} represents a divalent aliphatic group, a divalent alicyclic group or a divalent aromatic group.

Examples of the divalent aliphatic group for R_z^{210} include aliphatic groups having 1 to 8 carbon atoms, such as a methylene group, an ethylene group, a propylene group, a butylene group, a 2-methylpropylene group, and 2-methyl-3-ethoxybutylene group. Among these examples, a methylene group, an ethylene group or a propylene group is preferable.

Examples of the alicyclic group for R_z^{210} include alicyclic groups having 5 to 10 carbon atoms, such as a cyclohexylene group.

Examples of the divalent aromatic group for R_z^{210} include aryl groups having 6 to 14 carbon atoms, such as a phenylene group, a xylylene group, a toluylene group, and a cumenylene group.

[0237]

In formula (z2–r–4), examples of the acid dissociable group for R_z^{211} include groups represented by the aforementioned formulae (z2–r–1) to (z2–r–3).

[0238]

In formula (z2), R_z^{30} represents a hydrogen atom or an organic group.

Examples of the organic group for R_z^{30} include a hydrocarbon group which may have a substituent.

Examples of the hydrocarbon group for R_z^{30} a linear or branched alkyl group,

and a cyclic hydrocarbon group.

The linear alkyl group for R_z^{30} preferably has 1 to 5 carbon atoms, more preferably 1 to 4 carbon atoms, and still more preferably 1 or 2 carbon atoms. Specific examples include a methyl group, an ethyl group, an n-propyl group, an n-butyl group and an n-pentyl group.

The branched alkyl group for R_z^{30} preferably has 3 to 10 carbon atoms, and more preferably 3 to 5 carbon atoms. Specific examples include an isopropyl group, an isobutyl group, a tert-butyl group, an isopentyl group, a neopentyl group, a 1,1-diethylpropyl group, and a 2,2-dimethylbutyl group.

[0239]

The cyclic hydrocarbon group for R_z^{30} may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group, and may be polycyclic or monocyclic.

As the monocyclic aliphatic hydrocarbon group, a group in which 1 hydrogen atom has been removed from a monocycloalkane is preferable. The monocycloalkane preferably has 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

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

[0240]

Examples of the aromatic hydrocarbon group for R_z^{30} include a group in which one hydrogen atom has been removed from an aromatic hydrocarbon ring such as benzene, naphthalene, anthracene or phenanthrene; a group in which one hydrogen atom has been removed from an aromatic hetero ring such as a pyridine ring or a thiophene

ring; a group in which one hydrogen atom has been removed from an aromatic compound containing 2 or more aromatic rings (e.g., biphenyl or fluorene); and a group in which one hydrogen atom of the aforementioned aromatic hydrocarbon ring or aromatic hetero ring has been substituted with an alkyl group (arylalkyl groups, such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, and a 2-naphthylethyl group). The alkylene group which is bonded to the aforementioned aryl group or heteroaryl group preferably has 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and most preferably 1 carbon atom.

[0241]

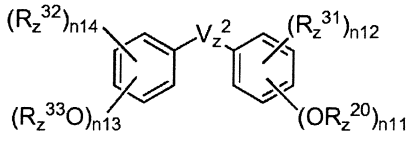
Examples of the substituent for the hydrocarbon group represented by R_z^{30} include a linear, branched or cyclic alkyl group, an aromatic hydrocarbon group, a linear or branched alkoxy group, a hydroxy group, a carboxy group, a halogen atom, and a group represented by any one of the aforementioned formulae (z2–r–1) to (z2–r–4). The aromatic hydrocarbon group as the substituent for the hydrocarbon group represented by R_z^{30} may further have a linear, branched or cyclic alkyl group or a group represented by any one of the aforementioned formulae (z2–r–1) to (z2–r–4) as a substituent.

[0242]

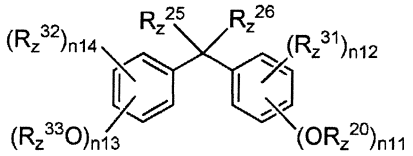
As the component (Z2), at least one member selected from the group consisting of groups represented by the following general formulae (z2–1) and (z2–2) is preferable.

[0243]

[Chemical Formula 57]



・・・ (z 2 − 1)



・・・ (z 2 − 2)

In the formulae, V_z^2 represents a divalent linking group; R_z^{20} and R_z^{33} each independently represents an acid dissociable group; R_z^{31} and R_z^{32} each independently represents a hydrogen atom or an organic group; R_z^{25} and R_z^{26} each independently represents a hydrogen atom or a hydrocarbon group which may have a substituent; n11 represents an integer of 1 to 5, and n12 represents an integer of 0 to 4, provided that n11+n12=5; n13 represents an integer of 1 to 5, and n14 represents an integer of 0 to 4, provided that n13+n14=5.

[0244]

In formula (z2−1), the divalent linking group for V_z^2 is the same as defined for the divalent linking group represented by Ya^{x1} in the aforementioned formula (a10-1). Among these examples, as the divalent linking group for V_z^2, a linear alkylene group having 1 to 10 carbon atoms is preferable, a methylene group [$-CH_2-$], an ethylene group [$-(CH_2)_2-$], a trimethylene group [$-(CH_2)_3-$], a tetramethylene group [$-(CH_2)_4-$] or a pentamethylene group [$-(CH_2)_5-$] is more preferable, and a methylene group is still more preferable.

[0245]

In formulae (z2−1) and (z2−2), the acid dissociable group for R_z^{20} and R_z^{33} is the same as defined for the acid dissociable group represented by R_z^{20} in the

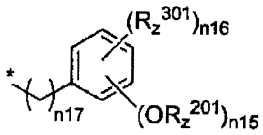
aforementioned formula (z2). Among these examples, as the acid dissociable group for R_z^{20} and R_z^{33}, a group represented by the aforementioned formula (z2–r–4) is preferable, and a group represented by the aforementioned formula (z2–r–4) in which the acid dissociable group for R_z^{211} is a group represented by the aforementioned formula (z2–r–1) is more preferable.

[0246]

In formulae (z2–1) and (z2–2), the organic group for R_z^{31} and R_z^{32} is the same as defined for the organic group represented by R_z^{30} in the aforementioned formula (z2). Among these examples, as the organic group for R_z^{31} and R_z^{32}, an aromatic hydrocarbon group which may have a substituent is preferable, and a group represented by the following general formula (z2–r–5) is more preferable.

[0247]

[Chemical Formula 58]



$\cdots$ (z2−r−5)

In the formula, R_z^{201} represents an acid dissociable group; R_z^{301} represents a hydrogen atom or an alkyl group;

n15 represents an integer of 1 to 6, and n16 represents an integer of 0 to 5; provided that n15+n16=6; n17 represents 0 or 1; and * indicates a bonding site.

[0248]

In formula (z2–r–5), the acid dissociable group for R_z^{201} is the same as defined for the acid dissociable group represented by R_z^{20} in the aforementioned formula (z2). Among these examples, as the acid dissociable group for R_z^{201}, a group represented by the aforementioned formula (z2–r–4) is preferable, and a group represented by the

aforementioned formula (z2–r–4) in which the acid dissociable group for R_z^{211} is a group represented by the aforementioned formula (z2–r–1) is more preferable.

In formula (z2–r–5), the alkyl group for R_z^{301} is preferably a methyl group, an ethyl group or a cyclohexyl group, and a methyl group or a cyclohexyl group is more preferable.

In formula (z2–r–5), n15 is preferably 1 or 2, and more preferably 1.

In formula (z2–r–5), n16 is preferably 4 or 5, and more preferably 5.

[0249]

In formula (z2–2), the hydrocarbon group for R_z^{25} and R_z^{26} is the same as defined for the hydrocarbon group as the organic group represented by R_z^{30} in the aforementioned formula (z2). Among these examples, as R_z^{25} and R_z^{26}, a hydrogen atom or an aromatic hydrocarbon group which may have a substituent is preferable, and a hydrogen atom or a group represented by the aforementioned formula (z2–r–5) is more preferable.

[0250]

In formulae (z2–1) and (z2–2), each of n11 and n13 is preferably 1 or 2, and more preferably 1.

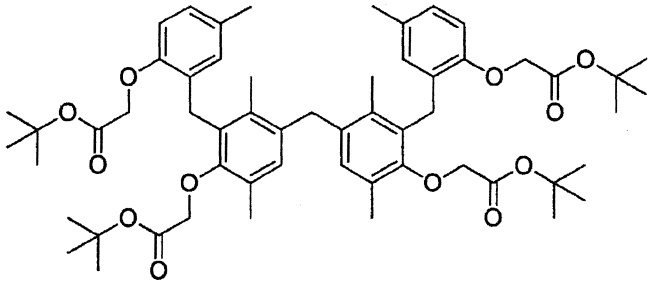
In formulae (z2–1) and (z2–2), n16 is preferably 4 or 5, and more preferably 5.

[0251]

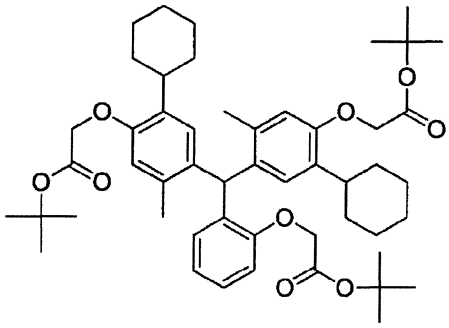
Specific examples of the component (Z2) include compounds represented by the following chemical formulae (Z2–1) and (Z2–2), and compounds described in paragraphs [0046]–[0050] of Japanese Unexamined Patent Application, First Publication No. 2005–122097.

[0252]

[Chemical Formula 59]



・・・（Z 2－1）



・・・（Z 2－2）

[0253]

Other examples of the component (Z2) include compounds described in paragraphs [0034], [0036] and [0037] of Japanese Unexamined Patent Application, First Publication No. Hei 9–278699, and compounds described in paragraphs [0119]–[0122] of Japanese Unexamined Patent Application, First Publication No. Hei 10–097075.

[0254]

In the resist composition, as the component (Z2), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

[0255]

In the resist composition of the present embodiment, the amount of the component (Z) relative to 100 parts by weight of the component (A) is preferably 30 parts by weight or less, and more preferably 10 to 30 parts by weight.

When the amount of the component (Z) is within the above-mentioned preferable range, the etching resistance may be improved, and a pattern having a good shape may be formed.

Further, in the resist composition of the present embodiment, the blend ratio (weight ratio) of the component (Z1) to the component (Z2) in the component (Z) is preferably Z1:Z2=75:25 to 25:75, more preferably Z1:Z2=70:30 to 40:60, and still more preferably Z1:Z2=67:33 to 45:55.

When the blend ratio (weight ratio) of the component (Z1) to the component (Z2) in the component (Z) is within the above-mentioned preferable range, the etching resistance may be improved, and a pattern having a good shape may be formed.

[0256]

<Optional components>

<<Component (B): acid-generator component>>

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

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

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

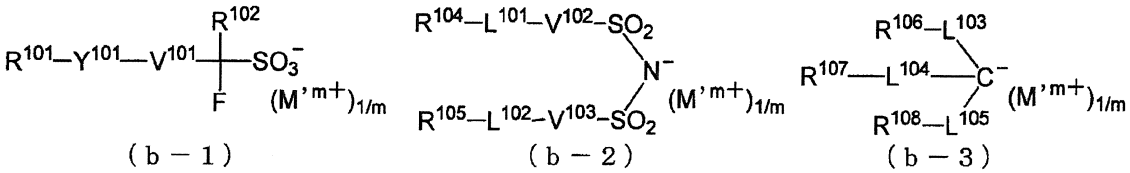
[0257]

As the onium salt acid generator, a compound represented by general formula (b-1) below (hereafter, sometimes referred to as "component (b-1)"), a compound represented by general formula (b-2) below (hereafter, sometimes referred to as

"component (b-2)") or a compound represented by general formula (b-3) below (hereafter, sometimes referred to as "component (b-3)") may be mentioned.

[0258]

[Chemical Formula 60]



(b − 1) (b − 2) (b − 3)

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

[0259]

{Anion moiety}

- Anion moiety of component (b-1)

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

[0260]

Cyclic group which may have a substituent:

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

[0261]

The aromatic hydrocarbon group for 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 carbon atoms, still more preferably 5 to 20 carbon atoms, still more preferably 6 to 15 carbon atoms, and most preferably 6 to 10 carbon atoms. Here, the number of carbon atoms within a substituent(s) is not included in the number of carbon atoms of the aromatic hydrocarbon group.

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

Specific examples of the aromatic hydrocarbon group represented by R^{101} include a group in which one hydrogen atom has been removed from the aforementioned aromatic ring (i.e., an aryl group, such as a phenyl group or a naphthyl group), and a group in which one hydrogen of the aforementioned aromatic ring has been substituted with an alkylene group (e.g., an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group or a 2-naphthylethyl group). The alkylene group (alkyl chain within the arylalkyl group)

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

[0262]

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

As examples of the hydrocarbon group containing a ring in the structure thereof, an alicyclic hydrocarbon group (a group in which one hydrogen atom has been removed from an aliphatic hydrocarbon ring), a group in which the alicyclic hydrocarbon group is bonded to the terminal of the aforementioned chain-like aliphatic hydrocarbon group, and a group in which the alicyclic group is interposed within the aforementioned linear or branched aliphatic hydrocarbon group, can be given.

The alicyclic hydrocarbon group preferably has 3 to 30 carbon atoms, and more preferably 3 to 20 carbon atoms.

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

[0263]

Among these examples, as the cyclic aliphatic hydrocarbon group for R^{101}, a

group in which one or more hydrogen atoms have been removed from a monocycloalkane or a polycycloalkane is preferable, a group in which one or more hydrogen atoms have been removed from a polycycloalkane is more preferable, an adamantyl group or a norbornyl group or a cyclic group having a steroid skeleton is still more preferable, and an adamantyl group or a cyclic group having a steroid skeleton is most preferable.

[0264]

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

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

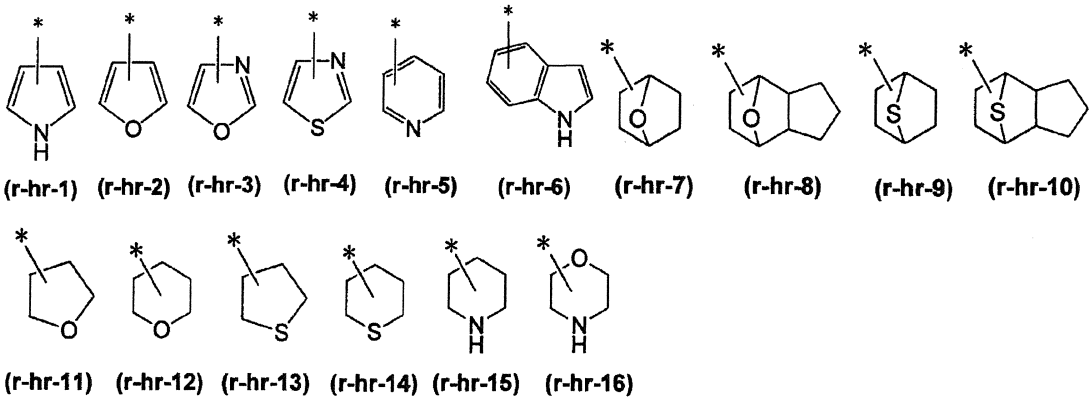
As the branched aliphatic hydrocarbon group, branched alkylene groups are preferred, and specific examples include various alkylalkylene groups, including alkylmethylene groups such as $-CH(CH_3)-$, $-CH(CH_2CH_3)-$, $-C(CH_3)_2-$, $-C(CH_3)(CH_2CH_3)-$, $-C(CH_3)(CH_2CH_2CH_3)-$, and $-C(CH_2CH_3)_2-$;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

[0265]

The cyclic hydrocarbon group for R^{101} may contain a hetero atom such as a heterocycle. Specific examples include lactone-containing cyclic groups represented by the aforementioned general formulae (a2–r–1) to (a2–r–7), the $-SO_2-$ containing cyclic group represented by the aforementioned formulae (a5–r–1) to (a5–r–4), and other heterocyclic groups represented by chemical formulae (r–hr–1) to (r–hr–16) shown below.

[0266]

[Chemical Formula 61]



[0267]

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

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

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

group or an ethoxy group.

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

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

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

[0268]

Chain alkyl group which may have a substituent:

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

The linear alkyl group preferably has 1 to 20 carbon atoms, more preferably 1 to 15 carbon atoms, and still more preferably 1 to 10 carbon atoms. Specific examples include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, an isotridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, an isohexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl 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 still more preferably 3 to 10 carbon atoms. Specific examples include a 1-methylethyl group, a 1-methylpropyl group, a 2-methylpropyl group, a 1-methylbutyl group, a 2-methylbutyl group, a 3-methylbutyl group, a 1-ethylbutyl group, a 2-ethylbutyl group, a 1-methylpentyl group, a 2-methylpentyl group, a 3-methylpentyl

group and a 4-methylpentyl group.

[0269]

Chain alkenyl group which may have a substituent:

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

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

[0270]

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

[0271]

Among these examples, as R^{101}, a cyclic group which may have a substituent is preferable, and a cyclic hydrocarbon group which may have a substituent is more preferable. Specifically, a phenyl group, a naphthyl group, a group in which one or more hydrogen atoms have been removed from a polycycloalkane, a lactone-containing cyclic group represented by any one of the aforementioned formula (a2–r–1), (a2–r–3) to (a2–r–7), and an $-SO_2-$ containing cyclic group represented by any one of the aforementioned formula (a5–r–1) to (a5–r–4).

[0272]

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

In the case where Y^{101} is 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 the divalent linking group containing an oxygen atom include divalent linking groups represented by the aforementioned general formula (y–al–1) to (y–al–8).

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

[0273]

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

[0274]

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

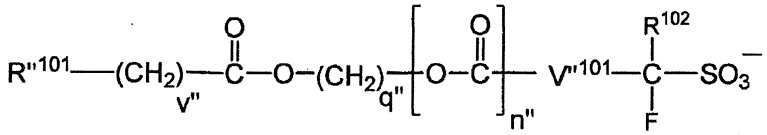
[0275]

As a specific example of the anion moiety for the component (b-1), in the case where Y^{101} a single bond, a fluorinated alkylsulfonate anion such as a

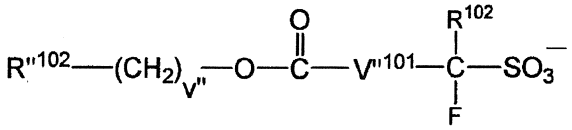
trifluoromethanesulfonate anion or a perfluorobutanesulfonate anion can be mentioned; and in the case where Y^{101} represents a divalent linking group containing an oxygen atom, anions represented by formulae (an-1) to (an-3) shown below can be mentioned.

[0276]

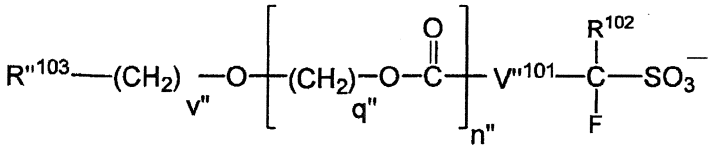
[Chemical Formula 62]



(an1)



(an2)



(an3)

In the formulae, R''^{101} represents an aliphatic cyclic group which may have a substituent, a monovalent heterocyclic group represented by any of Formulae (r-hr-1) to (r-hr-6), or a chain-like alkyl group which may have a substituent; R''^{102} represents an aliphatic cyclic group which may have a substituent, a lactone-containing cyclic group represented by any of Formulae (a2-r-1) and (a2-r-3) to (a2-r-7), or a $-SO_2-$containing cyclic group represented by any of formulae (a5-r-1) to (a5-r-4); R''^{103} represents an aromatic cyclic group which may have a substituent, an aliphatic cyclic group which may have a substituent, or a chain-like alkenyl group which may have a substituent;

V''^{101} represents a single bond, an alkylene group having 1 to 4 carbon atoms or a fluorinated alkylene group having 1 to 4 carbon atoms; R^{102} represents a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms; each v" independently represents an integer of 0 to 3; each q" independently represents an integer of 1 to 20; and n" represents 0 or 1.

[0277]

As the aliphatic cyclic group for R''^{101}, R''^{102} and R''^{103} which may have a substituent, the same groups as the cyclic aliphatic hydrocarbon group for R^{101} described above are preferable. As the substituent, the same groups as those described above for substituting the cyclic aliphatic hydrocarbon group for R^{101} can be mentioned.

[0278]

As the aromatic cyclic group for R''^{103} which may have a substituent, the same groups as the aromatic hydrocarbon group for the cyclic hydrocarbon group represented by R^{101} described above are preferable. The substituent is the same as defined for the substituent for the aromatic hydrocarbon group represented by R^{101}.

[0279]

As the chain-like alkyl group for R''^{101} which may have a substituent, the same groups as those described above for R^{101} are preferable. As the chain-like alkenyl group for R''^{104} which may have a substituent, the same groups as those described above for R^{101} are preferable.

[0280]

V''^{101} is preferably a single bond or a fluorinated alkylene group, and more preferably a single bond or a fluorinated alkylene group having 1 to 3 carbon atoms. In the case where V''^{101} is a fluorinated alkylene group, V''^{101} in $-V''^{101}-C(F)(R''^{102})-SO_3^-$ is preferably $-CF_2-$, $-CHF-$, $-CF_2CF_2-$, $-CHFCF_2-$, $-CF(CF_3)CF_2-$ or $-CH(CF_3)CF_2-$, and more preferably $-CF_2-$ or $-CHF-$.

[0281]

R^{102} represents a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms. R^{102} is preferably a fluorine atom or a perfluoroalkyl group of 1 to 5 carbon atoms, and more preferably a fluorine atom.

[0282]

V" represents an integer of 0 to 3, and preferably 0 or 1. q" represents an integer of 1 to 20, preferably an integer of 1 to 10, more preferably an integer of 1 to 5, still more preferably 1, 2 or 3, and most preferably 1 or 2. n" represents 0 or 1.

[0283]

- Anion moiety of component (b-2)

In formula (b-2), R^{104} and R^{105} each independently represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent or a chain-like alkenyl group which may have a substituent, and is the same as defined for R^{101} in formula (b-1).

R^{104} and R^{105} may be mutually bonded to form a ring.

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

The chain-like alkyl group preferably has 1 to 10 carbon atoms, more preferably 1 to 7 carbon atoms, and still more preferably 1 to 3 carbon atoms. The smaller the number of carbon atoms of the chain-like alkyl group for R^{104} and R^{105}, the more the solubility in a resist solvent is improved. Further, in the chain-like alkyl group for R^{104} and R^{105}, it is preferable that the number of hydrogen atoms substituted with fluorine atoms is as large as possible because the acid strength increases. The fluorination ratio of the chain-like alkyl group is preferably from 70 to 100%, more preferably from 90 to 100%, and it is particularly desirable that the chain-like alkyl group be a perfluoroalkyl group in which all hydrogen atoms are substituted with fluorine atoms.

In formula (b-2), V^{102} and V^{103} each independently represents a single bond, an alkylene group or a fluorinated alkylene group, and is the same as defined for V^{101} in

formula (b-1).

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

[0284]

- Anion moiety of component (b-3)

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

L^{103} to L^{105} each independently represents a single bond, –CO– or $-SO_2-$.

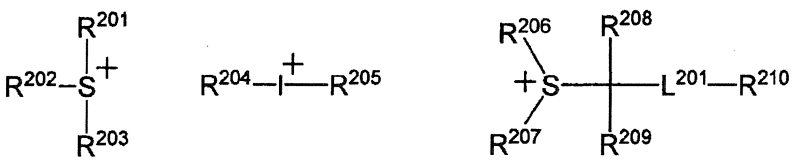
[0285]

{Cation moiety}

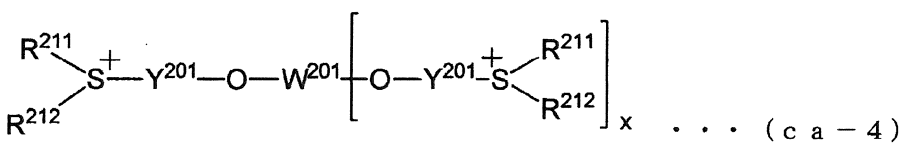
In formulae (b–1), (b–2) and (b–3), m represents an integer of 1 or more, M'^{m+} represents an onium cation having a valency of m, preferably a sulfonium cation or an iodonium cation, and examples thereof include an organic cation represented by any one of the aforementioned general formulae (ca–1) to (ca–4).

[0286]

[Chemical Formula 63]



(ca–1) (ca–2) (ca–3)



(ca–4)

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

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

[0287]

As the aryl group for R^{201} to R^{207} and R^{211} to R^{212}, an aryl group of 6 to 20 carbon atoms may be mentioned, and a phenyl group or a naphthyl group is preferable.

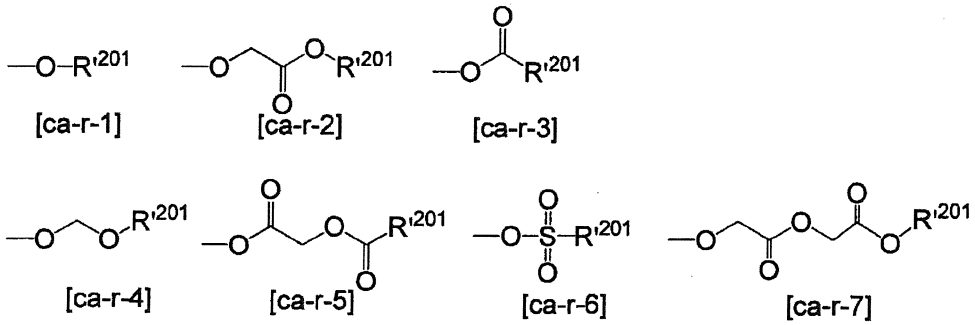
The alkyl group for R^{201} to R^{207}, R^{211} and R^{212} is preferably a chain-like or cyclic alkyl group having 1 to 30 carbon atoms.

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

Specific examples of the substituent which R^{201} to R^{207} and R^{211} to R^{212} may have include an alkyl group, a halogen atom, a halogenated alkyl group, a carbonyl group, a cyano group, an amino group, an aryl group, and groups represented by general formulae (ca-r-1) to (ca-r-7) shown below.

[0288]

[Chemical Formula 64]



In the formulae, each R'^{201} independently represents a hydrogen atom, a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent.

[0289]

As the cyclic group which may have a substituent, the chain-like alkyl group which may have a substituent and the chain-like alkenyl group which may have a substituent for R'^{201}, the same groups as those described later for R^{101} in formula (b-1) can be mentioned. As the cyclic group which may have a substituent and chain-like alkyl group which may have a substituent, the same groups as those described above for the acid dissociable group represented by the aforementioned formula (a1-r-2) can be also mentioned.

[0290]

When R^{201} to R^{203}, R^{206}, R^{207}, R^{211} and R^{212} are mutually bonded to form a ring with the sulfur atom, these groups may be mutually bonded via a hetero atom such as a sulfur atom, an oxygen atom or a nitrogen atom, or a functional group such as a carbonyl group, -SO-, $-SO_2-$, $-SO_3-$, –COO–, –CONH– or $-N(R_N)-$ (wherein R_N represents an alkyl group of 1 to 5 carbon atoms). The ring containing the sulfur atom in the skeleton thereof is preferably a 3 to 10-membered ring, and most preferably a 5 to 7-membered ring. Specific examples of the ring formed include a thiophene ring, a thiazole ring, a

benzothiophene ring, a thianthrene ring, a benzothiophene ring, a dibenzothiophene ring, a 9H-thioxanthene ring, a thioxanthone ring, a phenoxathiin ring, a tetrahydrothiophenium ring, and a tetrahydrothiopyranium ring.

[0291]

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

[0292]

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

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

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

The alkenyl group for R^{210} preferably has 2 to 10 carbon atoms.

As the $-SO_2-$ containing cyclic group for R^{210} which may have a substituent, an "$-SO_2-$ containing polycyclic group" is preferable, and a group represented by the aforementioned general formula (a5–r–1) is more preferable.

[0293]

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

Examples of the arylene group for Y^{201} include groups in which one hydrogen atom has been removed from an aryl group given as an example of the aromatic

hydrocarbon group for R^{101} in formula (b-1) described later.

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

[0294]

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

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

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

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

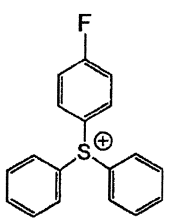
[0295]

Specific examples of preferable cations represented by formula (ca−1) include cations represented by formulae (ca−1−1) to (ca−1−78) and (ca−1−101) to (ca−1−149) shown below.

In the following chemical formulae, g1 represents a repeating number, and g1 is an integer of 1 to 5. g2 represents a repeating number, and g2 is an integer of 0 to 20. g3 represents a repeating number, and g3 is an integer of 0 to 20.

[0296]

[Chemical Formula 65]



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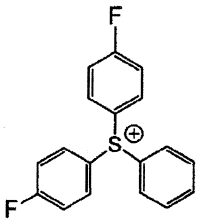

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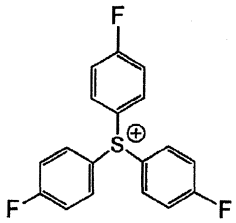

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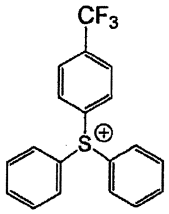

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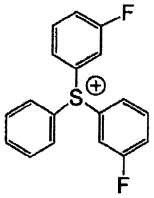

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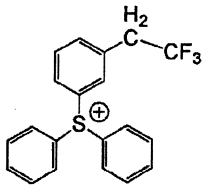
(ca-1-6)



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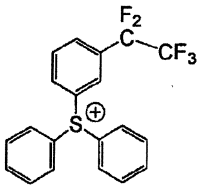

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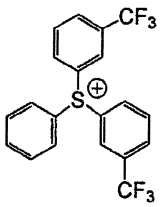

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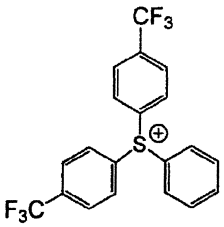

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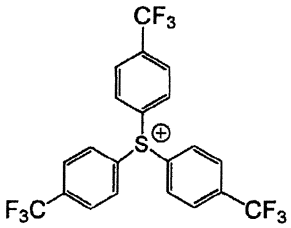

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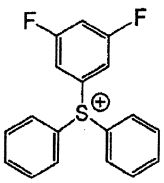

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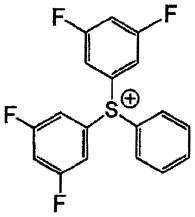

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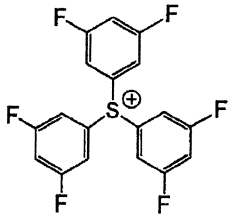

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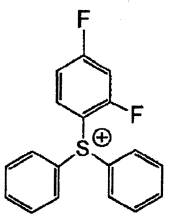

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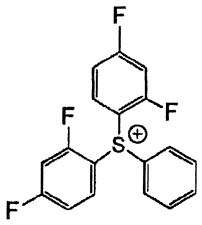

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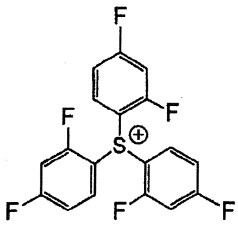

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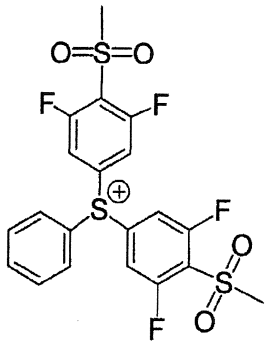
[0297]

[Chemical Formula 66]



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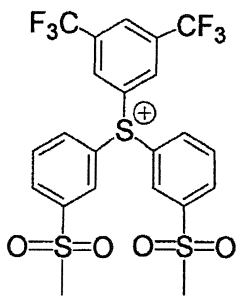

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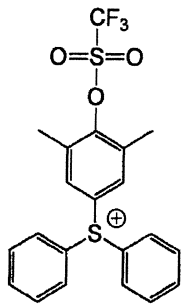

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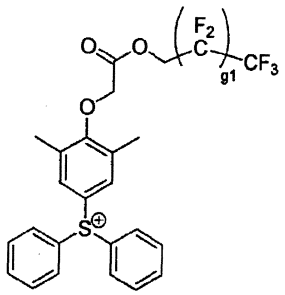

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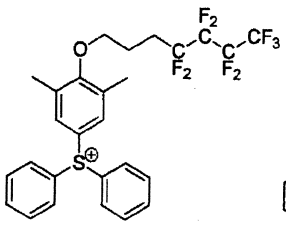

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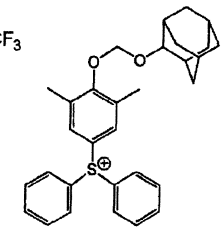

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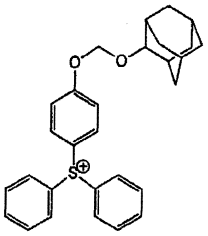

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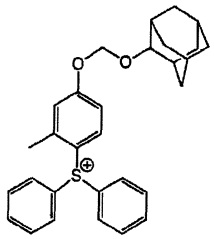

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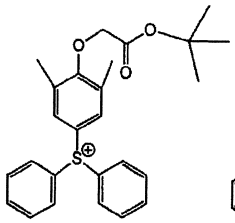

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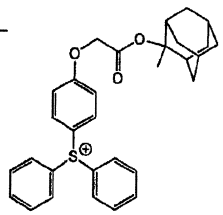

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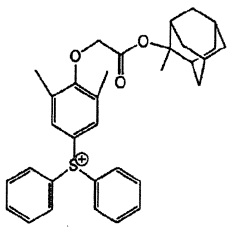

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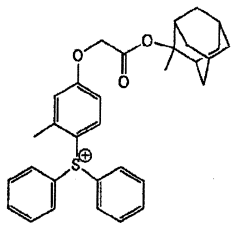
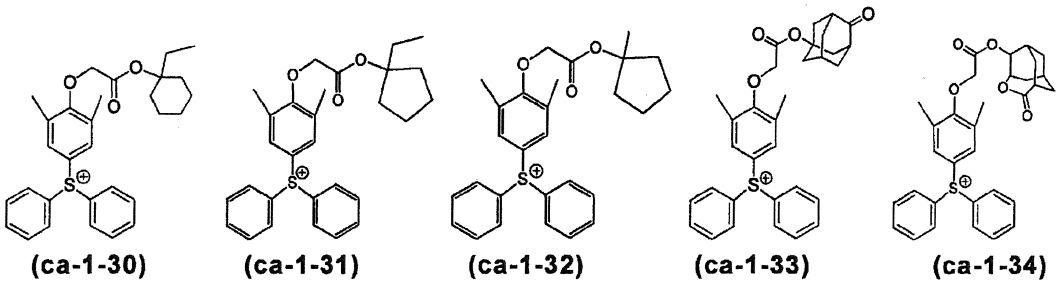


(ca-1-29)

[0298]

[Chemical Formula 67]



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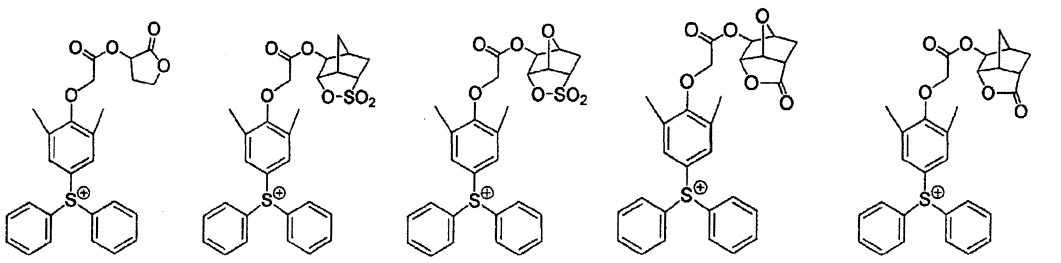

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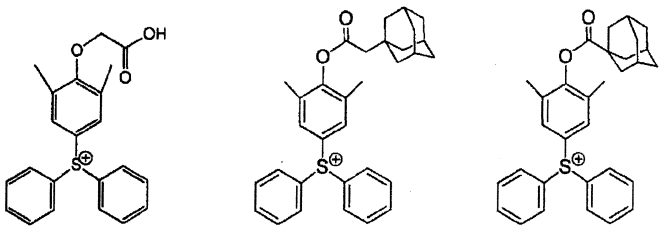
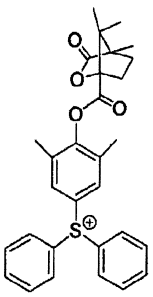


(ca-1-40) (ca-1-41) (ca-1-42)

[0299]

[Chemical Formula 68]



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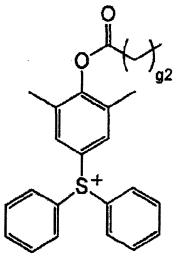

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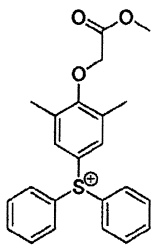

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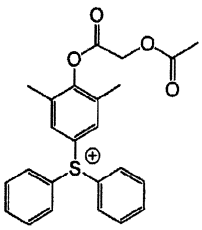

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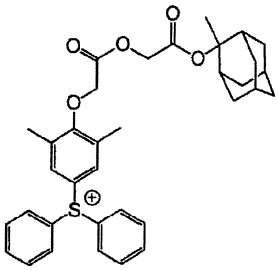

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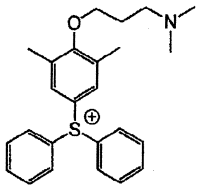

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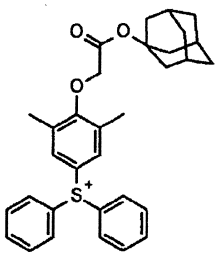

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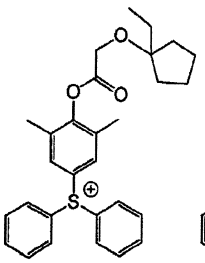
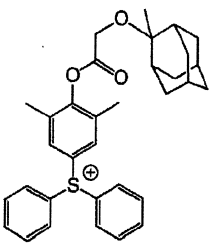


(ca-1-50)



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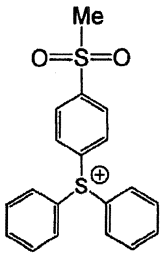

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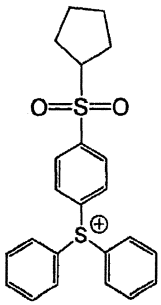

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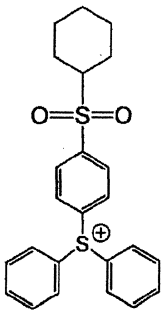
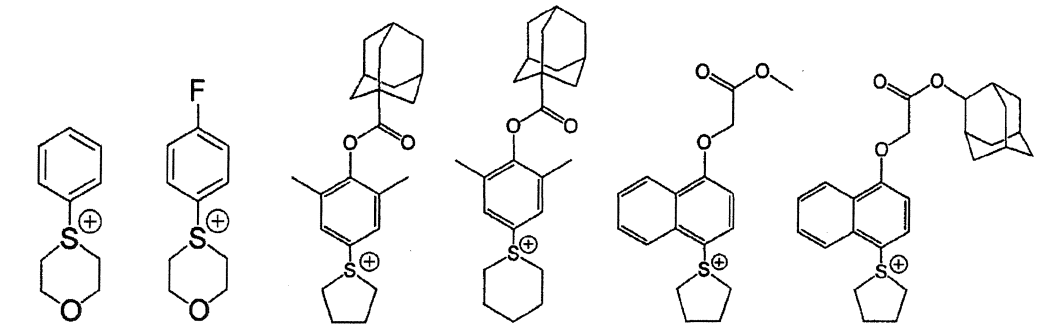


(ca-1-54)

[0300]

[Chemical Formula 69]



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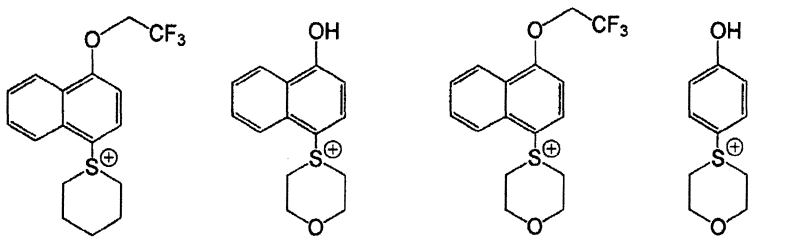

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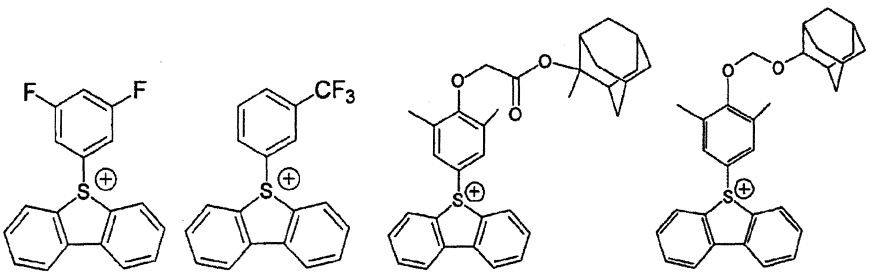
[0301]

[Chemical Formula 70]



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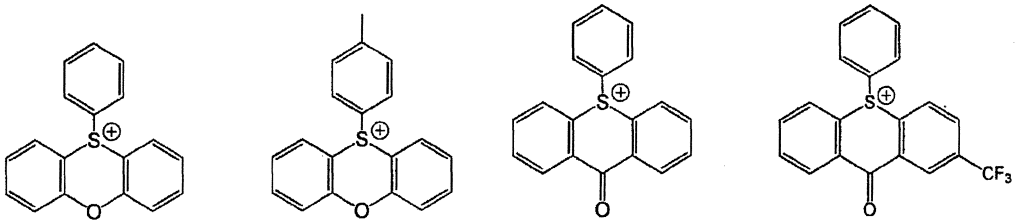

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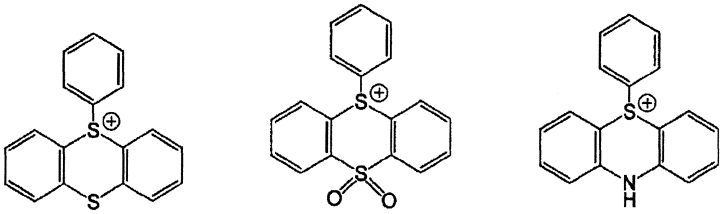
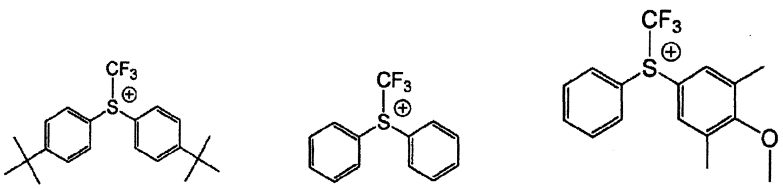


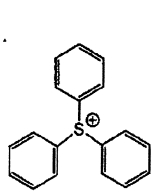
(ca-1-73) (ca-1-74) (ca-1-75)

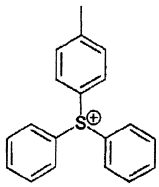


(ca-1-76) (ca-1-77) (ca-1-78)

[0302]

[Chemical Formula 71]


(ca-1-101)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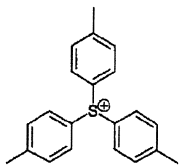
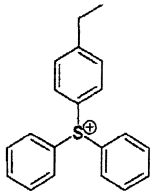
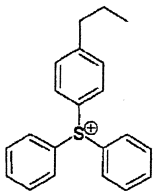

(ca-1-103)


(ca-1-104)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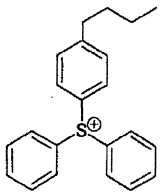
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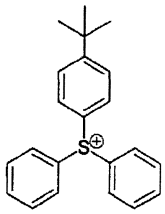
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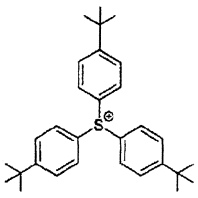
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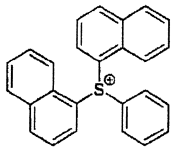
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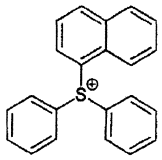
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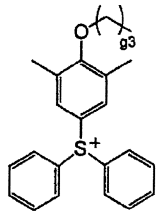
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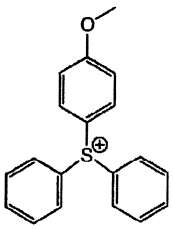
[0303]

[Chemical Formula 72]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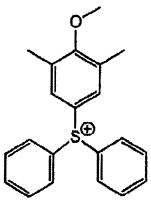
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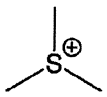
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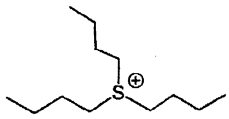
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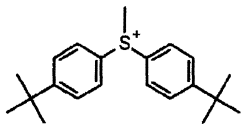
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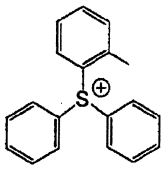
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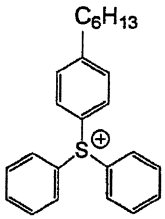
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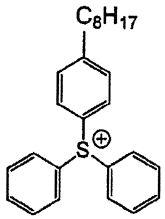
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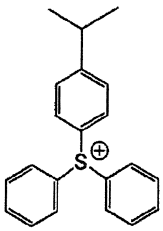
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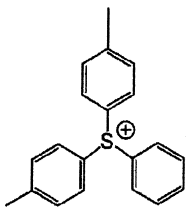
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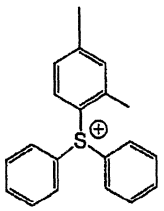
[0304]

[Chemical Formula 73]



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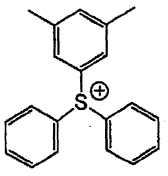

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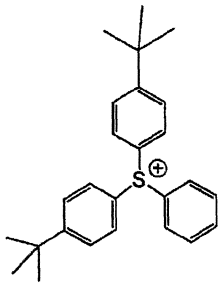
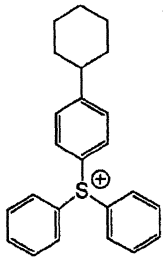
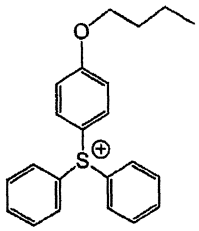


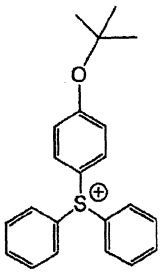
(ca-1-124)



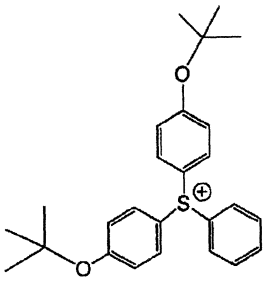
(ca-1-125)



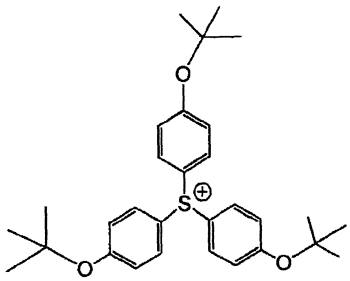
(ca-1-126)



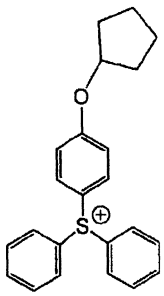
(ca-1-127)



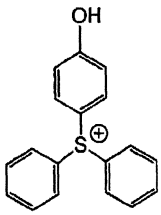
(ca-1-128)



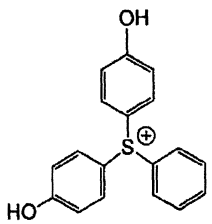
(ca-1-129)



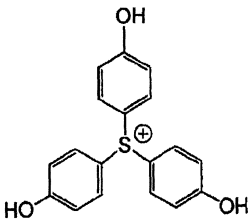
(ca-1-130)



(ca-1-131)



(ca-1-132)



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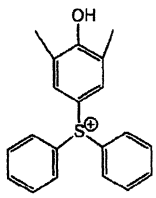
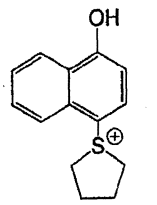
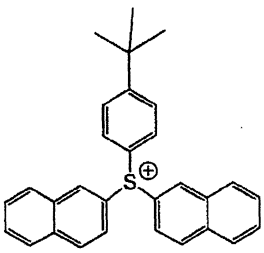


(ca-1-134)



(ca-1-135)



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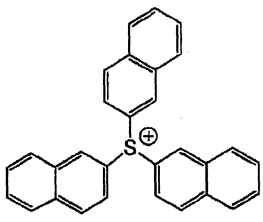
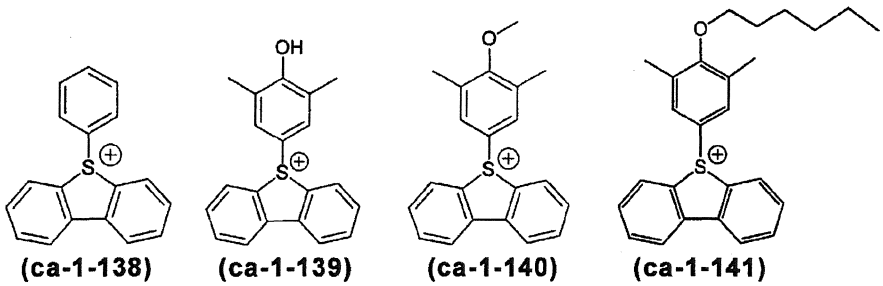


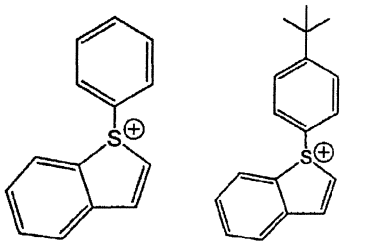
(ca-1-137)

[0305]

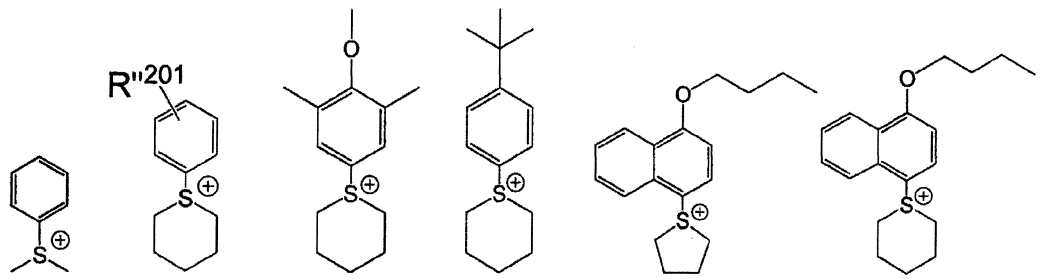
[Chemical Formula 74]



(ca-1-138) (ca-1-139) (ca-1-140) (ca-1-141)



(ca-1-142) (ca-1-143)



(ca-1-144) (ca-1-145) (ca-1-146) (ca-1-147) (ca-1-148) (ca-1-149)

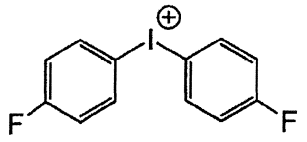
In the formulae, R"^{201} represents a hydrogen atom or a substituent. Examples of the substituent which R^{201} to R^{207}, R^{211} and R^{212} may have include an alkyl group, a halogen atom, a halogenated alkyl group, a carbonyl group, a cyano group, an amino group, an aryl group, and groups respectively represented by formulae (ca-r-1) to (ca-r-7).

[0306]

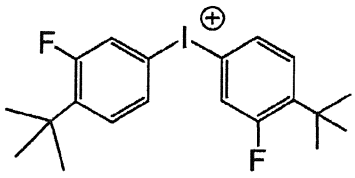
Specific examples of suitable cations represented by formula (ca-2) include cations respectively represented by the following formulae (ca-2-1) to (ca-2-3), a dihphenyliodonium cation and a bis(4-tert-butylphenyl)iodonium cation.

[0307]

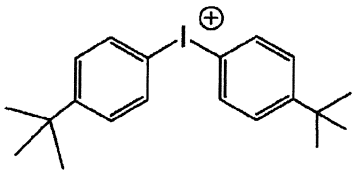
[Chemical Formula 75]



(ca-2-1)



(ca-2-2)



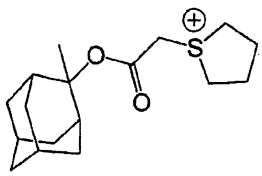
(ca-2-3)

[0308]

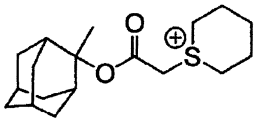
Specific examples of suitable cations represented by formula (ca-3) include cations respectively represented by formulae (ca-3-1) to (ca-3-7) shown below.

[0309]

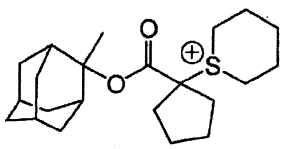
[Chemical Formula 76]



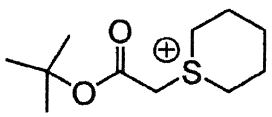
(ca-3-1)



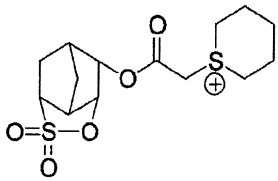
(ca-3-2)



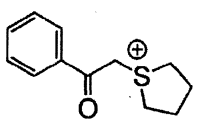
(ca-3-3)



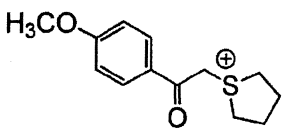
(ca-3-4)



(ca-3-5)



(ca-3-6)



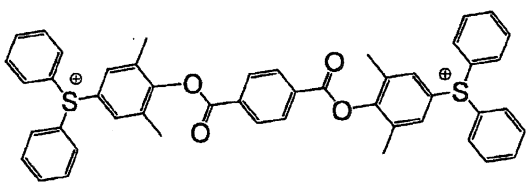
(ca-3-7)

[0310]

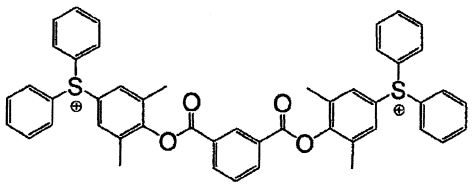
Specific examples of preferable cations represented by formula (ca-4) include cations represented by formulae (ca-4-1) and (ca-4-2) shown below.

[0311]

[Chemical Formula 77]



(ca-4-1)



(ca-4-2)

[0312]

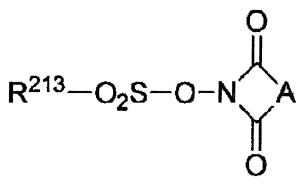
Among the above examples, as the cation moiety ($(M^{m+})_{1/m}$), a cation represented by general formula (ca–1)or (ca-2) is preferable, and a cation represented by any one of chemical formulae (ca–1–1) to (ca–1–78) and (ca–1–101) to (ca–1–149) or chemical formulae (ca–2–1) to (ca–2–3) is more preferable.

[0313]

As an example of the iminosulfonate acid generator, a compound represented by the following general formula (b-4) (hereafter, sometimes referred to as "component (b-4)") may be mentioned.

[0314]

[Chemical Formula 78]



・・・ (b－4)

In the formula, R^{213} represents an alkyl group which may have a substituent, or an aryl group which may have a substituent; A represents an alkylene group which may have a substituent, an alkenylene group which may have a substituent, or an arylene group which may have a substituent.

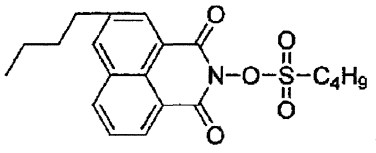
[0315]

Specific examples of the component (b–4) include a compound represented by the following chemical formula (B1–1), and compound described in paragraphs

[0089]–[0091] of Japanese Unexamined Patent Application, First Publication No. 10–097075.

[0316]

[Chemical Formula 79]



··· (B 1 − 1)

[0317]

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

In the case where the resist composition contains the component (B), the amount of the component (B) relative to 100 parts by weight of the component (A) is preferably 50 parts by weight or less, more preferably 0.1 to 40 parts by weight, still more preferably from 0.1 to 30 parts by weight, and still more preferably 0.1 to 20 parts by weight.

When the amount of the component (B) is within the above-mentioned range, formation of a resist pattern can be satisfactorily performed.

[0318]

<<Component (D)>>

The resist composition of the present invention may include, in addition to the components (A) and (Z), an acid diffusion control component (hereafter, sometimes referred to as "component (D)"). The component (D) functions as an acid diffusion control agent, i.e., a quencher which traps the acid generated in the resist composition upon exposure.

Examples of the component (D) include a nitrogen-containing organic compound (D1) (hereafter, referred to as "component (D1)"), and a photodegradable base (D2) (hereafter, referred to as "component (D2)") which is decomposable by exposure to lose the ability of controlling of acid diffusion, and does not fall under the definition of the component (D1).

When a resist pattern is formed using a resist composition containing the component (D), the contrast between exposed portions and unexposed portions of the resist film is further improved.

[0319]

- Component (D1)

The component (D1) is a basic component and is a nitrogen-containing organic compound component that acts as an acid diffusion control agent in the resist composition.

[0320]

The component (D1) is not particularly limited as long as it acts as an acid diffusion control agent, and examples thereof include aliphatic amines and aromatic amines.

[0321]

Among the aliphatic amines, secondary aliphatic amines and tertiary aliphatic amines are preferable.

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

Examples of these aliphatic amines include amines in which at least one hydrogen atom of ammonia (NH_3) has been substituted with an alkyl group or hydroxyalkyl group of no more than 12 carbon atoms (i.e., alkylamines or

alkylalcoholamines), and cyclic amines.

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

[0322]

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

Specific examples of the aliphatic monocyclic amine include piperidine, and piperazine.

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

[0323]

Examples of other aliphatic amines include tris(2-methoxymethoxyethyl)amine,

tris{2-(2-methoxyethoxy)ethyl}amine, tris{2-(2-methoxyethoxymethoxy)ethyl}amine, tris{2-(1-methoxyethoxy)ethyl}amine, tris{2-(1-ethoxyethoxy)ethyl}amine, tris{2-(1-ethoxypropoxy)ethyl}amine, tris[2-{2-(2-hydroxyethoxy)ethoxy}ethyl]amine and triethanolamine triacetate, and triethanolamine triacetate is preferable.

[0324]

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

[0325]

As the component (D1), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

Among the above examples, as the component (D1), an aromatic amine is preferable, and an aniline compound is more preferable. Examples of the aniline compound include 2,6-diisopropylaniline, N, N-dimethylaniline, N, N-dibutylaniline, and N, N-dihexylaniline.

[0326]

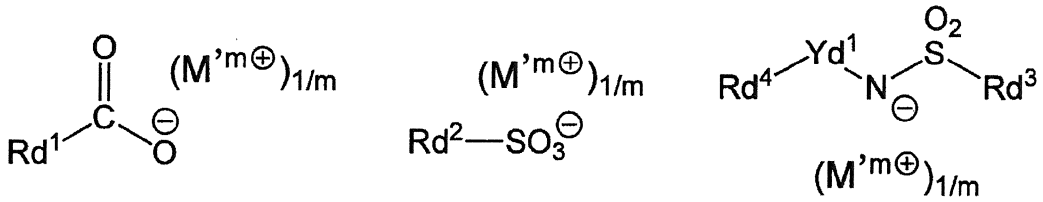
- Component (D2)

The component (D2) is not particularly limited, as long as it is decomposed upon exposure and then loses the ability of controlling of acid diffusion. As the component (D2), at least one compound selected from the group consisting of a compound represented by general formula (d2-1) shown below (hereafter, referred to as "component (d2-1)"), a compound represented by general formula (d2-2) shown below (hereafter, referred to as "component (d2-2)") and a compound represented by general formula (d2-3) shown below (hereafter, referred to as "component (d2-3)") is preferably used.

At exposed portions of the resist film, the components (d2-1) to (d2-3) are decomposed and then lose the ability of controlling of acid diffusion (i.e., basicity), and therefore the components (d2-1) to (d2-3) cannot function as a quencher, whereas at unexposed portions, the components (d2-1) to (d2-3) functions as a quencher.

[0327]

[Chemical Formula 80]



(d 2 − 1) (d 2 − 2) (d 2 − 3)

In the formulae, Rd^1 to Rd^4 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, provided that, the carbon atom adjacent to the sulfur atom within the Rd^2 in general formula (d2-2) has no fluorine atom bonded thereto; Yd^1 represents a single bond or a divalent linking group; m represents an integer of 1 or more, and each M'^{m+} independently represents an onium cation having a valency of m.

[0328]

{Component (d2-1)}

- Anion moiety

In formula (d2-1), 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, and is the same groups as those defined above for R^{101} in the aforementioned formula (b-1).

Among these, as the group for Rd^1, an aromatic hydrocarbon group which may have a substituent, an aliphatic cyclic group which may have a substituent and a

chain-like alkyl group which may have a substituent are preferable.

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

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

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

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

[0329]

In the case where the chain-like alkyl group is a fluorinated alkyl group having a

fluorine atom or a fluorinated alkyl group, the fluorinated alkyl group preferably has 1 to 11 carbon atoms, more preferably 1 to 8 carbon atoms, and still more preferably 1 to 4 carbon atoms. The fluorinated alkyl group may contain an atom other than fluorine. Examples of the atom other than fluorine include an oxygen atom, a sulfur atom and a nitrogen atom.

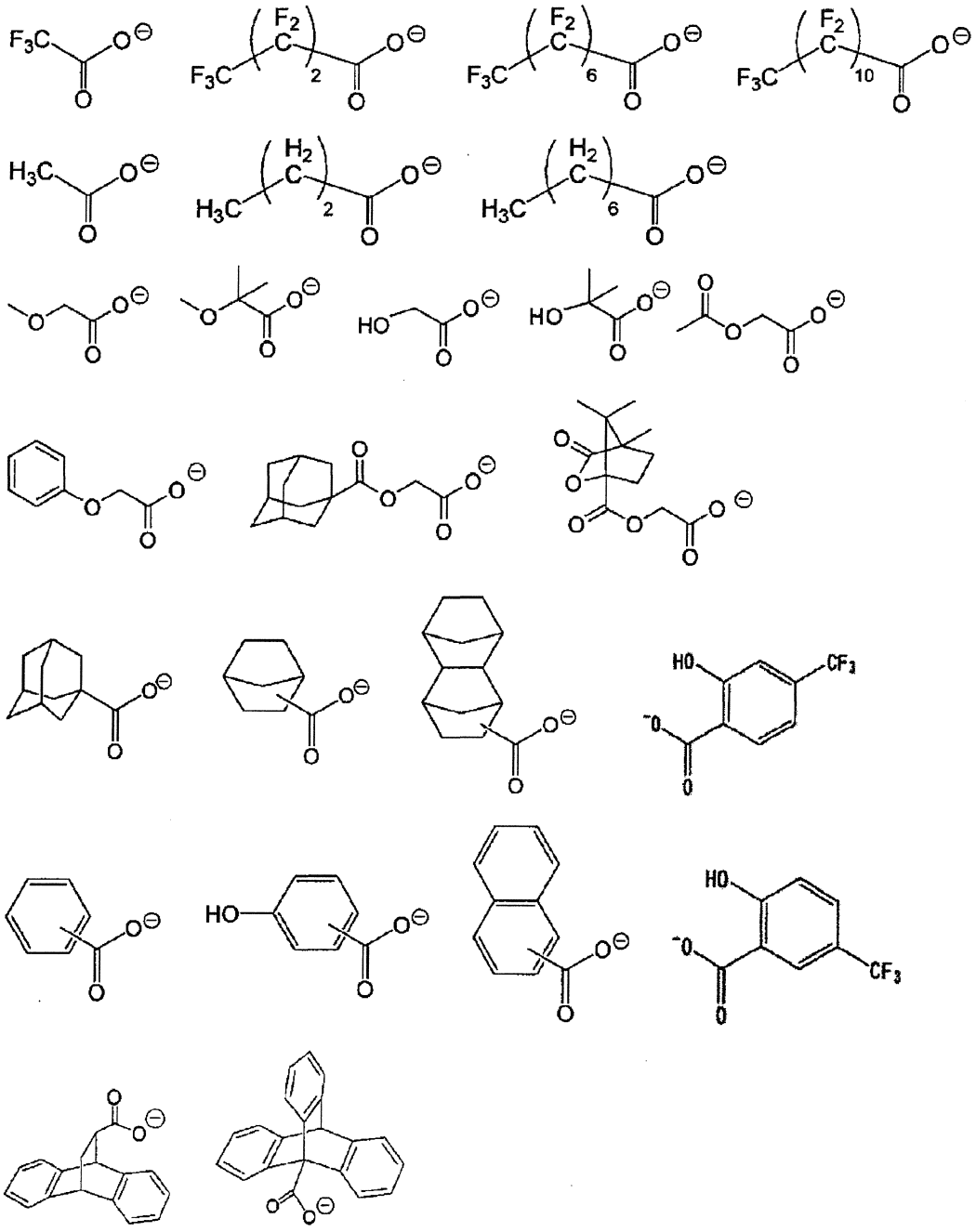
As Rd^1, a fluorinated alkyl group in which part or all of the hydrogen atoms constituting a linear alkyl group have been substituted with fluorine atom(s) is preferable, and a fluorinated alkyl group in which all of the hydrogen atoms constituting a linear alkyl group have been substituted with fluorine atoms (i.e., a linear perfluoroalkyl group) is particularly desirable.

[0330]

Specific examples of preferable anion moieties for the component (d2-1) are shown below.

[0331]

[Chemical Formula 81]



[0332]

- Cation moiety

In formula (d2-1), M'^{m+} represents an m-valent organic cation

As the organic cation for M^{m+}, for example, the same cation moieties as those represented by the aforementioned formulae (ca-1) to (ca-4) are preferable, cation

moieties represented by the aforementioned general formulae (ca-1) is preferable, and cation moieties represented by the aforementioned formulae (ca-1-1) to (ca-1-78), (ca−1−101) to (ca−1−149) are still more preferable.

As the component (d2-1), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

[0333]

{Component (d2-2)}

- Anion moiety

In formula (d2-2), 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 is the same groups as those defined above for R^{101} in the aforementioned formula (b-1).

However, the carbon atom adjacent to the sulfur atom within the Rd^2 has no fluorine atom bonded thereto. As a result, the anion of the component (d2-2) becomes an appropriately weak acid anion, thereby improving the quenching ability of the component (D2).

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

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

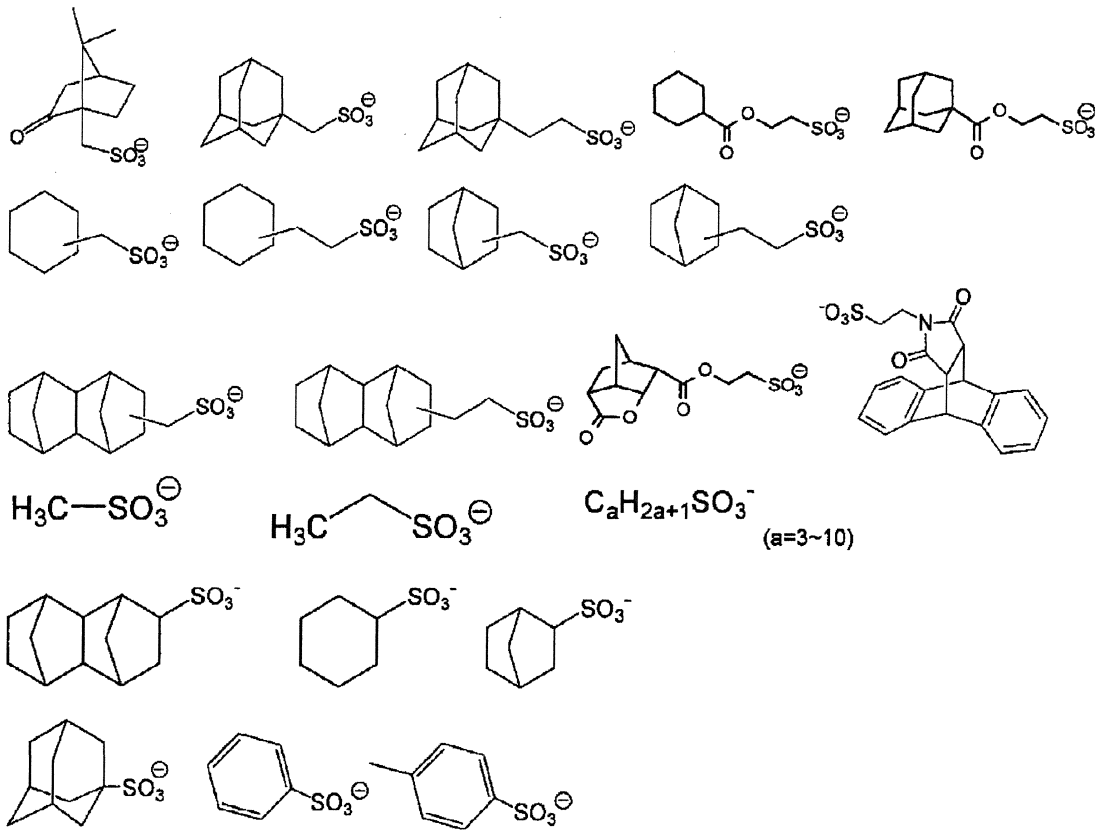
formula (d2-1) can be mentioned.

[0334]

Specific examples of preferable anion moieties for the component (d2-2) are shown below.

[0335]

[Chemical Formula 82]



[0336]

- Cation moiety

In formula (d2-2), M'^{m+} is an m-valent onium cation, and is the same as defined for M'^{m+} in the aforementioned formula (d2-1).

As the component (d2-2), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

[0337]

{Component (d2-3)}

- Anion moiety

In formula (d2-3), Rd^3 represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent or a chain-like alkenyl group which may have a substituent, and is the same groups as those defined above for R^{101} in the aforementioned formula (b-1), and a cyclic group containing a fluorine atom, a chain-like alkyl group or a chain-like alkenyl group is preferable. Among these, a fluorinated alkyl group is preferable, and more preferably the same fluorinated alkyl groups as those described above for Rd^1.

[0338]

In formula (d2-3), 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 is the same groups as those defined above for R^{101} in the aforementioned formula (b-1).

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

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

The alkoxy group for Rd^4 is preferably an alkoxy group of 1 to 5 carbon atoms,

and specific examples thereof include a methoxy group, an ethoxy group, an n-propoxy group, an iso-propoxy group, an n-butoxy group and a tert-butoxy group. Among these, a methoxy group and an ethoxy group are preferable.

[0339]

As the alkenyl group for Rd^4, the same groups as those described above for R^{101} in the aforementioned formula (b-1) may be mentioned, and a vinyl group, a propenyl group (an allyl group), a 1-methylpropenyl group and a 2-methylpropenyl group are preferable. These groups may have an alkyl group of 1 to 5 carbon atoms or a halogenated alkyl group of 1 to 5 carbon atoms as a substituent.

[0340]

As the cyclic group for Rd^4, the same groups as those described above for R^{101} in the aforementioned formula (b-1) may be mentioned. Among these, as the cyclic group, an alicyclic group (e.g., a group in which one or more hydrogen atoms have been removed from a cycloalkane such as cyclopentane, cyclohexane, adamantane, norbornane, isobornane, tricyclodecane or tetracyclododecane) or an aromatic group (e.g., a phenyl group or a naphthyl group) is preferable. When Rd^4 is an alicyclic group, the resist composition can be satisfactorily dissolved in an organic solvent, thereby improving the lithography properties.

[0341]

In formula (d2-3), Yd^1 represents a single bond or a divalent linking group.

The divalent linking group for Yd^1 is not particularly limited, and examples thereof include a divalent hydrocarbon group (aliphatic hydrocarbon group, or aromatic hydrocarbon group) which may have a substituent and a divalent linking group containing a hetero atom. The divalent linking groups are the same as defined for the divalent hydrocarbon group which may have a substituent and the divalent linking group

containing a hetero atom explained above as the divalent linking group for Ya^{x1} in the aforementioned formula (a10–1).

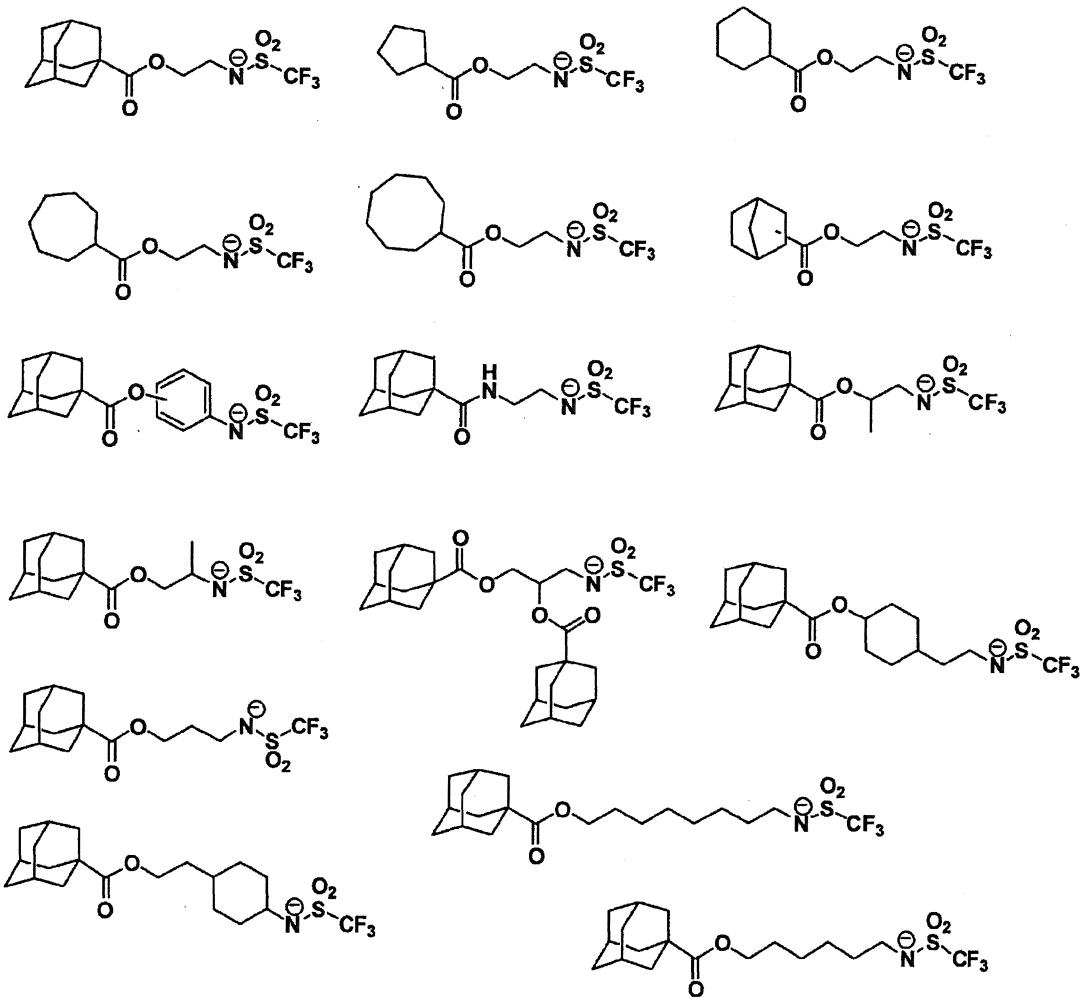
As Yd^1, a carbonyl group, an ester bond, an amide bond, an alkylene group or a combination of these is preferable. As the alkylene group, a linear or branched alkylene group is more preferable, and a methylene group or an ethylene group is still more preferable.

[0342]

Specific examples of preferable anion moieties for the component (d2-3) are shown below.

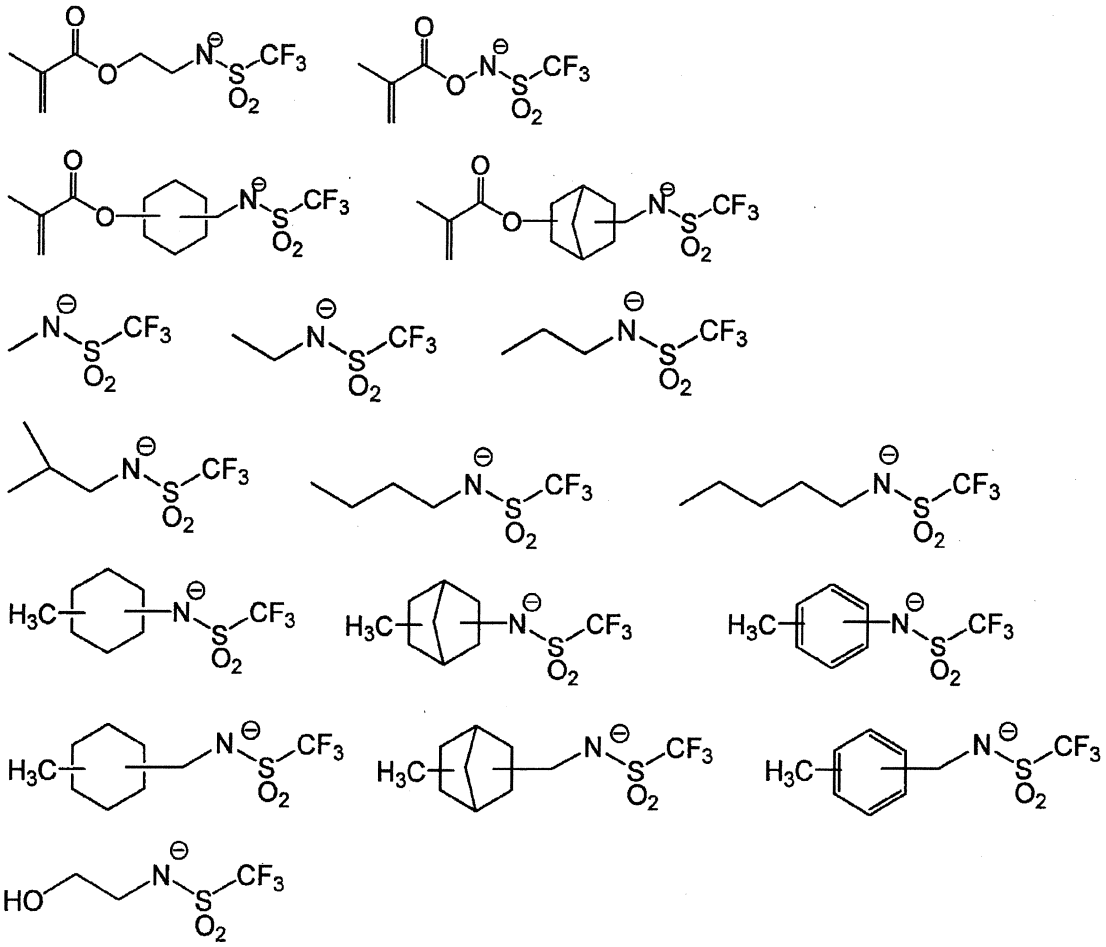
[0343]

[Chemical Formula 83]



[0344]

[Chemical Formula 84]



[0345]

- Cation moiety

In formula (d2-3), M'^{m+} is an m-valent onium cation, and is the same as defined for M'^{m+} in the aforementioned formula (d2-1).

As the component (d2-3), one kind of compound may be used, or two or more kinds of compounds may be used in combination.

[0346]

As the component (D2), one kind of the aforementioned components (d2-1) to (d2-3) may be used, or at least two kinds of the aforementioned components (d2-1) to (d2-3) may be used.

In the case where the resist composition contains the component (D2), the amount of the component (D2) relative to 100 parts by weight of the component (A) is preferably within a range from 0.5 to 35 parts by weight, more preferably from 1 to 25 parts by weight, still more preferably from 2 to 20 parts by weight, and still more preferably 3 to 15 parts by weight.

When the amount of the component (D2) is at least as large as the lower limit of the above-mentioned range, excellent lithography properties and excellent resist pattern shape can be more reliably obtained. On the other hand, when the amount of the component (D2) is no more than the upper limit of the above-mentioned preferable range, a good balance may be achieved with the other structural units, and the lithography properties may be improved.

[0347]

Production method of component (D2):

The production methods of the components (d2-1) and (d2-2) are not particularly limited, and the components (d2-1) and (d2-2) can be produced by conventional methods.

Further, the production method of the component (d2–3) is not particularly limited, and the component (d2-3) may be produced in the same manner as disclosed in US2012–0149916.

[0348]

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

In the resist composition of the present embodiment, for preventing any deterioration in sensitivity, and improving the resist pattern shape and the post exposure stability of the latent image formed by the pattern-wise exposure of the resist layer, at

least one compound (E) (hereafter referred to as the component (E)) selected from the group consisting of an organic carboxylic acid, or a phosphorus oxo acid or derivative thereof may be added.

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

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

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

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

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

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

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

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

[0349]

<<Component (F): Fluorine additive>>

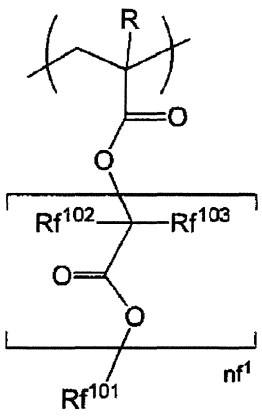
In the present embodiment, the resist composition may further include a fluorine additive (hereafter, referred to as "component (F)") for imparting water repellency to the resist film, or improving lithography properties.

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

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

[0350]

[Chemical Formula 85]



··· (f1-1)

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

[0351]

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

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

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

these examples, as Rf^{102} and Rf^{103}, a hydrogen atom, a fluorine atom or an alkyl group of 1 to 5 carbon atoms is preferable, and a hydrogen atom, a fluorine atom, a methyl group or an ethyl group is more preferable.

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

[0352]

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

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

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

Among these, as Rf^{101}, a fluorinated hydrocarbon group of 1 to 6 carbon atoms is preferable, and a trifluoromethyl group, $-CH_2-CF_3$, $-CH_2-CF_2-CF_3$, $-CH(CF_3)_2$, $-CH_2-CH_2-CF_3$, and $-CH_2-CH_2-CF_2-CF_2-CF_2-CF_3$ are most preferable.

[0353]

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

the lower limit of the above-mentioned range, the water repellency of the resist film may become satisfactory.

Further, the dispersity (Mw/Mn) of the component (F) is preferably 1.0 to 5.0, more preferably 1.0 to 3.0, and most preferably 1.2 to 2.5.

[0354]

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

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

[0355]

<<Component (S): organic solvent>>

The resist composition of the present embodiment may be prepared by dissolving the resist materials for the resist composition in an organic solvent (hereafter, referred to as "component (S)").

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

Examples thereof include lactones such as γ-butyrolactone; ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl-n-pentyl ketone, methyl isopentyl ketone, and 2-heptanone; polyhydric alcohols, such as ethylene glycol, diethylene glycol, propylene glycol and dipropylene glycol; compounds having an ester bond, such as ethylene glycol monoacetate, diethylene glycol monoacetate, propylene glycol

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

In the resist composition of the present embodiment, as the component (S), one kind of solvent may be used, or two or more kinds of compounds may be used as a mixed solvent.

Among these, PGMEA, PGME, γ-butyrolactone, EL and cyclohexanone are preferable.

Further, among the mixed solvents, a mixed solvent obtained by mixing PGMEA with a polar solvent is preferable. The mixing ratio (weight ratio) of the mixed solvent can be appropriately determined, taking into consideration the compatibility of the PGMEA with the polar solvent, but is preferably in the range of 1:9 to 9:1, more preferably from 2:8 to 8:2.

Specifically, when EL or cyclohexanone is mixed as the polar solvent, the PGMEA:EL or cyclohexanone weight ratio is preferably from 1:9 to 9:1, and more preferably from 2:8 to 8:2. Alternatively, when PGME is mixed as the polar solvent, the

PGMEA:PGME weight ratio is preferably from 1:9 to 9:1, more preferably from 2:8 to 8:2, and still more preferably 3:7 to 7:3. Furthermore, a mixed solvent of PGMEA, PGME and cyclohexanone is also preferable.

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

The amount of the component (S) is not particularly limited, and is appropriately adjusted to a concentration which enables coating of a coating solution to a substrate. In general, the component (S) is used in an amount such that the solid content of the resist composition becomes within the range from 0.1 to 50% by weight, and preferably from 10 to 50% by weight.

[0356]

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

[0357]

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

2016-155121.

[0358]

The resist composition of the present embodiment contains the base component (A) and the dissolution inhibitor (Z). The dissolution inhibitor contains the compound (Z1) and the compound (Z2).

Generally, in a resist film formed using a resist composition, spaces are formed between molecules constituting the base component. As the molecular weight of the base component becomes larger, the molecule itself constituting the base component becomes larger, such that the spaces formed between the molecules becomes larger. Such spaces formed within the resist film may deteriorate the adhesion of the resist film to a substrate.

In the resist composition of the present embodiment, both the compound (Z1) and the compound (Z2) have a weight average molecular weight of 3,000 or less, which means that the molecule size is relatively small. Therefore, in a resist film formed using the resist composition of the present embodiment, the compound (Z1) and the compound (Z2) may be appropriately dispersed in the spaces generated between molecules constituting the base component (A).

Since the compound (Z1) has a phenolic hydroxy group or a carboxy group in the molecule thereof, the compound (Z1) tends to segregate in the lower layer in the resist film. As a result, it is presumed that the compound (Z1) contributes to improvement in the adhesion of the resist film to the substrate interface, so as to improve the etching resistance.

On the other hand, since the compound (Z1) has a phenolic hydroxy group or a carboxy group in the molecule thereof, particularly in an alkali developing process, the compound (Z1) may cause film thickness loss of the resist film. However, the compound (Z2) has a higher hydrophobicity than the compound (Z1). Therefore, it is presumed that

the compound (Z2) contributes to suppressing film thickness loss which may be caused by the compound (Z1).

By virtue of the synergistic effect of the compound (Z1) and the compound (Z2) as described above, it is presumed that a resist pattern having good etching resistance and good shape may be obtained.

[0359]

(Method of forming a resist pattern)

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

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

[0360]

Step (i):

Firstly, a resist composition of the present embodiment is applied to a substrate using a spinner or the like, and a bake treatment (post applied bake (PAB)) is conducted at a temperature of 80 to 160°C for 40 to 200 seconds, preferably 60 to 150 seconds, to form a resist film.

[0361]

Step (ii):

Following selective exposure of the thus formed resist film by exposure through a mask having a predetermined pattern formed thereon (mask pattern) using an exposure apparatus such a KrF exposure apparatus, baking treatment (post exposure baking (PEB)) is conducted under temperature conditions of 80 to 150°C for 40 to 150 seconds, and

preferably 60 to 120 seconds.

[0362]

Step (iii)

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

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

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

[0363]

After the developing treatment or the rinse treatment, drying is conducted. If desired, bake treatment (post bake) can be conducted following the developing. The bake treatment (post bake) may be conducted, for example, at 80°C or higher, preferably 90 to 120°C for 10 to 120 seconds, preferably 30 to 90 seconds.

In this manner, a resist pattern can be formed.

[0364]

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

and glass. Suitable materials for the wiring pattern include copper, aluminum, nickel, and gold.

Further, as the substrate, any one of the above-mentioned substrates provided with an inorganic and/or organic film on the surface thereof may be used. As the inorganic film, an inorganic antireflection film (inorganic BARC) can be used. As the organic film, an organic antireflection film (organic BARC) and an organic film such as a lower-layer organic film used in a multilayer resist method can be used.

Here, a "multilayer resist method" is method in which at least one layer of an organic film (lower-layer organic film) and at least one layer of a resist film (upper resist film) are provided on a substrate, and a resist pattern formed on the upper resist film is used as a mask to conduct patterning of the lower-layer organic film. This method is considered as being capable of forming a pattern with a high aspect ratio. More specifically, in the multilayer resist method, a desired thickness can be ensured by the lower-layer organic film, and as a result, the thickness of the resist film can be reduced, and an extremely fine pattern with a high aspect ratio can be formed.

The multilayer resist method is broadly classified into a method in which a double-layer structure consisting of an upper-layer resist film and a lower-layer organic film is formed (double-layer resist method), and a method in which a multilayer structure having at least three layers consisting of an upper-layer resist film, a lower-layer organic 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).

[0365]

The method of forming a resist pattern according to the present embodiment is useful for forming a resist film having a large thickness. For example, even when the film thickness of the resist film formed in step (i) is 1 to 10μm, a resist pattern having a good

shape may be stably formed.

[0366]

The wavelength to be used for exposure is not particularly limited and the exposure may be conducted using radiation such as ultraviolet ray (e.g., g-line and i-line), ArF excimer laser, KrF excimer laser, F_2 excimer laser, extreme ultraviolet rays (EUV), vacuum ultraviolet rays (VUV), electron beam (EB), X-rays, and soft X-rays.

The resist composition according to the first aspect is effective for ultraviolet ray (such as g-line or i-line), KrF excimer laser, ArF excimer laser, EB or EUV, more effective for ultraviolet ray (such as g-line or i-line), KrF excimer laser or ArF excimer laser, and still more effective for ultraviolet ray (such as g-line or i-line) or KrF excimer laser . The method of forming a resist pattern according to the second aspect is preferable as a method in which the resist film is exposed to ultraviolet ray (such as g-line or i-line) or KrF excimer laser in step (ii).

[0367]

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

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

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

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

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

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

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

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

[0368]

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

As the organic solvent contained in the organic developing solution used in a solvent developing process, any of the conventional organic solvents can be used which

are capable of dissolving the component (A) (prior to exposure). Specific examples of the organic solvent include polar solvents such as ketone solvents, ester solvents, alcohol solvents, nitrile solvents, amide solvents and ether solvents, and hydrocarbon solvents.

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

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

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

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

[0369]

Examples of ketone solvents include 1-octanone, 2-octanone, 1-nonanone,

2-nonanone, acetone, 4-heptanone, 1-hexanone, 2-hexanone, diisobutyl ketone, cyclohexanone, methylcyclohexanone, phenylacetone, methyl ethyl ketone, methyl isobutyl ketone, acetylacetone, acetonylacetone, ionone, diacetonylalcohol, acetylcarbinol, acetophenone, methyl naphthyl ketone, isophorone, propylenecarbonate, γ-butyrolactone and methyl amyl ketone (2-heptanone). Among these examples, as a ketone solvent, methyl amyl ketone (2-heptanone) is preferable.

[0370]

Examples of ester solvents include methyl acetate, butyl acetate, ethyl acetate, isopropyl acetate, amyl acetate, isoamyl acetate, ethyl methoxyacetate, ethyl ethoxyacetate, propylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene glycol monobutyl ether acetate, ethylene glycol monophenyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monopropyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monophenyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, 2-methoxybutyl acetate, 3-methoxybutyl acetate, 4-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, 3-ethyl-3-methoxybutyl acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, 2-ethoxybutyl acetate, 4-ethoxybutyl acetate, 4-propoxybutyl acetate, 2-methoxypentyl acetate, 3-methoxypentyl acetate, 4-methoxypentyl acetate, 2-methyl-3-methoxypentyl acetate, 3-methyl-3-methoxypentyl acetate, 3-methyl-4-methoxypentyl acetate, 4-methyl-4-methoxypentyl acetate, propylene glycol diacetate, methyl formate, ethyl formate, butyl formate, propyl formate, ethyl lactate, butyl lactate, propyl lactate, ethyl carbonate, propyl carbonate, butyl carbonate, methyl pyruvate, ethyl pyruvate, propyl pyruvate, butyl pyruvate, methyl acetoacetate, ethyl acetoacetate, methyl propionate,

ethyl propionate, propyl propionate, isopropyl propionate, methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, methyl-3-methoxypropionate, ethyl-3-methoxypropionate, ethyl-3-ethoxypropionate and propyl-3-methoxypropionate. Among these examples, as an ester solvent, butyl acetate is preferable.

[0371]

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

[0372]

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

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

[0373]

The developing treatment may be performed by a conventional developing method. Examples thereof include a method in which the substrate is immersed in the developing solution for a predetermined time (a dip method), a method in which the developing solution is cast up on the surface of the substrate by surface tension and maintained for a predetermined period (a puddle method), a method in which the developing solution is sprayed onto the surface of the substrate (spray method), and a method in which the developing solution is continuously ejected from a developing solution ejecting nozzle while scanning at a constant rate to apply the developing

solution to the substrate while rotating the substrate at a constant rate (dynamic dispense method).

[0374]

As the organic solvent contained in the rinse liquid used in the rinse treatment after the developing treatment in the case of a solvent developing process, any of the aforementioned organic solvents contained in the organic developing solution can be used which hardly dissolves the resist pattern. In general, at least one solvent selected from the group consisting of hydrocarbon solvents, ketone solvents, ester solvents, alcohol solvents, amide solvents and ether solvents is used. Among these, at least one solvent selected from the group consisting of hydrocarbon solvents, ketone solvents, ester solvents, alcohol solvents and amide solvents is preferable, more preferably at least one solvent selected from the group consisting of alcohol solvents and ester solvents, and an alcohol solvent is particularly desirable.

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

As the organic solvent, one kind of solvent may be used alone, or two or more kinds of solvents may be used in combination. Further, an organic solvent other than the aforementioned examples or water may be mixed together. However, in consideration of the development characteristics, the amount of water within the rinse liquid, based on the total amount of the rinse liquid is preferably 30% by weight or less, more preferably 10% by weight or less, still more preferably 5% by weight or less, and most preferably 3% by

weight or less.

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

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

[0375]

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

[0376]

In the method of forming a resist pattern according to the present embodiment as described above, by virtue of using the resist composition of the first aspect, it is presumed that a resist pattern having improved etching resistance and good shape may be formed.

[0377]

The method of forming a resist pattern according to the present embodiment is useful in the formation of a resist film having a large film thickness. Such a resist composition and a resist pattern forming method are useful for processing a multi-step

staircase structure. By applying the present invention, stacking of memory films (three-dimensional, large-capacity memory manufacturing) may be realized with high accuracy.

EXAMPLES

[0378]

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

[0379]

<Production of resist composition>

(Examples 1 to 10, Comparative Examples 1 to 3)

The components shown in Table 1 were mixed together and dissolved to obtain each resist composition (solid content: 30 wt%).

[0380]

[Table 1]

	Component (A)	Component (B)	Component (Z)		Component (S)
			Component (Z1)	Component (Z2)	
Example 1	(A)-1 [100]	(B)-1 [0.5]	(Z1)-1 [5.90]	(Z2)-1 [5.90]	(S)-1 [290]
Example 2	(A)-1 [100]	(B)-1 [0.5]	(Z1)-1 [11.80]	(Z2)-1 [5.90]	(S)-1 [290]
Example 3	(A)-1 [100]	(B)-1 [0.5]	(Z1)-1 [17.70]	(Z2)-1 [5.90]	(S)-1 [290]
Example 4	(A)-1 [100]	(B)-1 [0.5]	(Z1)-1 [11.80]	(Z2)-1 [1.18]	(S)-1 [290]
Example 5	(A)-1 [100]	(B)-1 [0.5]	(Z1)-1 [11.80]	(Z2)-1 [11.80]	(S)-1 [290]
Example 6	(A)-1 [100]	(B)-1 [0.5]	(Z1)-2 [11.80]	(Z2)-1 [5.90]	(S)-1 [290]
Example 7	(A)-1 [100]	(B)-1 [0.5]	(Z1)-3 [11.80]	(Z2)-1 [5.90]	(S)-1 [290]
Example 8	(A)-1 [100]	(B)-1 [0.5]	(Z1)-1 [11.80]	(Z2)-2 [5.90]	(S)-1 [290]
Example 9	(A)-1 [100]	(B)-1 [0.5]	(Z1)-4 [11.80]	(Z2)-1 [5.90]	(S)-1 [290]
Example 10	(A)-1 [100]	(B)-1 [0.5]	(Z1)-5 [11.80]	(Z2)-1 [5.90]	(S)-1 [290]
Comparative Example 1	(A)-1 [100]	(B)-1 [0.5]	(Z1)-1 [11.80]	-	(S)-1 [290]
Comparative Example 2	(A)-1 [100]	(B)-1 [0.5]	-	(Z2)-1 [5.90]	(S)-1 [290]
Comparative Example 3	(A)-1 [100]	(B)-1 [0.5]	-	-	(S)-1 [290]

[0381]

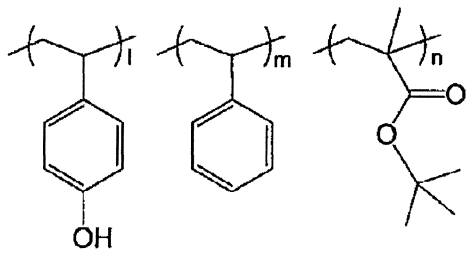
In Table 1, the reference characters indicate the following. The values in brackets [ ] indicate the amount (in terms of parts by weight) of the component added.

(A)–1:Polymeric compound represented by chemical formula (A1–1) shown below. The weight average molecular weight (Mw) and the dispersity (Mw/Mn) in terms of the polystyrene equivalent value measured by gel permeation chromatography (GPC) were 10,000 and 2.14, respectively. The composition of the copolymer (ratio (molar ratio) of the respective structural units within the structural formula) as determined by

^{13}C–NMR was l/m/n = 61/14/25.

[0382]

[Chemical Formula 86]



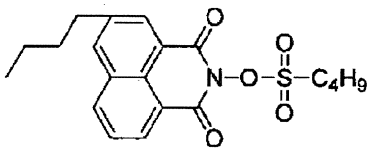
··· (A1−1)

[0383]

(B1)–1: a compound represented by chemical formula (B1–1) shown below

[0384]

[Chemical Formula 87]



··· (B1−1)

[0385]

(Z1)–1: a compound represented by chemical formula (Z1–1) shown below. Weight average molecular weight (Mw): 268.35.

(Z1)–2: a compound represented by chemical formula (Z1–2) shown below. Weight average molecular weight (Mw): 424.53.

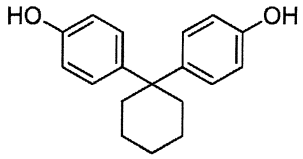
(Z1)–3: a compound represented by chemical formula (Z1–3) shown below. Weight average molecular weight (Mw): 352.43.

(Z1)–4: a compound represented by chemical formula (Z1–4) shown below. Weight average molecular weight (Mw): 246.31.

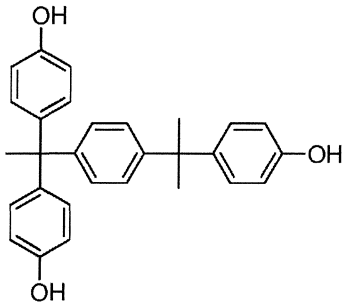
(Z1)–5: a compound represented by chemical formula (Z1–5) shown below. Weight average molecular weight (Mw): 292.29.

[0386]

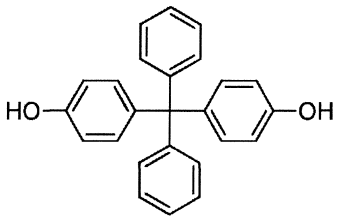
[Chemical Formula 88]



・・・（Ｚ１－１）



・・・（Ｚ１－２）



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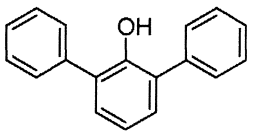
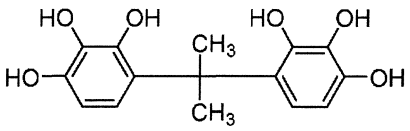


・・・（Ｚ１－４）



・・・（Ｚ１－５）

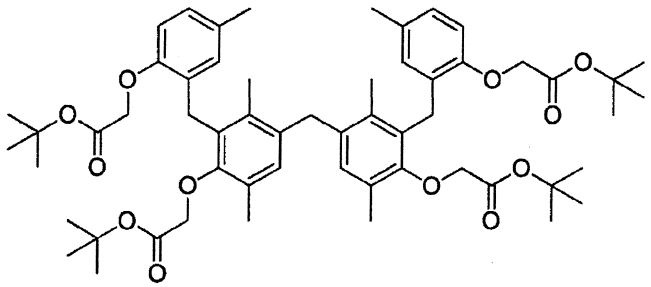
[0387]

(Z2)–1: a compound represented by chemical formula (Z2–1) shown below. Weight average molecular weight (Mw): 953.21.

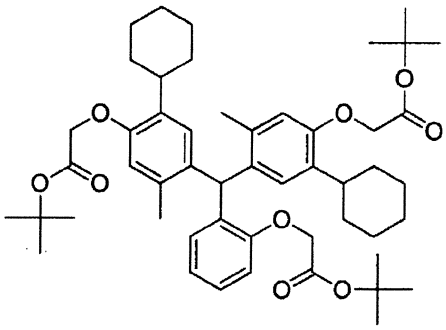
(Z2)–2: a compound represented by chemical formula (Z2–2) shown below. Weight average molecular weight (Mw): 827.1.

[0388]

[Chemical Formula 89]



・・・ (Z 2 − 1)



・・・ (Z 2 − 2)

[0389]

(S)-1: a mixed solvent of propylene glycol monomethyl ether acetate/propylene glycol monomethyl ether = 50/50 (weight ratio).

[0390]

<Method of forming resist pattern>

Step (i):

Each of the resist compositions of examples and comparative examples was applied to a silicon substrate which had been treated with hexamethyldisilazane (HMDS) using a spinner, and was then prebaked (PAB) on a hot plate at 90°C for 120 seconds and dried, so as to form a resist film having a film thickness of 5.0μm.

Step (ii):

Subsequently, the resist film was selectively irradiated with high-pressure mercury lamp (365 nm) through a mask pattern (6% half-tone), using an i-line stepper (NSR−2205i14E (manufactured by Nikon; NA (numerical aperture) = 0.57, σ = 0.67)).

Then, a post exposure bake (PEB) treatment was conducted at 110°C for 60 seconds.

Step (iii)

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

Finally, a bake treatment (post bake) was conducted at 100°C for 60 seconds.

As a result, an isolated line patter (hereafter, sometimes referred to as "IS pattern") having a space width of 3μm and a pitch of 15μm was formed.

[0391]

<Evaluation of dry etching resistance>

Using an etching apparatus manufactured by Tokyo Ohka Kogyo Co., Ltd., the IS pattern formed in the above "Method of forming resist pattern" was subjected to dry etching under the following conditions.

Conditions:

Kind of etching gas and flow rate; a mixture of tetrafluoromethane 30cc/min., trifluoromethane 30cc/min. and helium 100cc/min. pressure; 300mmTorr

Output; 600w

Time; 120 seconds

The cross-sectional shape of the IS pattern after the dry etching was observed using a scanning electron microscope (product name: S4500; manufactured by Hitachi), and the presence or absence of undercut (etching of a lower portion of the pattern) was

evaluated. The results are shown in Table 2.

[0392]

<Evaluation of wet etching resistance>

A portion of the substrate having an IS pattern formed thereon in the above "Method of forming resist pattern" was cut out, and immersed in a 23% buffered hydrofluoric acid for 12 minutes.

The cross-sectional shape of the IS pattern after the immersing was observed using a scanning electron microscope (product name: S4500; manufactured by Hitachi), and the amount of side etching (μm) was evaluated. The results are shown in Table 2.

[0393]

(Evaluation of film thickness loss of pattern)

The resist composition of each example was applied to an 8-inch silicon wafer using a spinner, and was then prebaked (PAB) and dried on a hotplate at 120°C for 90 seconds, so as to form a resist film having a film thickness of 5.0μm.

Then, using a 2.38% by weight aqueous solution of tetramethylammonium hydroxide (TMAH) (product name: NMD-3; manufactured by Tokyo Ohka Kogyo Co., Ltd.) as a developing solution, the resist film was developed at 23°C for 60 seconds.

Thereafter, the resist film was dried using a spinner, and the film thickness (nm) of the resist film was measured using Nanospec 6100A (manufactured by Nanometrics). The results are shown in Table 2.

[0394]

[Table 2]

	Undercut	Amount of side etching (μm)	Amount of film thickness loss (nm)
Example 1	Not observed	2.9	18
Example 2	Not observed	2.3	20
Example 3	Not observed	2.1	50
Example 4	Not observed	3.3	45
Example 5	Not observed	2.3	14
Example 6	Not observed	2.4	22
Example 7	Not observed	2.5	21
Example 8	Not observed	2.4	24
Example 9	Not observed	2.4	18
Example 10	Not observed	2.3	50
Comparative Example 1	Not observed	2.6	280
Comparative Example 2	Observed	4.0	12
Comparative Example 3	Not observed	5.7	30

[0395]

As seen from the results shown in Table 2, it was confirmed that, in the case where a resist pattern was formed using the resist compositions of Examples 1 to 10, film thickness loss of the pattern could be suppressed, and both dry etching resistance and wet etching resistance were satisfactory.

[0396]

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.

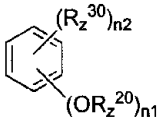
What is claimed is:

1. A resist composition which generates acid upon exposure and exhibits changed solubility in a developing solution under action of acid, the resist composition comprising:

a polymer (A1) having a structural unit (a10) containing a hydroxystyrene skeleton, and

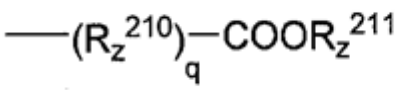
a dissolution inhibitor (Z) which suppresses dissolution in a developing solution,the dissolution inhibitor (Z) comprising a compound (Z1) having a weight average molecular weight of 3,000 or less and containing a phenolic hydroxy group in a molecule thereof, and a compound (Z2) having a weight average molecular weight of 3,000 or less and being represented by general formula (z2) shown below,

wherein the amount of the dissolution inhibitor (Z) relative to 100 parts by weight of the polymer (A1) is 30 parts by weight or less:



・・・ (z2)

wherein R_z^{20} is a group represented by general formula (z2-r-4); R_z^{30} represents a hydrogen atom or an organic group; n1 represents an integer of 1 to 6, and n2 represents an integer of 0 to 5, provided that n1+n2=6;



・・・ (z2-r-4)

wherein R_z^{210} represents a divalent aliphatic group, a divalent alicyclic group or a divalent aromatic group; R_z^{211} represents an acid dissociable group; and q represents 0 or 1.

2. The resist composition according to Claim 1, wherein the blend ratio (weight ratio) of the compound (Z1) to the compound (Z2) is Z1:Z2=75:25 to 25:75.

3. A method of forming a resist pattern, comprising:

using the resist composition of Claim 1 to form a resist film,

exposing the resist film, and

developing the exposed resist film to form a resist pattern.