

[DESCRIPTION]

[TITLE OF INVENTION]

METHOD OF FORMING RESIST PATTERN

[Technical Field]

5 [0001]

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

Priority is claimed on Japanese Patent Application No. 2017-254871, filed December 28, 2017, the content of which is incorporated herein by reference.

[Background Art]

10 [0002]

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

In recent years, in the production of semiconductor elements and liquid crystal display elements, advances in lithography techniques have led to progress in the field of pattern miniaturization. Typically, these miniaturization techniques involve shortening the wavelength (increasing the energy) of the light source for exposure. Specifically, ultraviolet radiation typified by g-line and i-line radiation has been used in the related art, 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 beams (EB), extreme ultraviolet rays (EUV), and X rays.

[0003]

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

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

For example, in a case where the developing solution is an alkali developing solution (alkali developing process), as a positive-tone chemically amplified resist composition, a composition which contains a resin component (base resin) whose solubility in an alkali developing solution is increased due to an action of an acid and an acid generator component has been typically used. In a case where a resist film formed using such a resist composition is selectively exposed at the time of forming a resist pattern, in light-exposed portions, an 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 light-exposed portions of the resist film soluble in the alkali developing solution. Thus, by conducting alkali development, and the light-unexposed portions of the resist film remain to form a positive-tone resist pattern.

On the other hand, in a case where such a chemically amplified resist composition is applied to a solvent developing process using a developing solution containing an organic solvent (organic developing solution), since the solubility in an organic developing solution is relatively decreased at the time of an increase in polarity

of the base resin, the light-unexposed portions of the resist film are dissolved and removed by the organic developing solution, and a negative-tone resist pattern in which the light-exposed portions of the resist film are remaining is formed. Such a solvent developing process for forming a negative-tone resist pattern is also referred to as a

5 "negative-tone developing process".

[0004]

Up till now, as a base resin of a chemically amplified resist composition, for example, for KrF excimer laser (248 nm), a resin having high transparency such as polyhydroxystyrene (PHS) and a resin (a PHS-based resin) in which a hydroxyl group of

10 PHS is protected by an acid dissociable and dissolution inhibiting group has been used. In addition, for example, for ArF excimer laser (193 nm), a resin (a (meth)acrylic resin) in which a hydroxyl group of a carboxy group of (meth)acrylic acid is protected by an acid dissociable and dissolution inhibiting group has been used (for example, Japanese Unexamined Patent Application, First Publication No. 2003-241385).

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

20 [0005]

In addition, a wide variety of acid generators have been proposed as the acid generator component used in the chemically amplified resist composition, and for example, onium salt-based acid generators such as iodonium salts and sulfonium salts, oxime sulfonate-based acid generators, diazomethane-based acid generators,

25 nitrobenzylsulfonate-based acid generators, iminosulfonate-based acid generators,

disulfone-based acid generators, and the like are known.

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

[0006]

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

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

[Citation List]

[Patent Literature]

[0007]

[Patent Literature 1]

Japanese Unexamined Patent Application, First Publication No. 2003-241385

[Summary of Invention]

[Technical Problem]

[0008]

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

a thick resist film having a film thickness greater than that of the related art, for example, a film thickness of 7 μm or more is formed on the surface of the processing target, a resist pattern is formed, and etching or the like is performed is included. In a case where a chemically amplified resist composition is used in this process, it becomes more difficult to maintain the sensitivity during light exposure as the film thickness of the resist increases. In a case of attempting to form a thick resist film using a conventional chemically amplified resist composition, there is a problem that a large amount of light exposure is required and thus the sensitivity is reduced. In addition, there is a problem that the resolution for development is reduced and it is difficult to obtain a desired resist pattern shape.

[0009]

The present invention has been made in consideration of the above circumstances, and an object of the present invention is to provide a method of forming a resist pattern, by which high sensitivity is exhibited and a pattern having a good shape is formed even in a case where a thick resist film having a film thickness of 7 μm or more is formed.

[Solution to Problem]

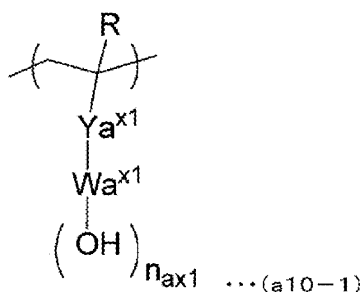
[0010]

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

That is, the method of forming a resist pattern according to one aspect of the present invention is a method of forming a resist pattern including, step (i) of forming a resist film having a film thickness of 7 μm or more on a supporting body using a resist composition, a step (ii) of exposing the resist film to light, and a step (iii) of developing the exposed resist film to form a resist pattern, in which in the resist composition, an acid

is generated upon light exposure, the solubility of the resist composition in a developing solution is changed due to an action of the acid, and a resin component (A1) having a constitutional unit (a10) represented by General Formula (a10-1), a constitutional unit (a4) including an acid non-dissociable aliphatic cyclic group, and a constitutional unit
 5 (a1) including an acid decomposable group having a polarity that is increased by an action of an acid is contained.

[0011]



[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5
 10 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. $\text{Y}^{\text{a}^{\text{x}1}}$ represents a single bond or a divalent linking group. $\text{W}^{\text{a}^{\text{x}1}}$ represents an $(n_{\text{ax}1} + 1)$ -valent aromatic hydrocarbon group. $n_{\text{ax}1}$ represents an integer of 1 to 3.]

[Advantageous Effects of Invention]

[0012]

15 According to the present invention, a method of forming a resist pattern, by which high sensitivity is exhibited and a pattern having a good shape is formed even in a case where a thick resist film having a film thickness of 7 μm or more is formed, can be provided.

[Description of Embodiments]

20 [0013]

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

The term “alkyl group” includes linear, branched or cyclic, monovalent
5 saturated hydrocarbon, unless otherwise specified. The same applies to the alkyl group in 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 some or all hydrogen atoms of
10 an alkyl group are substituted with halogen atoms. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.

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

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

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

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

[0014]

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

25 The “acrylic acid ester” indicates a compound in which the terminal hydrogen

atom of the carboxy group of acrylic acid ($\text{CH}_2=\text{CH}-\text{COOH}$) has been substituted with an organic group.

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

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

[0015]

A "constitutional unit derived from acrylamide" indicates a constitutional 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 at 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 at the α -position of acrylamide indicates the carbon atom bonded to the carbonyl group of acrylamide, unless otherwise specified.

- 5 As the substituent which substitutes the hydrogen atom bonded to the carbon atom at the α -position of acrylamide, the same substituents as those described above for the substituent ($R^{\alpha 0}$) at the α -position of the above-described α -position of the α -substituted acrylic acid ester can be exemplified.

[0016]

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

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

- As the substituent which substitutes the hydrogen atom at the α -position of
- 25 hydroxystyrene, the same substituents as those described above for the substituent at the

α -position of the above-described α -substituted acrylic acid ester can be exemplified.

[0017]

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

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

[0018]

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

Specific examples of the halogenated alkyl group as the substituent at the α -position include groups in which some or all hydrogen atoms of the above-described “alkyl group as the substituent at the α -position” are substituted with halogen atoms.
25 Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom

and, an iodine atom, and a fluorine atom is particularly preferable.

Specific examples of the hydroxyalkyl group as the substituent at the α -position include groups in which some or all hydrogen atoms of the above-described “alkyl group as the substituent at the α -position” are substituted with a hydroxyl group. The number
5 of hydroxyl groups in the hydroxyalkyl group is preferably 1 to 5, and most preferably 1.
[0019]

In the present specification and the scope of the present patent claims, asymmetric carbons may be present or enantiomers or diastereomers may be present depending on the structures of the chemical formulae. In that case, these isomers are
10 represented by one formula. These isomers may be used alone or in the form of a mixture.
[0020]

(Method of forming resist pattern)

A method of forming a resist pattern according to the present embodiment has a
15 step (i) of forming a resist film having a film thickness of 7 μm or more on a supporting body using a resist composition, a step (ii) of exposing the resist film to light, and a step (iii) of developing the exposed resist film to form a resist pattern, In the method of forming a resist pattern according to the aspect of the present invention, a specific resist composition is selected in the step (i).

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

[0021]

Step (i):

First, a specific resist composition to be described later is applied onto a
25 supporting body with a spinner or the like and is subjected to a bake (post-apply bake

(PAB)) treatment, for example, under a temperature condition of 80°C to 150°C and preferably 100°C to 150°C (more preferably more than 100°C and 150°C or less), for 40 to 120 seconds and preferably 60 to 120 seconds (more preferably 80 to 100 seconds) to form a resist film having a film thickness of 7 μm or more.

5 [0022]

Step (ii):

Following selective light exposure of the thus formed resist film, for example, by light exposure through a mask having a predetermined pattern formed thereon (mask pattern) using a light exposure apparatus or the like, baking treatment (post exposure baking (PEB)) is conducted, for example, under temperature conditions of 80°C to 150°C and preferably 90°C to 130°C, for 40 to 120 seconds and preferably 60 to 100 seconds.

[0023]

Step (iii):

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

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

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

25 [0024]

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

In this manner, a resist pattern can be formed.

[0025]

5 The supporting body is not specifically limited and a conventionally known supporting body 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,
10 aluminum, nickel, and gold.

 Further, as the supporting body, any one of the above-described supporting bodies 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
15 organic film such as a lower-layer organic film used in a multilayer resist method can be used.

 Here, the multilayer resist method is a method in which at least one layer of an organic film (lower-layer organic film) and at least one layer of a resist film (upper-layer resist film) are provided on a substrate, and a resist pattern formed on the upper-layer
20 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.

25 The multilayer resist method is classified into a method in which a double-layer

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

[0026]

The method of forming a resist pattern according to the aspect is useful in a case of forming a resist film having a high film thickness, and the film thickness of the resist film formed in the step (i) is 7 μm or more.

The film thickness of the resist film formed in the step (i) is more preferably 8 μm or more, particularly preferably 10 μm or more, and the upper limit of the film thickness is substantially 30 μm or less.

[0027]

The wavelength to be used for light exposure is not particularly limited and the light exposure can be conducted using radiation such as an ArF excimer laser, a KrF excimer laser, an F₂ excimer laser, extreme ultraviolet rays (EUV), vacuum ultraviolet rays (VUV), electron beams (EB), X-rays, and soft X-rays.

The method of forming a resist pattern according to the present aspect is a particularly suitable method in a case where the resist film is irradiated with KrF excimer laser light in the step (ii).

[0028]

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

In liquid immersion lithography, the region between the resist film and the lens

at the lowermost point of the immersion light exposure apparatus is pre-filled with a solvent (liquid immersion medium) that has a larger refractive index than the refractive index of air, and the light exposure (immersion light exposure) is conducted in this state.

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

Examples of this solvent which exhibits a refractive index that is larger than the refractive index of air but smaller than the refractive index of the resist film include
10 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, and the boiling point is preferably in a range of 70° to 180°C and more
15 preferably in a range of 80° to 160°C. A fluorine-based inert liquid having a boiling point in the above-described range is advantageous in that the removal of the immersion medium after the light 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
20 preferable. Examples of these perfluoroalkyl compounds include perfluoroalkylether compounds and perfluoroalkylamine compounds.

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

25 As the immersion medium, water is preferable in terms of cost, safety,

environment, and versatility.

[0029]

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

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

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

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

A hydrocarbon solvent consists of a hydrocarbon which may be halogenated and

does not have any substituent other than a halogen atom. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom, and a fluorine atom is preferable.

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

[0030]

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.

[0031]

Examples of ester solvents include methyl acetate, butyl acetate, ethyl acetate, isopropyl acetate, amyl acetate, isoamyl acetate, ethyl methoxyacetate, ethyl ethoxyacetate, ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene glycol monobutyl ether acetate, ethylene glycol monophenyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monopropyl ether acetate, diethylene glycol monophenyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, 2-methoxybutyl acetate, 3-methoxybutyl acetate, 4-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, 3-ethyl-3-methoxybutyl acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, 2-

ethoxybutyl acetate, 4-ethoxybutyl acetate, 4-propoxybutyl acetate, 2-methoxypentyl acetate, 3-methoxypentyl acetate, 4-methoxypentyl acetate, 2-methyl-3-methoxypentyl acetate, 3-methyl-3-methoxypentyl acetate, 3-methyl-4-methoxypentyl acetate, 4-methyl-4-methoxypentyl acetate, propylene glycol diacetate, methyl formate, ethyl formate, butyl formate, propyl formate, ethyl lactate, butyl lactate, propyl lactate, ethyl carbonate, propyl carbonate, butyl carbonate, methyl pyruvate, ethyl pyruvate, propyl pyruvate, butyl pyruvate, methyl acetoacetate, ethyl acetoacetate, methyl propionate, ethyl propionate, propyl propionate, isopropyl propionate, methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, methyl-3-methoxypropionate, ethyl-3-methoxypropionate, ethyl-3-ethoxypropionate, and propyl-3-methoxypropionate. Among these examples, as an ester solvent, butyl acetate is preferable.

[0032]

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

15 [0033]

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

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

25 [0034]

The developing treatment can 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 upon the surface of the supporting body 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 supporting body (spray method), and a method in which the developing solution is continuously ejected from a developing solution ejecting nozzle while scanning at a constant rate to apply the developing solution to the supporting body while rotating the substrate at a constant rate (dynamic dispense method).

[0035]

As the organic solvent contained in the rinse liquid used in the rinse treatment after the developing treatment in a case of a solvent developing process, any of the above-described 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 preferable.

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

Among these, 1-hexanol, 2-heptanol and 2-hexanol are preferable, and 1-hexanol and 2-hexanol are more preferable.

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

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

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

[0036]

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 supporting body while rotating it at a constant rate (rotational coating method), a method in which the supporting body is immersed in the rinse liquid for a predetermined time (dip method), and a method in which the rinse liquid is sprayed onto the surface of the supporting body (spray method).

[0037]

<Resist composition>

In the above-described method of forming a resist pattern of the present embodiment, a specific resist composition is used in the step (i).

In the specific resist composition, an acid is generated upon light exposure, the solubility of the resist composition in a developing solution is changed due to an action
5 of the acid. As the resist composition, an embodiment containing a base material component (hereinafter, also referred to as a “component (A)”) whose solubility in a developing solution is changed due to an action of an acid may be mentioned.

[0038]

The resist composition of the present embodiment is suitable for forming a resist
10 pattern that is exposed to KrF excimer laser light.

In addition, the resist composition of the present embodiment is useful as a resist agent for forming a high-thickness resist film on a supporting body and is suitable for forming a resist film having a film thickness of 7 μm or more.

[0039]

15 In a case where a resist film is formed using the resist composition according to the present embodiment and the formed resist film is subjected to a selective light exposure, an acid is generated at light-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
20 solution is not changed at light-unexposed portions of the resist film, thereby generating the difference in solubility in a developing solution between the light-exposed portions of the resist film and the light-unexposed portions. Therefore, by subjecting the resist film to development, the light-exposed portions of the resist film are dissolved and removed to form a positive-tone resist pattern in a case where the resist composition is of a
25 positive-tone, whereas the light-unexposed portions of the resist film are dissolved and

removed to form a negative-tone resist pattern in a case where the resist composition is of a negative-tone.

[0040]

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

The resist composition of the present embodiment may be a positive-tone resist
10 composition or a negative-tone resist composition.

Further, in the formation of a resist pattern, the resist composition of the present embodiment can be applied to an alkali developing process using an alkali developing solution in the developing treatment, or a solvent developing process using a developing solution containing an organic solvent (organic developing solution) in the developing
15 treatment.

That is, the resist composition of the present embodiment is a “positive-tone resist composition for an alkaline developing process” that forms a positive-tone resist pattern in an alkali developing process and is a “negative-tone resist composition for a solvent developing process” that forms a negative-tone resist pattern in a solvent
20 developing process.

[0041]

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

Specifically, the resist composition of the embodiment may (1) contain an acid generator component (B) (hereinafter, referred to as “component (B)”) that generates an acid upon light exposure; (2) have a component (A) that generates an acid upon light exposure; and (3) have a component (A) that generates an acid upon light exposure and
 5 further contains component (B).

That is, in a case of (2) or (3) described above, the component (A) becomes a “base material component which generates an acid upon light exposure and whose solubility in a developing solution is changed due to the action of the acid”. In a case where the component (A) is a base material component which generates an acid upon
 10 light exposure and whose solubility in a developing solution is changed due to the action of the acid, it is preferable that a component (A1) described below is a high molecular compound which generates an acid upon light exposure and whose solubility in a developing solution is changed due to the action of the acid. As such a high molecular compound, a copolymer having a constitutional unit that generates an acid upon light
 15 exposure can be used.

Examples of the constitutional units that generate an acid upon light exposure include, for example, known constitutional units.

The resist composition of the present embodiment is particularly preferably the case of the above (1).

20 [0042]

<<Component (A)>>

The component (A) is a base material component whose solubility in a developing solution is changed due to an action of an acid.

In the present embodiment, the “base material component” is an organic
 25 compound having a film forming ability, and an organic compound having a molecular

weight of 500 or more is preferably used. In a case where the molecular weight of the organic compound is 500 or more, the film forming ability is improved, and in addition, a nano-level resist pattern is easily formed.

The organic compounds used as the base material component are roughly
5 classified into a non-polymer and a polymer.

As the non-polymer, those having a molecular weight of 500 or more and less than 4,000 are usually used. Hereinafter, a “low molecular compound” refers to a non-polymer having a molecular weight of 500 or more and less than 4,000.

As the polymer, those having a molecular weight of 1,000 or more are usually
10 used. Hereinafter, “resin”, “high molecular compound”, or “polymer” refers to a polymer having a molecular weight of 1,000 or more.

As the molecular weight of the polymer, a weight-average molecular weight in terms of polystyrene by gel permeation chromatography (GPC) is used.

[0043]

15 As the component (A) of the resist composition of the present embodiment, a resin component (A1) (hereinafter, also referred to as a “component (A1)”) whose solubility in a developing solution is changed due to an action of an acid is included.

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

[0044]

The component (A1) in the present embodiment has a constitutional unit (a10) represented by General Formula (a10-1), a constitutional unit (a4) including an acid non-dissociable aliphatic cyclic group, and a constitutional unit (a1) including an acid
25 decomposable group having a polarity that is increased by an action of an acid. The

component (A1) may have other constitutional units as necessary in addition to the constitutional unit (a10), a constitutional unit (a4), and the constitutional unit (a1).

[0045]

In the resist composition of the present embodiment, since the constitutional unit (a1) contains an acid dissociable group, the use of the component (A1) changes the polarity of the resin component before and after light exposure and requires only an alkali developing process. Moreover, even in the solvent developing process, a good development contrast can be obtained between the light-exposed and light-unexposed portions of the resist film.

10 [0046]

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

Meanwhile, in a case of a solvent developing process, the component (A1) exhibits high solubility in an organic developing solution prior to light exposure, and in a case where acid is generated from the component (B) upon light exposure, the polarity of the component (A1) is increased by the action of the generated acid, thereby decreasing

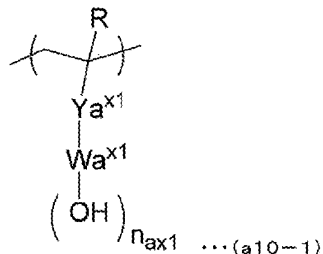
the solubility of the component (A1) in an organic developing solution. Therefore, in the formation of a resist pattern, by conducting selective light exposure of a resist film formed by applying the resist composition to a supporting body, the light-exposed portions of the resist film change from a soluble state to an insoluble state in an organic developing solution, whereas the light-unexposed portions of the resist film remain soluble and not change, and hence, a negative-tone resist pattern is formed by developing in the organic developing solution.

[0047]

· In regard to constitutional unit (a10):

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

[0048]



[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. $\text{Y}^{\text{a}^{\text{x}1}}$ represents a single bond or a divalent linking group. $\text{W}^{\text{a}^{\text{x}1}}$ represents an $(n_{\text{ax}1} + 1)$ -valent aromatic hydrocarbon group. $n_{\text{ax}1}$ represents an integer of 1 to 3.]

[0049]

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

As the alkyl group having 1 to 5 carbon atoms represented by R, a linear or

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

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

[0050]

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

Examples of the divalent linking group as $Y^{a^{x1}}$ include a divalent hydrocarbon group which may have a substituent and a divalent linking group having a hetero atom.

[0051]

· Divalent hydrocarbon group which may have substituent:

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

[0052]

·· Aliphatic hydrocarbon group as $Y^{a^{x1}}$

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

[0053]

5 ... Linear or branched aliphatic hydrocarbon group

The linear or branched aliphatic hydrocarbon group has preferably 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.

10 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 has preferably 2 to 10 carbon atoms, more preferably 3 to 6 carbon atoms, still more preferably 3 or 4 carbon atoms, and most
15 preferably 3 carbon atoms.

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

25 [0054]

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

5 [0055]

... Aliphatic hydrocarbon group containing ring in structure thereof

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

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

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

tricyclodecane, and tetracyclododecane.

[0056]

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

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

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

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

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

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

In the cyclic aliphatic hydrocarbon group, some carbon atoms constituting the ring structure thereof may be substituted with a substituent containing a hetero atom.

20 As the substituent containing a hetero atom, -O-, -C(=O)-O-, -S-, -S(=O)₂-, or -S(=O)₂-O- is preferable.

[0057]

.. Aromatic hydrocarbon group as Ya^{x1}

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

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

Specific examples of the aromatic hetero ring include a pyridine ring and a thiophene ring.

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

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

[0058]

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

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

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

[0059]

· Divalent linking group containing hetero atom

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

In a case where the divalent linking group containing a hetero atom is -C(=O)-NH-, -C(=O)-NH-C(=O)-, -NH-, or -NH-C(=NH)-, H may be substituted with a

substituent such as an alkyl group, an acyl group, or the like. The substituent (an alkyl group, an acyl group, or the like) has preferably 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms, and most preferably 1 to 5 carbon atoms.

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

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

As 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 in the alkylmethylene group is preferably a linear alkyl group having 1 to 5 carbon atoms, more preferably a linear alkyl group having 1 to 3 carbon atoms, and most preferably a methyl group.

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

preferably an integer of 1 to 5, still more preferably 1 or 2, and most preferably 1.

[0060]

As Y^{x1} , a single bond, an ester bond $[-C(=O)-O-]$, an ether bond $(-O-)$, $-C(=O)-$
 NH-, a linear or branched alkylene group, or a combination of these is preferable, and a
 5 single bond is particularly more preferable among these.

[0061]

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

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

[0062]

In Formula (a10-1), n_{ax1} represents an integer of 1 to 3, preferably 1 or 2, and
 more preferably 1.

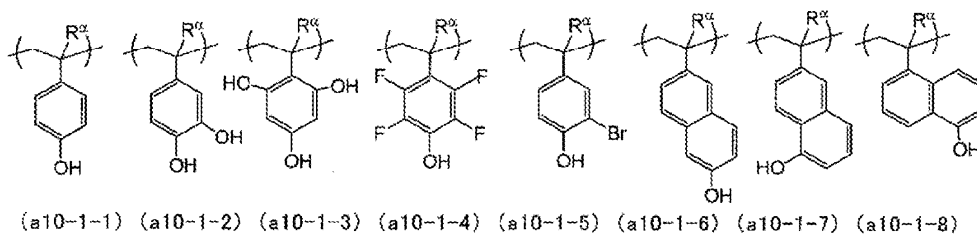
[0063]

25 Specific examples of the constitutional unit represented by General Formula

(a10-1) are shown below.

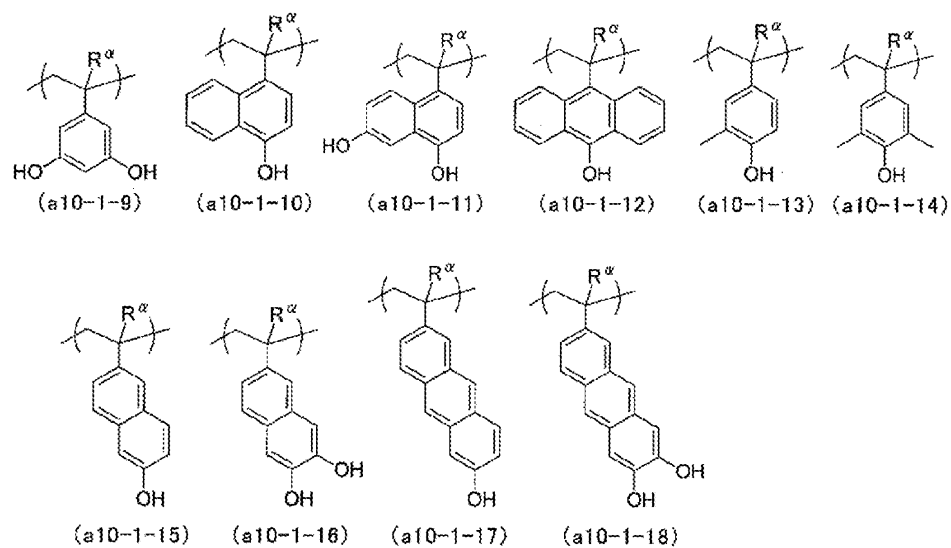
In the following formulae, R^a represents a hydrogen atom, a methyl group, or a trifluoromethyl group.

[0064]

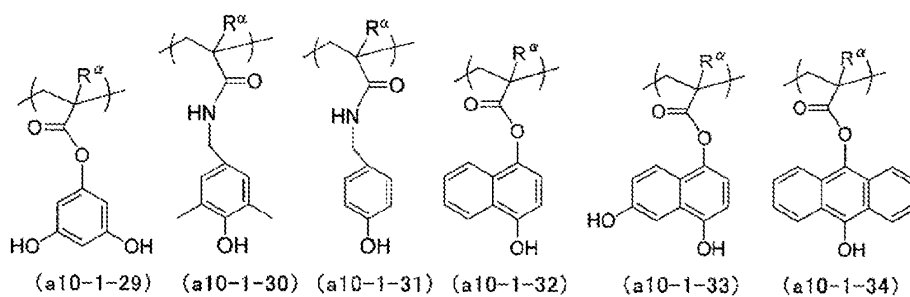
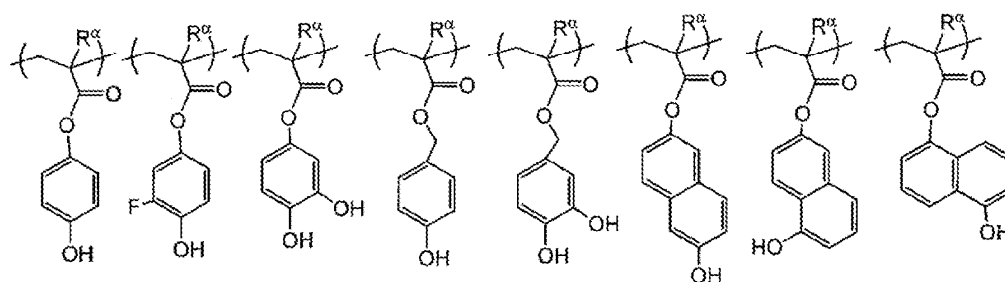


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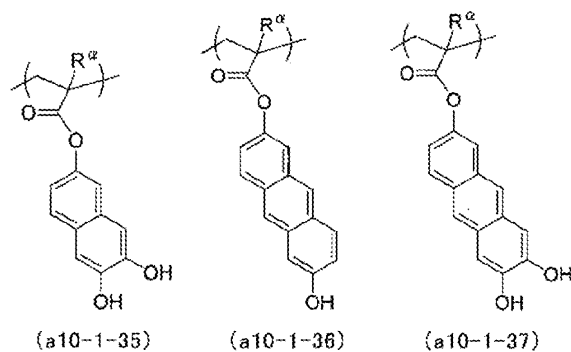
[0065]



[0066]



[0067]

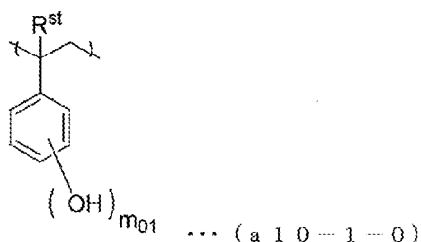


[0068]

- 5 The constitutional unit (a10) in the component (A1) may be used alone or in combination of two or more kinds thereof.

Among the above, the constitutional unit (a10) is preferably a constitutional unit including a hydroxystyrene skeleton and particularly preferably a constitutional unit represented by General Formula (a10-1-0).

10 [0069]



[In the formula, R^{st} represents a hydrogen atom or a methyl group. m_{01} represents an integer of 1 to 3.]

[0070]

5 The proportion of the constitutional unit (a10) in the component (A1) is preferably in a range of 40% to 80% by mole, more preferably in a range of 45% to 75% by mole, and particularly preferably in a range of 50% to 70% by mole with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

10 In a case where the proportion of the constitutional unit (a10) is equal to or more than the lower limit of the above preferred range, sensitivity, development characteristics, the effect of suppressing the occurrence of defects, and the like are further improved. On the other hand, in a case where the proportion of the constitutional unit (a10) is equal to or lower than the upper limit of the above preferred range, lithography
15 characteristics such as critical dimensional uniformity are further improved.

[0071]

· In regard to constitutional unit (a4):

The constitutional unit (a4) is a constitutional unit containing an acid non-dissociable aliphatic cyclic group.

20 In a case where the component (A1) has the constitutional unit (a4), the light transmittance of the resist film can be increased as compared with a case where a

component has a constitutional unit including an aromatic cyclic group. Further, the dry etching resistance of the formed resist pattern is improved, and in addition, the hydrophobicity of the component (A) is increased. The improvement in hydrophobicity contributes to the improvement in resolution, resist pattern shape, and the like,
5 particularly in the case of forming a resist pattern by a solvent developing process.

The “acid non-dissociable cyclic group” in the constitutional unit (a4) is a cyclic group that remains in the constitutional unit without being dissociated even when an acid acts in a case where the acid is generated in the resist composition by light exposure (for example, in a case where an acid is generated from the component (B) described later).

10 [0072]

The acid non-dissociable aliphatic cyclic group in the constitutional unit (a4) may be a monocyclic group, a polycyclic group, or preferably a monocyclic group.

In this case, as the monocyclic group, a group in which one or more hydrogen atoms have been removed from a monocycloalkane is preferable. The

15 monocycloalkane has more preferably 3 to 8 carbon atoms and still more preferably 5 to 8 carbon atoms, and specific examples thereof include cyclopentane, cyclohexane, and cyclooctane. In this case, a group in which one or more hydrogen atoms have been removed from a polycycloalkane is preferable as the polycyclic group. As the
20 examples thereof include adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane.

The monocyclic group and the polycyclic group each may have as a substituent, for example, a linear or branched alkyl group having 1 to 5 carbon atoms.

[0073]

25 Examples of the constitutional unit (a4) include a constitutional unit derived

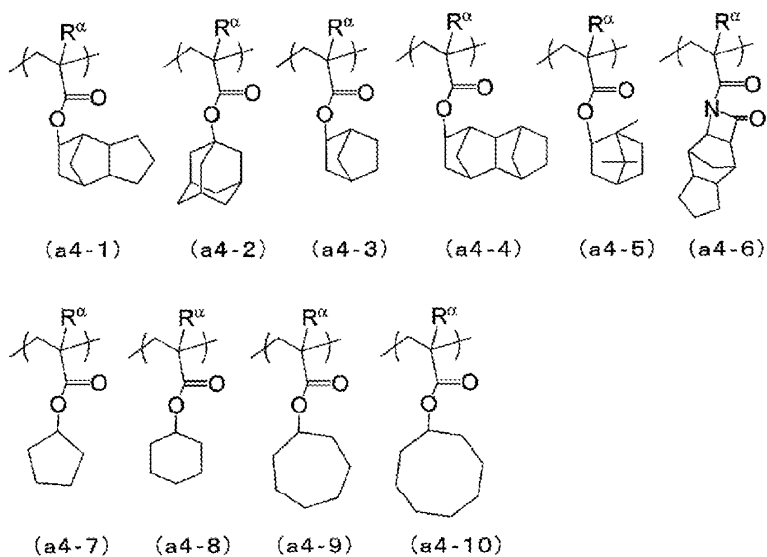
from an acrylate ester in which a hydrogen atom bonded to a carbon atom at the α -position may be substituted with a substituent and a constitutional unit derived from acrylamide, and the constitutional unit derived from an acrylate ester in which a hydrogen atom bonded to a carbon atom at the α -position may be substituted with a substituent is preferable.

[0074]

Hereinafter, specific examples of the constitutional unit (a4) will be described.

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

10 [0075]



[0076]

The constitutional unit (a4) in the component (A1) may be used alone or in combination of two or more kinds thereof.

15 Among the above, the constitutional unit (a4) is preferably a constitutional unit including an acid non-dissociable and monocyclic aliphatic cyclic group and more preferably at least one selected from the group consisting of constitutional units

represented by any of Chemical Formulae (a4-7) to (a4-10).

[0077]

The proportion of the constitutional unit (a4) in the component (A1) is preferably in a range of 1% to 50% by mole, more preferably in a range of 2% to 50% by mole, and still more preferably in a range of 5% to 45% by mole with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

By setting the proportion of the constitutional unit (a4) to be equal to or more than the lower limit of the above preferred range, the light transmittance of the resist film is further increased, and higher sensitivity and higher resolution are achieved. On the other hand, by setting the proportion of the constitutional unit (a4) to be equal to or lower than the upper limit of the preferred range, it is easy to balance with other constitutional units.

[0078]

· In regard to constitutional unit (a1):

The constitutional unit (a1) is a constitutional unit that contains an acid decomposable group whose polarity is increased due to an action of an acid.

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

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

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

preferable, a carboxy group or a hydroxyl group is more preferable, and a carboxy group is particularly preferable.

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

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

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

[0079]

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

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

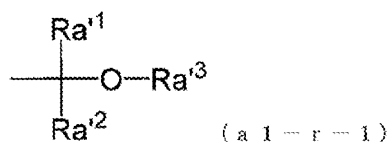
5 [0080]

· Acetal-type acid dissociable group:

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

10

[0081]



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

15

[0082]

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

20

In a case where Ra'¹ or Ra'² represents an alkyl group, examples of the alkyl group include the same alkyl groups exemplified as the substituent which may be bonded to the carbon atom at the α -position in the description on the α -substituted acrylic acid

ester. Among these, an alkyl group having 1 to 5 carbon atoms is preferable. Specific examples thereof include linear or branched alkyl groups. Specific examples of the alkyl group include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, and a neopentyl group. Among these, a methyl group or an ethyl group is preferable, and a methyl group is particularly preferable.

[0083]

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

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

15 [0084]

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

[0085]

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

25 As the aliphatic hydrocarbon group which is a monocyclic group, a group in

which one hydrogen atom has been removed from a monocycloalkane is preferable.

The monocycloalkane has preferably 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

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

[0086]

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

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

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

Specific examples of the aromatic hydrocarbon group as Ra'^3 include a group in
 25 which one hydrogen atom has been removed from the above-described aromatic

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

10 [0087]

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

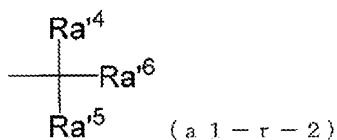
15 [0088]

· Tertiary alkyl ester-type acid dissociable group:

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

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

[0089]



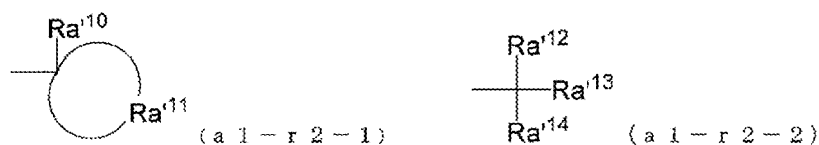
[In the formula, Ra'^4 to Ra'^6 each independently represent a hydrocarbon group, provided that Ra'^5 and Ra'^6 may be bonded to each other to form a ring.]

[0090]

- 5 Examples of the hydrocarbon group as Ra'^4 or Ra'^6 are the same as those exemplified above as Ra'^3 .

It is preferable that Ra'^4 represents an alkyl group having 1 to 5 carbon atoms. In a case where Ra'^5 to Ra'^6 are bonded to each other to form a ring, a group represented by General Formula (a1-r2-1) can be mentioned. Meanwhile, Ra'^4 to Ra'^6 are not bonded to one another and represent an independent hydrocarbon group, examples thereof include a group represented by General Formula (a1-r2-2).

[0091]



- [In the formula, Ra'^{10} represents an alkyl group having 1 to 10 carbon atoms, Ra'^{11} represents a group forming an aliphatic cyclic group together with the carbon atom to which Ra'^{10} is bonded, and Ra'^{12} to Ra'^{14} each independently represent a hydrocarbon group.]

[0092]

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

are preferable.

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

[0093]

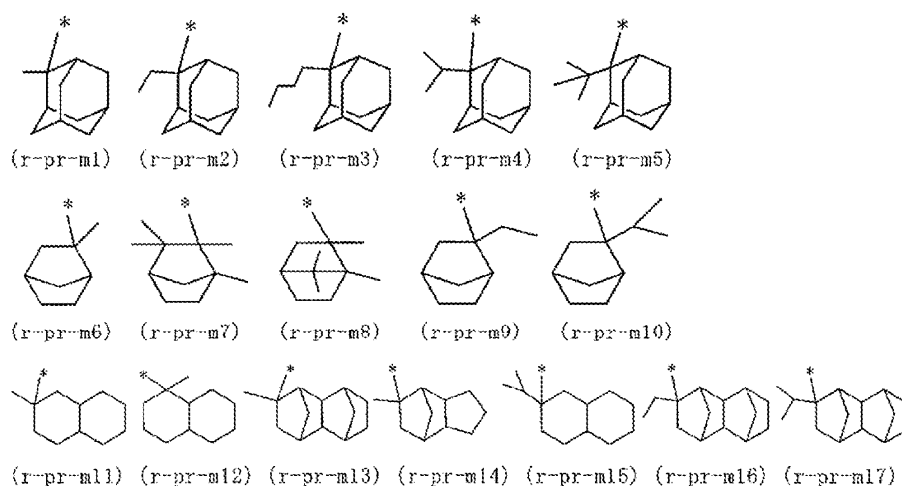
In Formula (a1-r2-2), Ra'^{12} and Ra'^{14} are preferably each independently an alkyl group having 1 to 10 carbon atoms, and the alkyl group is more preferably the group exemplified as a linear or branched alkyl group of Ra'^3 Formula (a1-r-1), still more preferably a linear alkyl group having 1 to 5 carbon atoms, and particularly preferably a methyl group or an ethyl group.

In Formula (a1-r2-2), Ra'^{13} is preferably a linear or branched alkyl group exemplified as the hydrocarbon group of Ra'^3 in Formula (a1-r-1) and an aliphatic hydrocarbon group which is a monocyclic group or a polycyclic group. Among these, the group exemplified as the aliphatic hydrocarbon group which is a monocyclic group or a polycyclic group of Ra'^3 is more preferable.

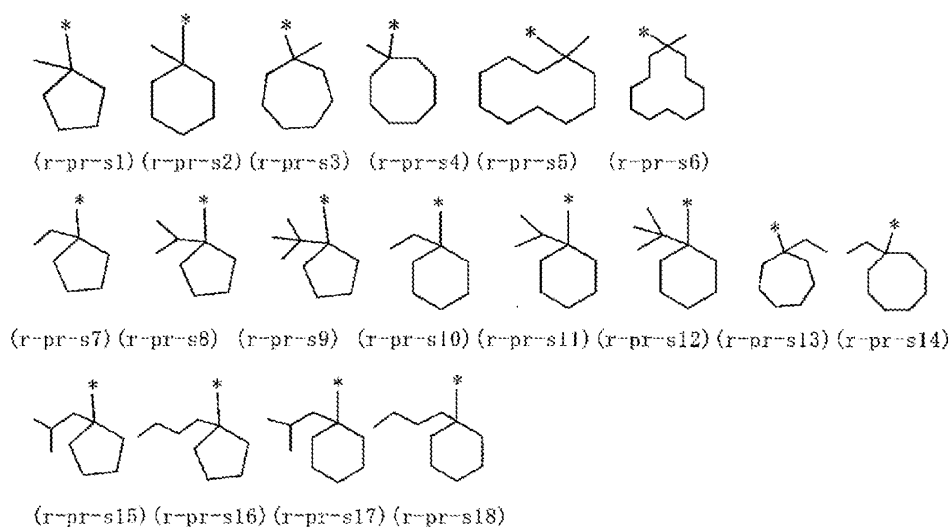
[0094]

Specific examples of the group represented by Formula (a1-r2-1) are shown below. * indicates a bond (hereinafter, the same in the present specification).

[0095]



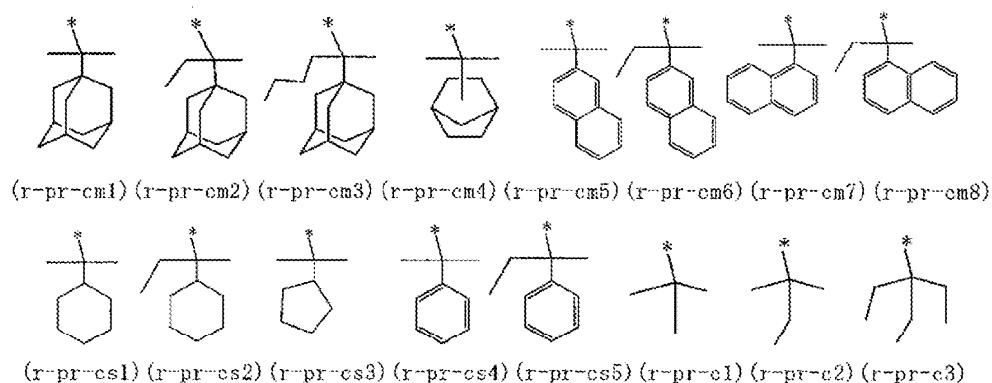
[0096]



[0097]

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

[0098]

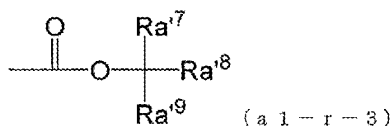


[0099]

· Tertiary alkyloxycarbonyl acid dissociable group:

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

[0100]



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

[0101]

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

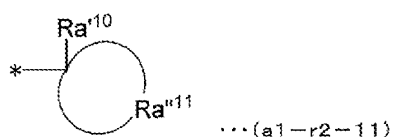
Further, the total number of carbon atoms in each alkyl group is preferably in a
 15 range of 3 to 7, more preferably in a range of 3 to 5, and most preferably 3 or 4.

[0102]

Among the above, the acid decomposable group in the constitutional unit (a1) is

preferably a group including an aliphatic cyclic group and more preferably a group which is the acid dissociable group and in which a polar group (such as a carboxy group, a hydroxyl group, an amino group, and a sulfo group) is protected, since the degradability by an action of an acid is higher. Among these, the acid decomposable group in the constitutional unit (a1) is preferably a group including an acid dissociable group represented by General Formula (a1-r2-1) is preferable, and a group including an acid dissociable group represented by General Formula (a1-r2-11) is more preferable, since the resolution is improved and a pattern having a better shape is easily formed.

[0103]



10

[In the formula, Ra'^{10} represents a hydrocarbon group having 1 to 10 carbon atoms. Ra''^{11} represents a group that forms a monocyclic aliphatic cyclic group together with the carbon atom to which Ra'^{10} is bonded. * represents a bond.]

[0104]

15 In Formula (a1-r2-11), as the alkyl group having 1 to 10 carbon atoms as Ra'^{10} , the groups exemplified as the linear or branched alkyl group as Ra'^3 in Formula (a1-r-1) are preferable.

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

20

The branched alkyl group has preferably 3 to 10 carbon atoms and more

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

5 [0105]

In Formula (a1-r2-11), preferred examples of the aliphatic cyclic group that is formed by Ra'^{11} together with a carbon atom to which Ra'^{10} is bonded include the group exemplified as the aliphatic hydrocarbon group which is a monocyclic group as Ra'^3 in Formula (a1-r-1).

10 As the aliphatic hydrocarbon group which is a monocyclic group, a group in which one hydrogen atom has been removed from a monocycloalkane is preferable. The monocycloalkane has preferably 3 to 8 carbon atoms and more preferably 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.
[0106]

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

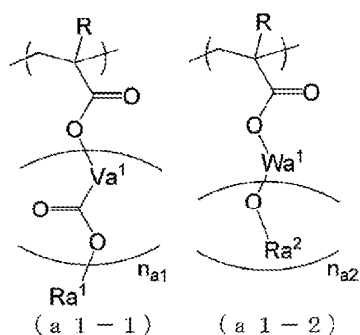
[0107]

25 Among the examples, as the constitutional unit (a1), a constitutional unit derived

from acrylic acid ester in which the hydrogen atom bonded to the carbon atom at the α -position may be substituted with a substituent is preferable.

Specific preferred examples of such a constitutional unit (a1) include constitutional units represented by General Formula (a1-1) or General Formula (a1-2) shown below.

[0108]



[In the formula, R represents a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, or a halogenated alkyl group having 1 to 5 carbon atoms. Va¹ represents a divalent hydrocarbon group which may have an ether bond, n_{a1} represents 0 to 2, and Ra¹ represents an acid dissociable group represented by Formula (a1-r-1) or (a1-r-2). Wa¹ represents a (n_{a2} + 1)-valent hydrocarbon group, n_{a2} represents 1 to 3, and Ra² represents an acid dissociable group represented by Formula (a1-r-1) or (a1-r-3)]

[0109]

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

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

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

[0110]

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

10 [0111]

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

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

[0112]

The linear or branched aliphatic hydrocarbon group has preferably 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 $[-(CH_2)_5-]$.

25 As the branched aliphatic hydrocarbon group, a branched alkylene group is

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

[0113]

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

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

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

25 cyclohexane. As the polycyclic alicyclic hydrocarbon group, a group in which two

hydrogen atoms have been removed from a polycycloalkane is preferable. As the polycycloalkane, a group having 7 to 12 carbon atoms is preferable. Specific examples of the polycycloalkane include adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane.

5 [0114]

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

The aromatic hydrocarbon group has preferably 3 to 30 carbon atoms, more preferably 5 to 30 carbon atoms, still more preferably 5 to 20 carbon atoms, particularly
10 preferably 6 to 15 carbon atoms, and most preferably 6 to 10 carbon atoms. Here, the number of carbon atoms in a substituent is not included in the number of carbon atoms.

Specific examples of the aromatic ring 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 some
15 carbon atoms constituting the above-described aromatic hydrocarbon rings have been substituted with hetero atoms. Examples of the hetero atom in the aromatic hetero rings include an oxygen atom, a sulfur atom, and a nitrogen atom.

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

group) has preferably 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and particularly preferably 1 carbon atom.

[0115]

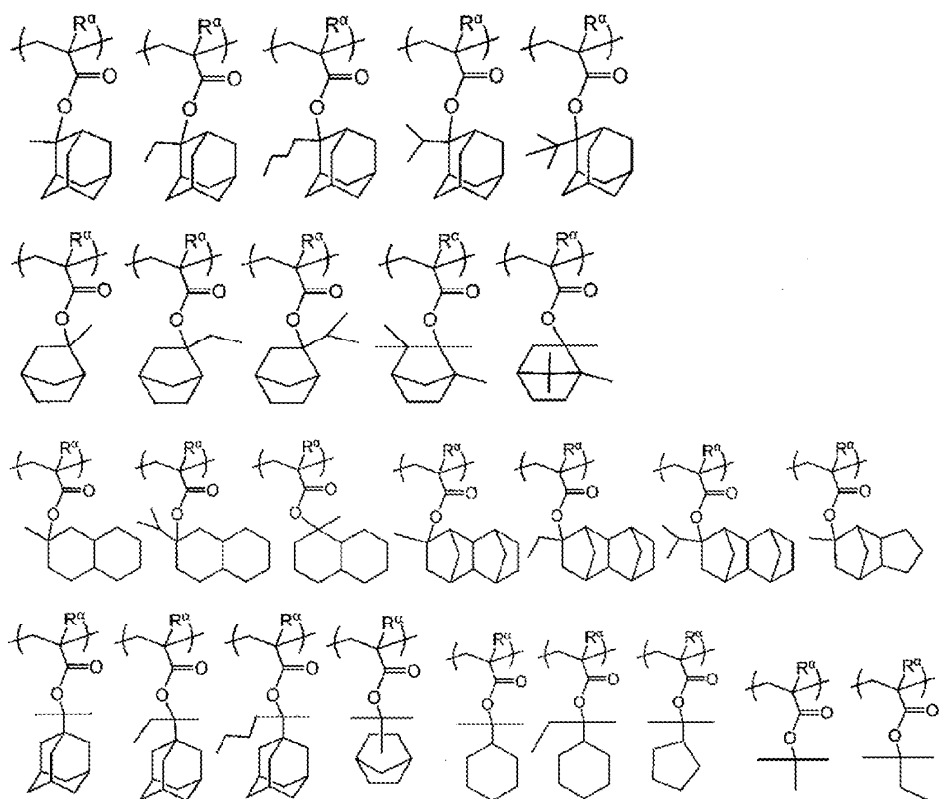
In Formula (a1-2), the $(n_{a2}+1)$ -valent hydrocarbon group as W^{a1} may be an
 5 aliphatic hydrocarbon group or an aromatic hydrocarbon group. The aliphatic
 hydrocarbon group indicates a hydrocarbon group that has no aromaticity, and may be
 saturated or unsaturated. In general, it is preferable that the aliphatic hydrocarbon group
 is saturated. Examples of the aliphatic hydrocarbon group include a linear or branched
 aliphatic hydrocarbon group, an aliphatic hydrocarbon group containing a ring in the
 10 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.

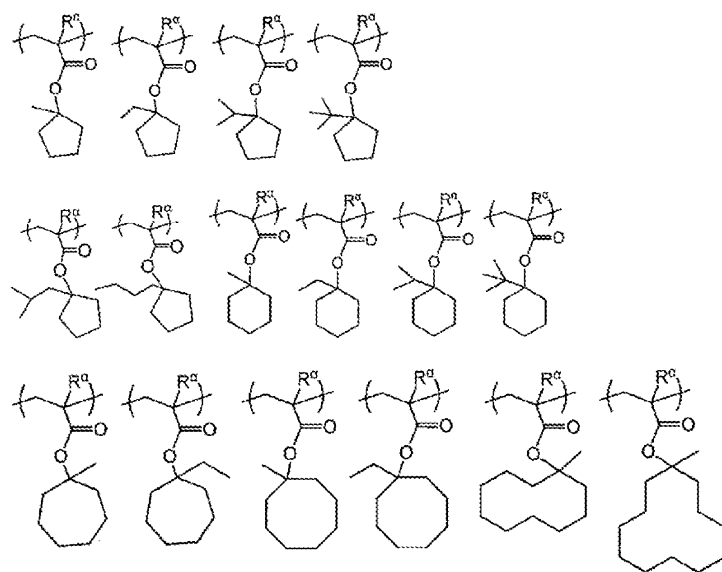
[0116]

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

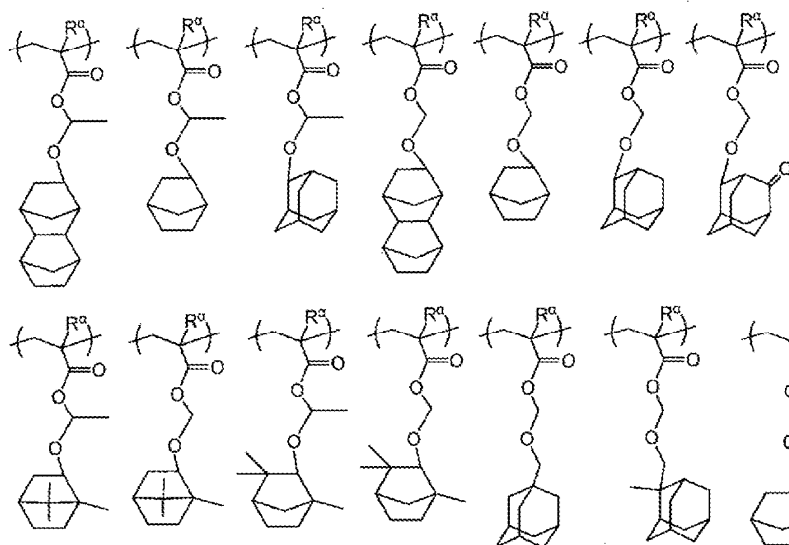
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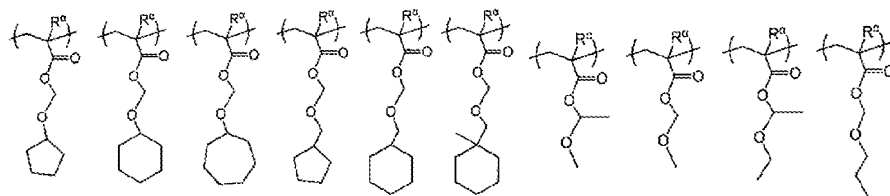
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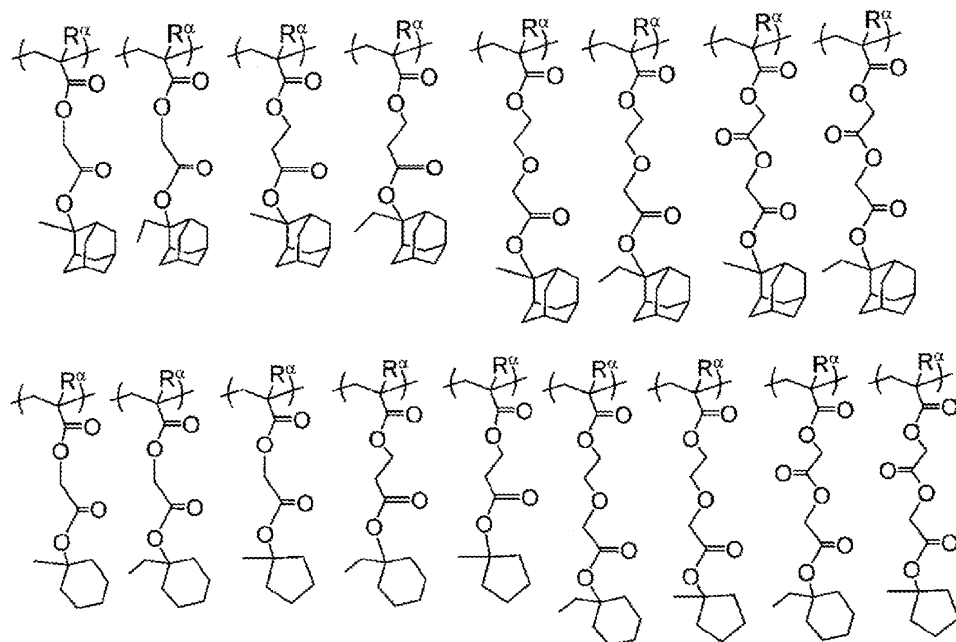
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[0120]



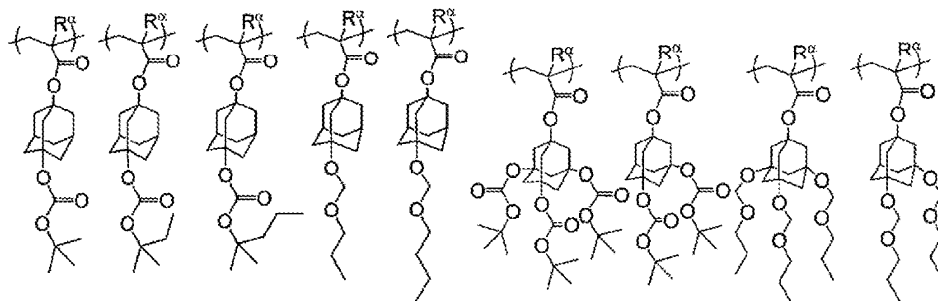
[0121]



[0122]

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

[0123]



5

[0124]

As the constitutional unit (a1), among above, a constitutional unit represented by General Formula (a1-1) is more preferable, and the constitutional unit which is represented by General Formula (a1-1) and in which Ra^1 is an acid dissociable group represented by Formula (a1-r2-11) is particularly preferable.

10

[0125]

The constitutional unit (a1) included in the component (A1) may be used alone or two or more kinds thereof.

The proportion of the constitutional unit (a1) in the component (A1) is preferably in a range of 5% to 20% by mole, more preferably in a range of 7% to 20% by mole, and still more preferably in a range of 10% to 20% by mole with respect to the all constitutional units (100% by mole) constituting the component (A1).

15

By setting the proportion of the constitutional unit (a1) to be equal to or greater than the lower limit of the above preferred range, a resist pattern can be easily obtained, the resolution is further improved, and a pattern having a good shape is easily formed.

20

By setting the proportion of the constitutional unit (a1) to be equal to or lower than the upper limit of the above-described preferable range, the constitutional unit (a1) and other constitutional units can be balanced.

[0126]

5 · In regard to other constitutional units:

The component (A1) may have other constitutional units as necessary in addition to the constitutional unit (a10), a constitutional unit (a4), and the constitutional unit (a1).

Examples of other constitutional units include: a constitutional unit (a2)
 10 containing a lactone-containing cyclic group, a -SO₂-containing cyclic group, or a carbonate-containing cyclic group; a constitutional unit (a3) (here, a constitutional unit corresponding to the constitutional unit (a1) or a constitutional unit (a2) is excluded) containing a polar group-containing aliphatic hydrocarbon group; and a constitutional unit derived from styrene or a derivative thereof.

15 [0127]

·· Constitutional unit (a2)

The component (A1) may have, as necessary, a constitutional unit (a2) containing a lactone-containing cyclic group, a -SO₂--containing cyclic group, or a carbonate-containing cyclic group, in addition to the constitutional unit (a10), the
 20 constitutional unit (a4) and the constitutional unit (a1).

In a case where the component (A1) is used for forming a resist film, the lactone-containing cyclic group, the -SO₂--containing cyclic group, or the carbonate-containing cyclic group in the constitutional unit (a2) is effective for improving the adhesiveness of the resist film to the substrate. Further, by having the constitutional
 25 unit (a2), in the alkali developing process, the solubility of the resist film in an alkali

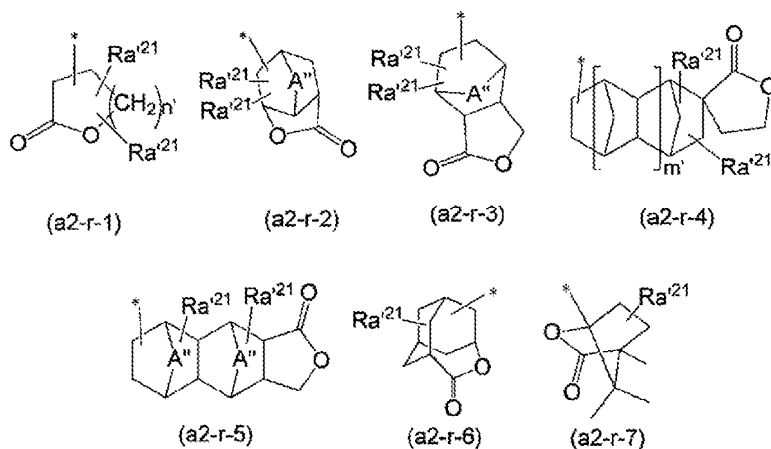
developing solution during development is enhanced.

[0128]

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

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

[0129]



[In the formulae, each Ra'^{21} independently represents a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, -COOR'', -OC(=O)R'', a hydroxyalkyl group, or a cyano group. R'' represents a

hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group, or a -SO₂--containing cyclic group. A'' represents an oxygen atom, a sulfur atom, or an alkylene group having 1 to 5 carbon atoms, which may contain an oxygen (-O-) atom or a sulfur atom (-S-). n' represents an integer of 0 to 2, and m' is 0 or 1]

[0130]

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

The alkoxy group as Ra'²¹ is preferably an alkoxy group having 1 to 6 carbon atoms.

Further, the alkoxy group is preferably a linear or branched alkoxy group. Specific examples of the alkoxy groups include a group formed by linking the above-described alkyl group exemplified as the alkyl group represented by Ra'²¹ to an oxygen atom (-O-).

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

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

[0131]

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

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

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

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

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

- The carbonate-containing cyclic group as R'' has the same definition as that for the carbonate-containing cyclic group described below. Specific examples of the
- 25 carbonate-containing cyclic group include groups represented by General Formulae (ax3-

r-1) to (ax3-r-3).

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

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

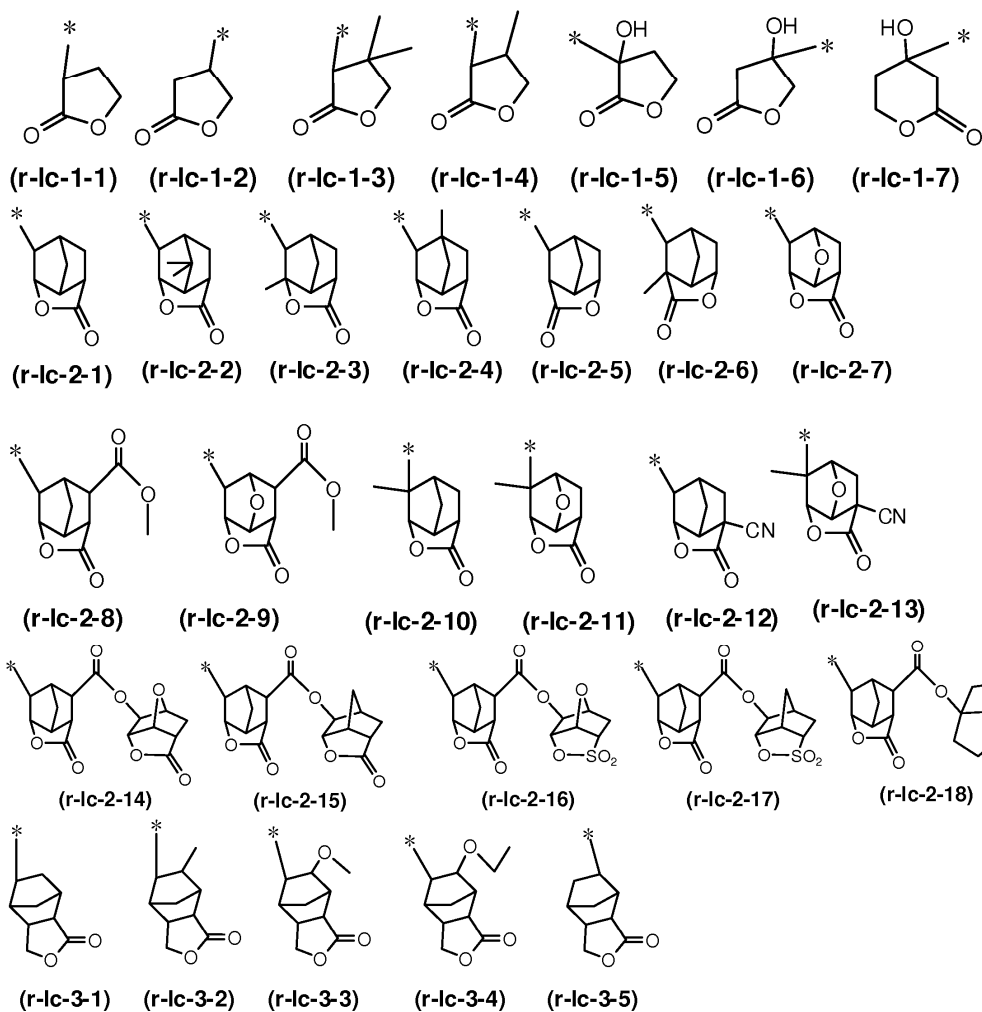
[0132]

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

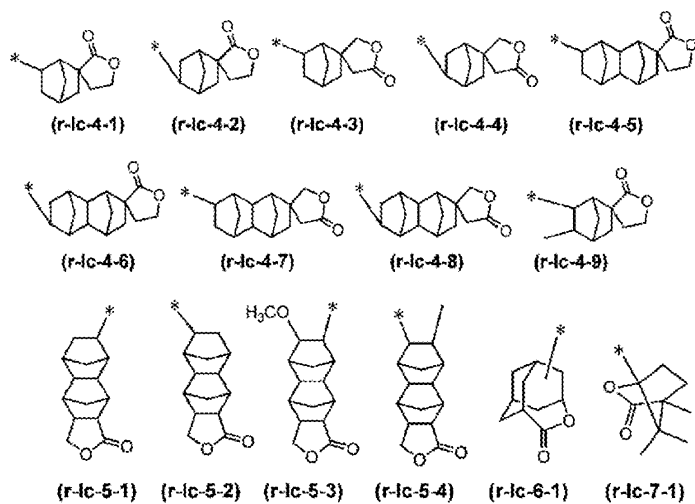
[0133]

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

[0134]



5 [0135]



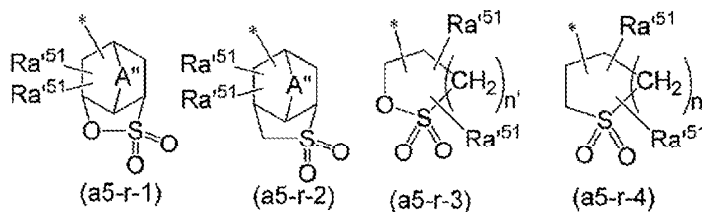
[0136]

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

As the -SO₂--containing cyclic group, a cyclic group containing -O-SO₂- in the ring skeleton thereof, in other words, a cyclic group containing a sultone ring in which -O-S- in the -O-SO₂- group forms a part of the ring skeleton thereof is particularly preferable.

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

15 [0137]



[In the formulae, Ra'⁵¹'s each independently represent a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, -COOR'', -OC(=O)R'', a hydroxyalkyl group, or a cyano group. Ra'' represents a hydrogen atom, an alkyl group, a lactone-containing cyclic group, a carbonate-containing cyclic group, or a -SO₂--containing cyclic group. A'' represents an alkylene group having 1 to 5 carbon atoms, which may contain an oxygen atom or a sulfur atom, an

oxygen atom, or a sulfur atom.

n' represents an integer of 0 to 2.]

[0138]

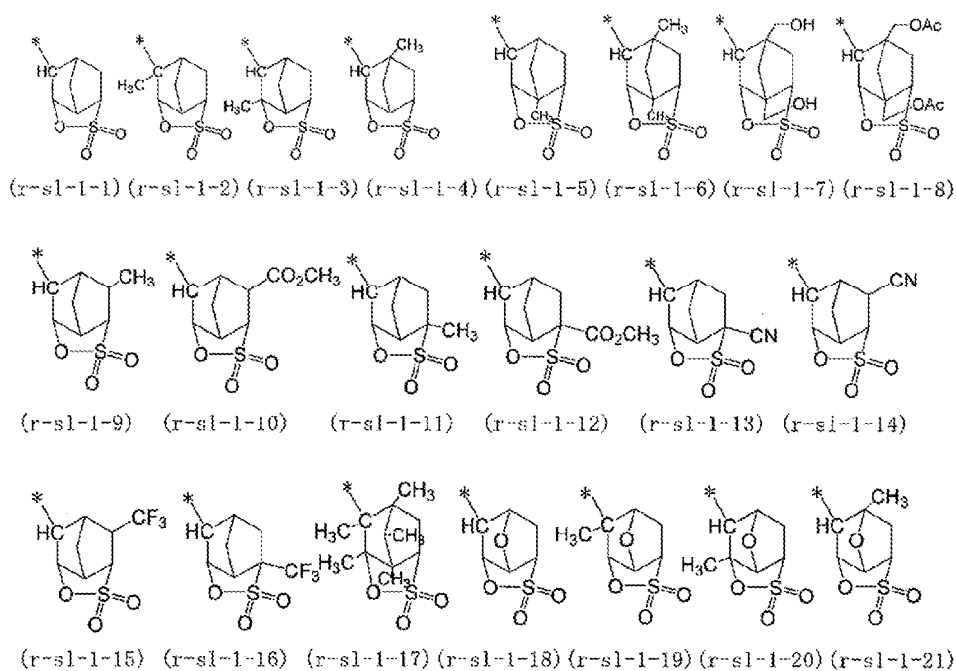
In General Formulae (a5-r-1) and (a5-r-2), A'' has the same definition as that for

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

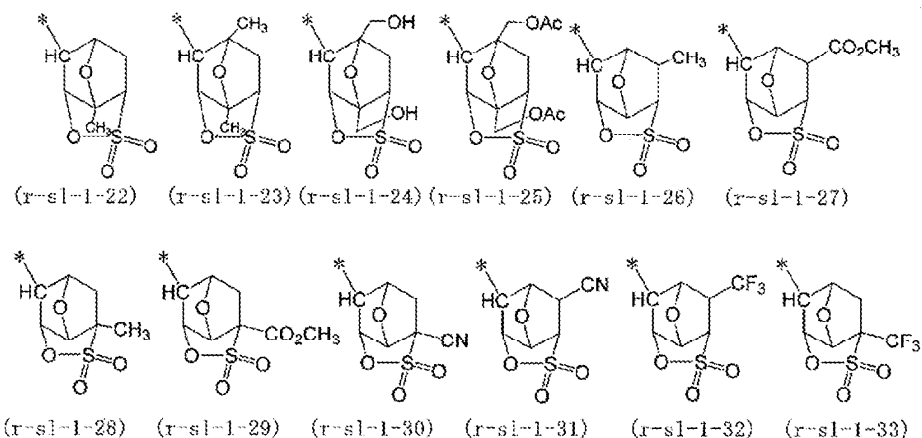
Examples of the alkyl group, the alkoxy group, the halogen atom, the halogenated alkyl group, -COOR'', -OC(=O)R'', and the hydroxyalkyl group as Ra'⁵¹ include the same groups as those described above in the explanation of Ra'²¹ in General Formulae (a2-r-1) to (a2-r-7).

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

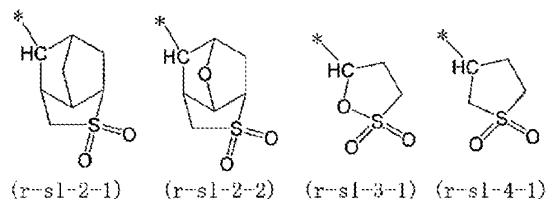
[0139]



15 [0140]



[0141]

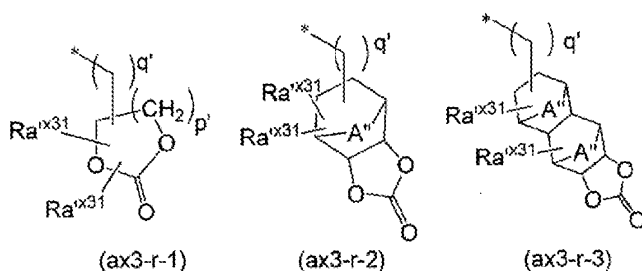


[0142]

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

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

15 [0143]



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

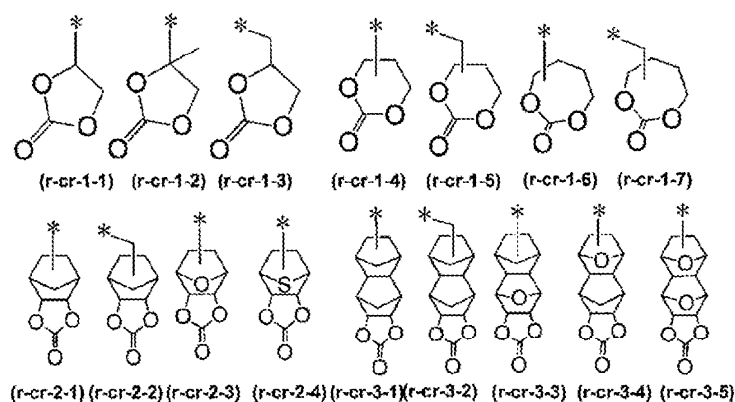
[0144]

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

Examples of the alkyl group, the alkoxy group, the halogen atom, the halogenated alkyl group, $-COOR''$, $-OC(=O)R''$, and the hydroxyalkyl group as Ra^{x31} include the same groups as those described above in the explanation of Ra^{x21} in General Formulae (a2-r-1) to (a2-r-7).

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

[0145]

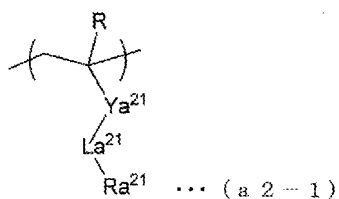


[0146]

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

Specific preferred examples of such a constitutional unit (a2) include constitutional units represented by General Formula (a2-1) shown below.

[0147]



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

[0148]

In Formula (a2-1), R has the same definition as described above.

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

[0149]

In Formula (a2-1), the divalent linking group as Y^{a21} is not particularly limited, and suitable examples thereof include a divalent hydrocarbon group which may have a substituent and a divalent linking group having hetero atoms.

10 [0150]

Examples of the divalent hydrocarbon group as Y^{a21} include the same groups as those described for the divalent hydrocarbon group as V^{a1} in Formula (a1-1). Examples of the substituents which the divalent hydrocarbon group as Y^{a21} may have include an alkyl group having 1 to 5 carbon atoms, an alkoxy group, a halogen atom, a halogenated alkyl group having 1 to 5 carbon atoms, a hydroxyl group, and a carbonyl group.

[0151]

Preferred examples of the divalent hydrocarbon group as Y^{a21} , which contains a hetero atom, 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, an acyl group, or the like), -S-, -S(=O)₂-, -S(=O)₂-O-, and a group represented by General Formula: - Y^{21} -O- Y^{22} -, - Y^{21} -O-, - Y^{21} -C(=O)-O-, -C(=O)-O- Y^{21} -, -[Y^{21} -C(=O)-O]_m- Y^{22} -, - Y^{21} -O-C(=O)- Y^{22} - or - Y^{21} -S(=O)₂-O- Y^{22} - [in the formulae, Y^{21} and Y^{22} each independently represent a divalent hydrocarbon group which may have a substituent, O represents an oxygen atom, and m'' represents an integer of 0 to 3].

25 In a case where the divalent linking group containing a hetero atom is -C(=O)-

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

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

10 described divalent linking group.

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

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

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

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

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

25 to 8, more preferably an integer of 1 to 5, still more preferably 1 or 2, and most

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

[0152]

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

[0153]

In Formula (a2-1), La^{21} represents $-O-$, $-COO-$, $-CON(R')-$, $-OCO-$, $-CONHCO-$
or $-CONHCS-$.

R' represents a hydrogen atom or a methyl group.

10 In a case where La^{21} represents $-O-$, Ya^{21} does not represent $-CO-$.

[0154]

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

Preferred examples of the lactone-containing cyclic group, the $-SO_2-$ --containing
15 cyclic group, and the carbonate-containing cyclic group as 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 examples, Ra^{21} represents preferably a lactone-containing cyclic
20 group or a $-SO_2-$ --containing cyclic group and more preferably a group represented by
General Formula (a2-r-1), (a2-r-2), (a2-r-6), or (a5-r-1). 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 more preferable.

[0155]

25 The constitutional unit (a2) included in the component (A1) may be used alone

or two or more kinds thereof.

In a case where the component (A1) has the constitutional unit (a2), the proportion of the constitutional unit (a2) in the component (A1) is preferably in a range of 1% to 80% by mole, more preferably in a range of 3% to 70% by mole, still more preferably in a range of 5% to 60% by mole, and even still more preferably in a range of 10% to 50% by mole with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

In a case where the proportion of the constitutional unit (a2) is equal to or greater than the lower limit of the above-described preferable range, the effect obtained by allowing the component (A1) to contain the constitutional unit (a2) can be satisfactorily achieved. On the contrary, in a case where the proportion of the constitutional unit (a2) is equal to or lower than the upper limit of the above-described preferable range, the constitutional unit (a2) and other constitutional units can be balanced, and various lithography characteristics and pattern shape are improved.

[0156]

.. Constitutional unit (a3)

The component (A1) may further have, as necessary, a constitutional unit (a3) containing a polar group-containing aliphatic hydrocarbon group (here, a constitutional unit corresponding to any of the constitutional unit (a0), the constitutional unit (a1), or the constitutional unit (a2) is excluded), in addition to the constitutional unit (a10), the constitutional unit (a4), and the constitutional unit (a1).

In a case where the component (A1) has the constitutional unit (a3), the hydrophilicity of the component (A) is increased, which contributes to an improvement in resolution.

[0157]

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

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

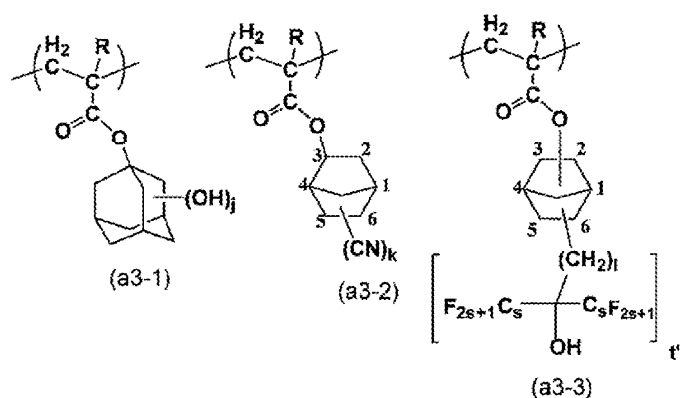
- Among the examples, constitutional units derived from acrylic acid ester that includes an aliphatic polycyclic group containing a hydroxyl group, cyano group, carboxy group, or a hydroxyalkyl group in which some hydrogen atoms of the alkyl
- 15 group have been substituted with fluorine atoms are particularly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

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

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

As the constitutional unit (a3), in a case where the hydrocarbon group in the polar group-containing aliphatic hydrocarbon group is a linear or branched hydrocarbon group having 1 to 10 carbon atoms, a constitutional unit derived from hydroxyethyl ester of acrylic acid is preferable, and in a case where the hydrocarbon group is a polycyclic group, a constitutional unit represented by Formula (a3-1), a constitutional unit represented by Formula (a3-2), and a constitutional unit represented by Formula (a3-3) are preferable.

15 [0159]



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

[0160]

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

It is preferable that j represents 1, and it is particularly preferable that the hydroxyl group is bonded to the 3-position of the adamantyl group.

[0161]

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

[0162]

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

[0163]

The constitutional unit (a3) included in the component (A1) may be used alone or two or more kinds thereof.

20 In a case where the component (A1) has the constitutional unit (a3), the proportion of the constitutional unit (a3) in the component (A1) is preferably in a range of 1% to 50% by mole, more preferably in a range of 3% to 40% by mole, still more preferably in a range of 5% to 30% by mole, and particularly preferably in a range of 10% to 30% by mole with respect to the total amount (100% by mole) of all
25 constitutional units constituting the component (A1).

By setting the proportion of the constitutional unit (a3) to be equal to or lower than the lower limit, the resolution in forming a resist pattern is further improved. On the other hand, by setting the proportion of the constitutional unit (a3) to be equal to or lower than the upper limit, it is easy to balance with other constitutional units.

5 [0164]

.. Constitutional unit (constitutional unit (st)) derived from styrene or its derivative

The term “styrene” is a concept including those obtained by substituting a hydrogen atom of styrene and a hydrogen atom at the α -position of styrene with other
10 substituents such as an alkyl group and a halogenated alkyl group. The alkyl group as the substituent herein includes an alkyl group having 1 to 5 carbon atoms, and the halogenated alkyl group as the substituent includes a halogenated alkyl group having 1 to 5 carbon atoms.

Examples of the “styrene derivatives” include those obtained by bonding a
15 substituent to a benzene ring of styrene in which a hydrogen atom at the α -position may be substituted with a substituent.

Further, the α -position (carbon atom at the α -position) indicates the carbon atom having the benzene ring bonded thereto, unless otherwise specified.

The term “constitutional unit derived from styrene” or “constitutional unit
20 derived from a styrene derivative” indicates a constitutional unit formed by cleavage of an ethylenic double bond of styrene or a styrene derivative.

The constitutional unit (st) included in the component (A1) may be used alone or two or more kinds thereof.

In a case where the component (A1) has the constitutional unit (st), the
25 proportion of the constitutional unit (st) is preferably in a range of 1% to 30% by mole

and more preferably in a range of 3% to 20% by mole with respect to the total amount (100% by mole) of all constitutional units constituting the component (A1).

[0165]

In the resist composition of the present embodiment, the resin component as the
5 component (A1) has the constitutional unit (a10), the constitutional unit (a4), and the constitutional unit (a1) and may use a single polymer or two or more kinds of polymers in combination.

Preferred examples of the component (A1) include a copolymer having the constitutional unit (a10), the constitutional unit (a4), and the constitutional unit (a1).

10 Among these, a copolymer composed of the unit (a10), the constitutional unit (a4), and the constitutional unit (a1) is particularly preferable.

[0166]

The weight-average molecular weight (M_w) (in terms of polystyrene determined by gel permeation chromatography (GPC)) of the component (A1) is preferably in a
15 range of 5,000 to 30,000, more preferably in a range of 6,000 to 25,000, and still more preferably in a range of 10,000 to 20,000.

In a case where the M_w of the component (A1) is equal to or lower than the upper limit of the preferred range, it is easy to suppress the viscosity of the resist composition from becoming too high. In addition, there is sufficient solubility in a
20 resist solvent when used as a resist, and in a case where the solubility is equal to or greater than the lower limit of the above preferred range, a resist film having a high film thickness is easily formed. In addition, the dry etching resistance and the cross-sectional shape of the resist pattern is improved.

Further, the dispersity (M_w/M_n) of the component (A1) is not particularly
25 limited, but is preferably in a range of 1.0 to 4.0, more preferably in a range of 1.0 to 3.0,

and particularly preferably in a range of 1.5 to 2.5. Further, M_n represents the number average molecular weight.

[0167]

The component (A1) can be produced, for example, by dissolving a monomer
5 from which the constitutional unit (a10) (a monomer in which at least a part of hydrogen atoms in the hydroxyl group bonded to the benzene ring are protected) is derived, a monomer from which the constitutional unit (a4) is derived, and a monomer from which a constitutional unit (a1) is derived, and, as necessary, a monomer from which another constitutional unit is derived in a polymerization solvent, adding a radical polymerization
10 initiator such as azobisisobutyronitrile (AIBN) and dimethyl azobisisobutyrate (for example, V-601) to the resultant mixture to perform polymerization, and then performing the deprotection reaction.

Further, a $-C(CF_3)_2-OH$ group may be introduced into the terminal of the component (A1) during the polymerization using a chain transfer agent such as $HS-CH_2-$
15 $CH_2-CH_2-C(CF_3)_2-OH$ together. As described above, a copolymer into which a hydroxyalkyl group, formed by substitution of some hydrogen atoms in the alkyl group with fluorine atoms, has been introduced is effective for reducing development defects and reducing line edge roughness (LER: uneven irregularities of a line side wall).

[0168]

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

The proportion of the component (A1) in the component (A) is preferably 25% by mass or greater, more preferably 50% by mass or greater, still more preferably 75% by mass or greater, and may be 100% by mass with respect to the total mass of the
25 component (A). In a case where the proportion of the component (A1) is equal to or

greater than the lower limit of the above preferred range, it is easy to form a resist pattern having a good shape, high sensitivity, high resolution, excellent critical dimension uniformity (CDU) in the supporting body surface (Shot), and other excellent lithography characteristics.

5 [0169]

The component (A) of the resist composition of the present embodiment is a resin component whose solubility in a developing solution is changed due to an action of an acid and may include another component other than the component (A1).

In the resist composition of the present embodiment, the content of the
10 component (A) may be appropriately adjusted according to the thickness of a resist film intended to be formed.

[0170]

<<Other component>>

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

[0171]

20 In regard to acid generator component (B)

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

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

used.

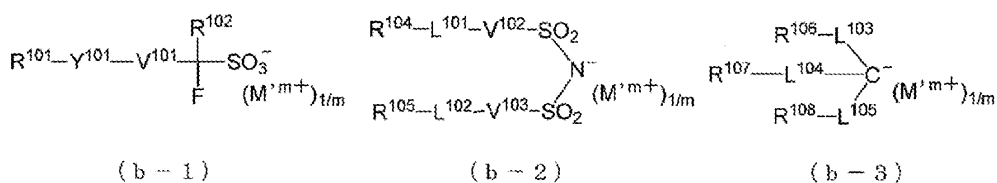
Examples of these acid generators are numerous and include onium salt-based acid generators such as iodonium salts and sulfonium salts; oxime sulfonate-based acid generators; diazomethane-based acid generators such as bisalkyl or bisaryl sulfonyl
 5 diazomethanes and poly(bis-sulfonyl)diazomethanes;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

Among these, it is preferable to use an onium salt-based acid generator.

[0172]

As the onium salt-based acid generators, for examples, a compound represented
 10 by General Formula (b-1) (hereinafter, also referred to as "component (b-1)"), a compound represented by General Formula (b-2) (hereinafter, also referred to as "component (b-2)"), or a compound represented by General Formula (b-3) (hereinafter, also referred to as "component (b-3)") can be used.

[0173]



15

[In the formulae, R¹⁰¹ and R¹⁰⁴ to R¹⁰⁸ each independently represent a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent. R¹⁰⁴ and R¹⁰⁵
 may be bonded to each other to form a ring.

20

R¹⁰² represents a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms. Y¹⁰¹ represents a single bond or a divalent linking group containing an oxygen

atom. V^{101} to V^{103} each independently represent a single bond, an alkylene group, or a fluorinated alkylene group. L^{101} and L^{102} each independently represent a single bond or an oxygen atom. L^{103} to L^{105} each independently represent a single bond, -CO- or -SO₂-. m represents an integer of 1 or greater, and M'^{m+} represents an m-valent onium cation.]

[0174]

{ Anion moiety }

· Anion moiety of component (b-1)

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

[0175]

Cyclic group which may have substituent:

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

[0176]

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

Specific examples of the aromatic ring contained in the aromatic hydrocarbon group as R¹⁰¹ include benzene, fluorene, naphthalene, anthracene, phenanthrene, biphenyl, or an aromatic hetero ring in which some carbon atoms constituting any of these aromatic rings have been substituted with hetero atoms. Examples of the hetero atom in the aromatic hetero rings include an oxygen atom, a sulfur atom, and a nitrogen atom.

Specific examples of the aromatic hydrocarbon group as R¹⁰¹ include a group in which one hydrogen atom has been removed from the above-described aromatic ring (an aryl group such as a phenyl group or a naphthyl group) and a group in which one hydrogen atom in the aromatic ring has been substituted with an alkylene group (an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, 1-naphthylethyl group, or a 2-naphthylethyl group). The alkylene group (an alkyl chain in the arylalkyl group) has preferably 1 to 4 carbon atoms, more preferably 1 or 2 carbon atoms, and particularly preferably 1 carbon atom.

[0177]

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

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

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

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

[0178]

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

[0179]

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

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 $[-(\text{CH}_2)_5-]$.

As the branched aliphatic hydrocarbon group, a branched alkylene group is preferred, and specific examples thereof include alkylalkylene groups, for example, alkylmethylene groups such as $-\text{CH}(\text{CH}_3)-$, $-\text{CH}(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2-$, -

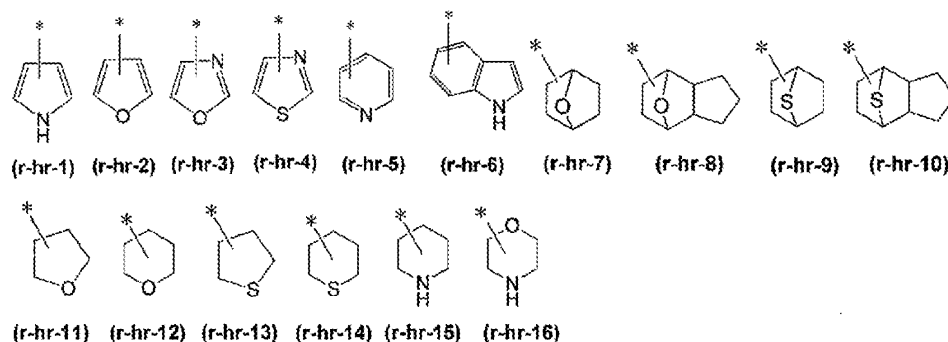
- 5 $\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_3)-$, and $-\text{C}(\text{CH}_2\text{CH}_3)_2-$; alkylethylene groups such as $-\text{CH}(\text{CH}_3)\text{CH}_2-$, $-\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2\text{CH}_2-$,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

[0180]

The cyclic hydrocarbon group as R^{101} may contain a hetero atom such as a hetero ring. Specific examples thereof include lactone-containing cyclic groups represented by General Formulae (a2-r-1) to (a2-r-7), the $-\text{SO}_2-$ -containing cyclic group

15 represented by General Formulae (a5-r-1) to (a5-r-4), and other heterocyclic groups represented by Chemical Formulae (r-hr-1) to (r-hr-16).

[0181]



[0182]

- 20 Examples of the substituent for the cyclic group as R^{101} include an alkyl group,

an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, a carbonyl group, and a nitro group.

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

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

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

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

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

[0183]

Chain-like alkyl group which may have substituent:

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

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

pentadecyl group, a hexadecyl group, an isohexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl group, an icosyl group, a hencicosyl group, and a docosyl group.

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

10 [0184]

Chain-like alkenyl group which may have substituent:

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

Among the 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 particularly preferable.

[0185]

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

25 [0186]

Among the 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. More specific examples of the cyclic hydrocarbon group include a phenyl group, a naphthyl group, a group in which one or more hydrogen atoms have been removed from a polycycloalkane, a lactone-containing cyclic group represented by any of General Formulae (a2-r-1) to (a2-r-7), and a $-SO_2$ -containing cyclic group represented by any of General Formulae (a5-r-1) to (a5-r-4).

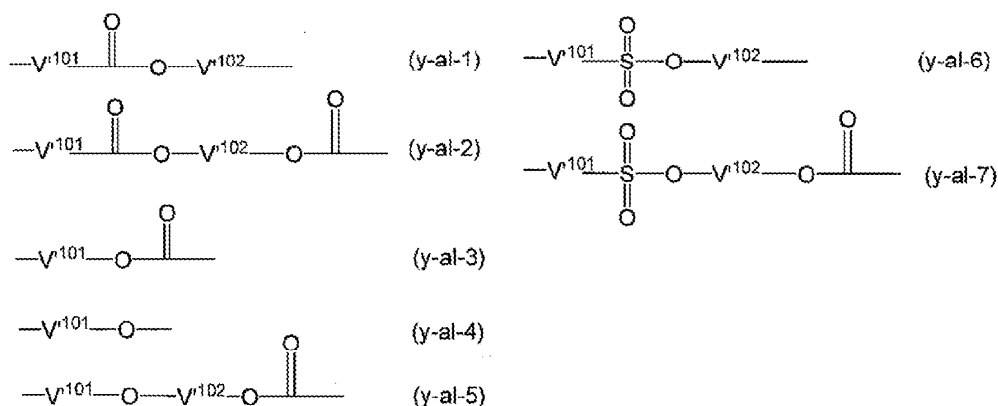
[0187]

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

In a case where Y^{101} represents a divalent linking group containing an oxygen atom, Y^{101} may contain an atom other than an oxygen atom. Examples of atoms other than an oxygen atom include a carbon atom, a hydrogen atom, a sulfur atom, and a nitrogen atom.

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

[0188]



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

5 [0189]

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

[0190]

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

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

15

group $[-CH_2CH_2CH_2CH_2CH_2-]$.

Further, a part of methylene group in the alkylene group as V^{101} and V^{102} may be substituted with a divalent aliphatic cyclic group having 5 to 10 carbon atoms. The aliphatic cyclic group is preferably a divalent group in which one hydrogen atom has been removed from the cyclic aliphatic hydrocarbon group (a monocyclic alicyclic hydrocarbon group or a polycyclic alicyclic hydrocarbon group) as R^{101} in Formula (b-1), and a cyclohexylene group, a 1,5-adamantylene group, or a 2,6-adamantylene group is more preferable.

[0191]

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

[0192]

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

20 [0193]

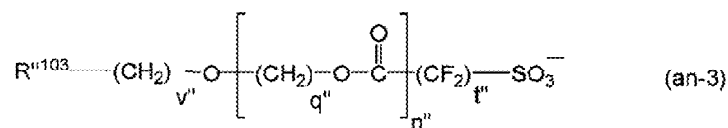
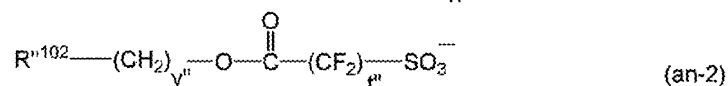
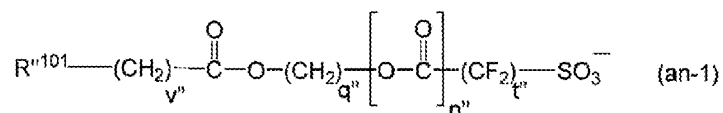
In Formula (b-1), R^{102} represents a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms. R^{102} represents preferably a fluorine atom or a perfluoroalkyl group having 1 to 5 carbon atoms and more preferably a fluorine atom.

[0194]

25 As a specific example of the anion moiety for the component (b-1), in a case

where Y^{101} represents a single bond, a fluorinated alkylsulfonate anion such as a trifluoromethanesulfonate anion or a perfluorobutanesulfonate anion can be exemplified; and in a 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 exemplified.

5 [0195]



[In the formula, $R^{''101}$ represents an aliphatic cyclic group which may have a substituent, a group represented by each of the 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 each of General Formulae (a2-r-1) to (a2-r-7), or a $-SO_2-$ -containing cyclic group represented by each of General Formulae (a5-r-1) to (a5-r-4); $R^{''103}$ represents an aromatic cyclic group which may have a substituent, an aliphatic cyclic group which may have a substituent, or a chain alkenyl group which may have a substituent; and v'' 's each independently represent an integer of 0 to 3, q'' 's each independently represent an integer of 1 to 20, t'' is an integer of 1 to 3, and n'' is 0 or 1.]

[0196]

As the aliphatic cyclic group as $R^{''101}$, $R^{''102}$, and $R^{''103}$ which may have a substituent, the same groups as the cyclic aliphatic hydrocarbon group as R^{101} described above are preferable. As the substituent, the same groups as the substituents which may

substitute the cyclic aliphatic hydrocarbon group as R^{101} can be exemplified.

[0197]

As the aromatic cyclic group as 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. As the substituent, the same groups as the substituents which may substitute the aromatic hydrocarbon group as R^{101} can be exemplified.

[0198]

As the chain-like alkyl group as R'^{101} which may have a substituent, the same groups exemplified as the chain-like alkyl groups represented by R^{101} are preferable.

As the chain-like alkenyl group as R'^{103} which may have a substituent, the same groups exemplified as the chain-like alkenyl groups represented by R^{101} are preferable.

[0199]

· Anion moiety of component (b-2)

In Formula (b-2), R^{104} and R^{105} each independently represent a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent or a chain-like alkenyl group which may have a substituent, and has the same definition as that for R^{101} in Formula (b-1). R^{104} and R^{105} may be bonded to each other to form a ring.

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

The chain-like alkyl group has preferably 1 to 10 carbon atoms, more preferably 1 to 7 carbon atoms, and still more preferably 1 to 3 carbon atoms. It is preferable that the number of carbon atoms in the chain-like alkyl group as R^{104} and R^{105} is small

because the solubility in a solvent for a resist is also excellent in the range of the number of carbon atoms. Further, in the chain-like alkyl group as R^{104} and R^{105} , it is preferable that the number of hydrogen atoms substituted with fluorine atoms is as large as possible because the acid strength increases and the transparency to high energy radiation of 200 nm or less or electron beams is improved.

The proportion of fluorine atoms in the chain-like alkyl group, that is, the fluorination ratio is preferably in a range of 70% to 100% and more preferably in a range of 90% to 100%, and it is most preferable that the chain-like alkyl group is a perfluoroalkyl group in which all hydrogen atoms are substituted with fluorine atoms.

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

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

15 [0200]

· Anion moiety of component (b-3)

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

20

L^{103} to L^{105} each independently represent a single bond, -CO-, or -SO₂-.

[0201]

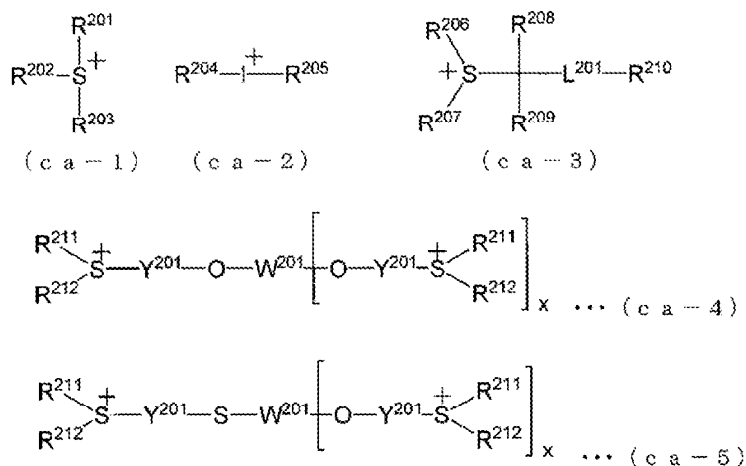
{ Cation moiety }

In Formulae (b-1), (b-2), and (b-3), m is an integer of 1 or more. M^{m+} is an m-valent onium cation, and a sulfonium cation or an iodonium cation is suitably mentioned.

25

For example, M^{m+} is particularly preferably an organic cation represented by any of General Formulae (ca-1) to (ca-5).

[0202]



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

[0203]

- 15 Examples of the aryl group as R^{201} to R^{207} , R^{211} , and R^{212} include an unsubstituted aryl group having 6 to 20 carbon atoms, and a phenyl group or a naphthyl group is preferable.

The alkyl group as R^{201} to R^{207} , R^{211} , and R^{212} is a chain-like or cyclic alkyl

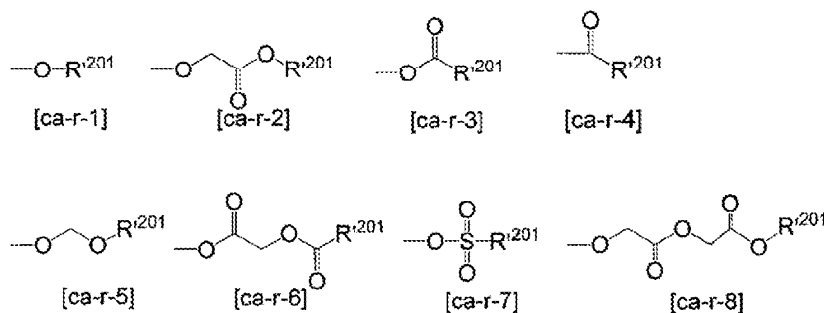
group, and the number of carbon atoms thereof is preferably in a range of 1 to 30.

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

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

- 5 R^{212} include an alkyl group, a halogen atom, a halogenated alkyl group, a carbonyl group, a cyano group, an amino group, an aryl group, and groups represented by Formulae (ca-r-1) to (ca-r-8) shown above.

[0204]



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

[0205]

Examples of the cyclic group which may have a substituent, the chain-like alkyl

- 15 group which may have a substituent, and the chain-like alkenyl group which may have a substituent as R'^{201} are the same as those represented by R^{101} in Formula (b-1), and examples of the cyclic group which may have a substituent and the chain-like alkyl group which may have a substituent are the same as those exemplified as the acid dissociable group represented by Formula (a1-r-2).

20 [0206]

R^{201} to R^{203} , R^{206} and R^{207} , and R^{211} and R^{212} are bonded to each other to form a ring with a sulfur atom in the formula, these groups may be bonded to one another via a hetero atom such as a sulfur atom, an oxygen atom or a nitrogen atom, or a functional group such as a carbonyl group, -SO-, -SO₂-, -SO₃-, -COO-, -CONH- or -N(R_N)- (here, R_N represents an alkyl group having 1 to 5 carbon atoms). As a ring to be formed, a ring containing the sulfur atom in the formula in the ring skeleton thereof is preferably a 3- to 10-membered ring and most preferably a 5- to 7-membered ring including the sulfur atom. Specific examples of the ring to be formed include a thiophene ring, a thiazole ring, a benzothiophene ring, a thianthrene ring, a benzothiophene ring, a dibenzothiophene ring, a 9H-thioxanthene ring, a thioxanthone ring, a thianthrene ring, a phenoxathiin ring, a tetrahydrothiophenium ring, and a tetrahydrothiopyranium ring.

[0207]

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

[0208]

R^{210} represents an alkyl group which may have a substituent, an alkenyl group which may have a substituent, or a -SO₂-containing cyclic group which may have a substituent.

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

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

The -SO₂--containing cyclic group as R^{210} which may have a substituent includes a group which is the same as the -SO₂--containing cyclic group represented by

any of General Formulae (a5-r-1) to (a5-r-4). Among these, a “-SO₂--containing polycyclic group” is preferable, and a group represented by General Formula (a5-r-1) is more preferable.

[0209]

- 5 In Formulae (ca-4) and (ca-5), Y²⁰¹'s each independently represent an arylene group, an alkylene group, or an alkenylene group.

Examples of the arylene group as Y²⁰¹ include groups in which one hydrogen atom has been removed from an aryl group exemplified as the aromatic hydrocarbon group represented by R¹⁰¹ in Formula (b-1).

- 10 Examples of the alkylene group and alkenylene group as Y²⁰¹ include groups in which one hydrogen atom has been removed from the chain-like alkyl group or the chain-like alkenyl group as R¹⁰¹ in Formula (b-1).

[0210]

In Formulae (ca-4) and (ca-5), x represents 1 or 2.

- 15 W²⁰¹ represents an (x + 1)-valent linking group, that is, a divalent or trivalent linking group.

- As the divalent linking group represented by W²⁰¹, a divalent hydrocarbon group which may have a substituent is preferable, and as examples thereof, the same divalent hydrocarbon groups (which may have a substituent) as those described above represented by Ya²¹ in General Formula (a2-1) can be exemplified. The divalent linking group as W²⁰¹ may be linear, branched or cyclic, and cyclic is more preferable. Among these, an arylene group having two carbonyl groups, each bonded to the terminal thereof is preferable. Examples of the arylene group include a phenylene group and a naphthylene group, and a phenylene group is particularly preferable.

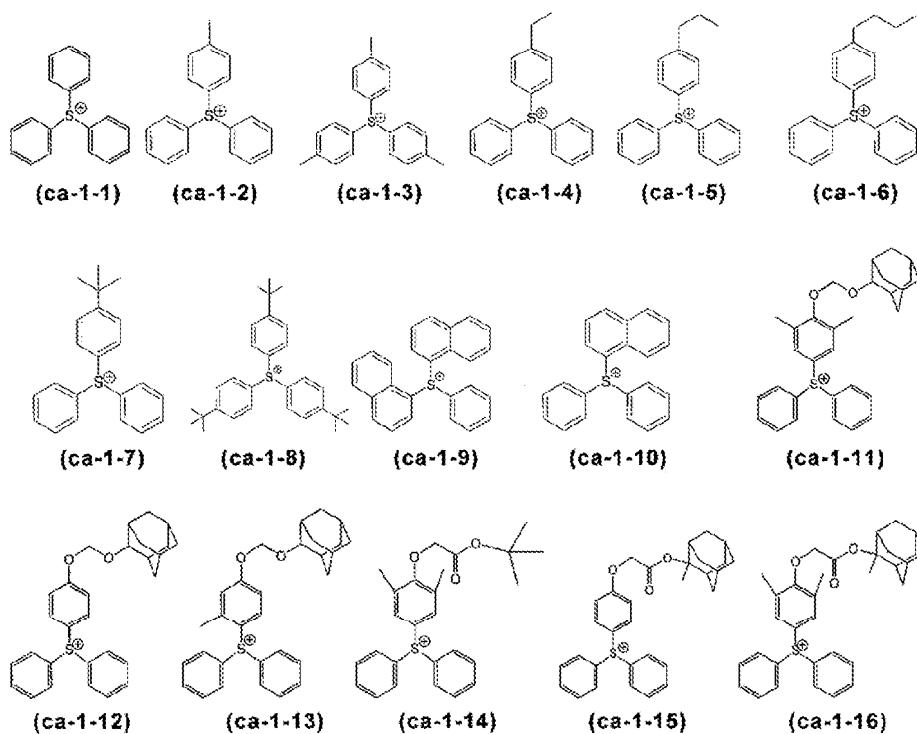
- 25 As the trivalent linking group as W²⁰¹, a group in which one hydrogen atom has

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

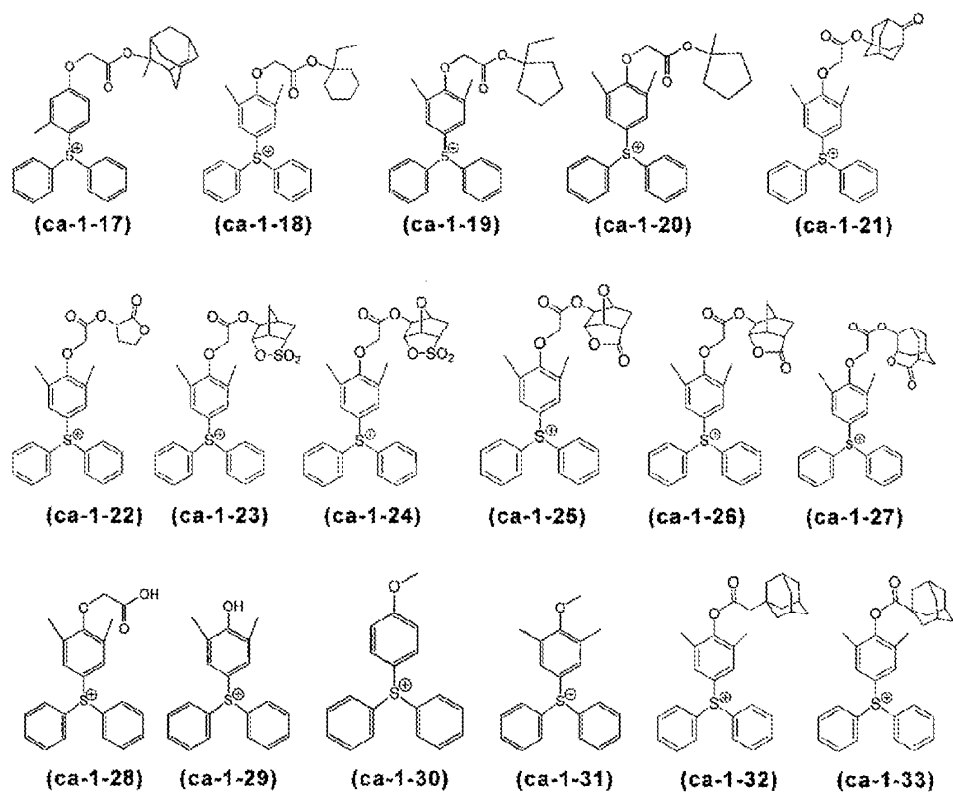
5 [0211]

Specific examples of suitable cations represented by Formula (ca-1) include cations represented by Formulae (ca-1-1) to (ca-1-129) shown below.

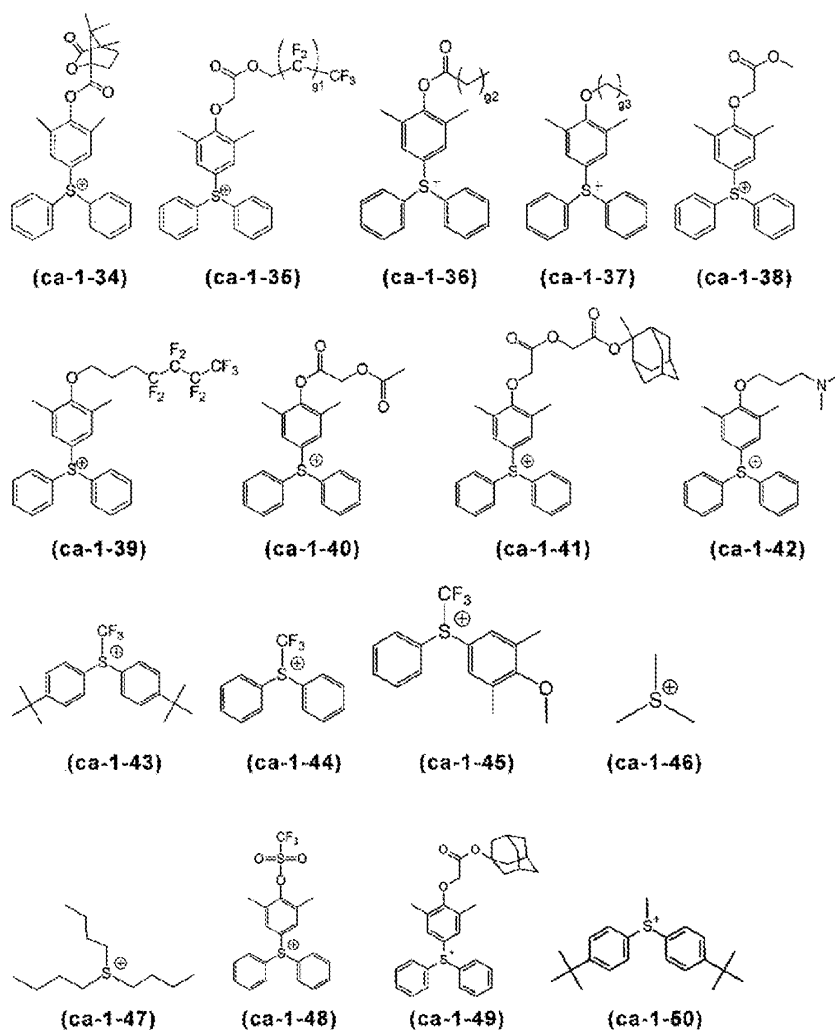
[0212]



10 [0213]

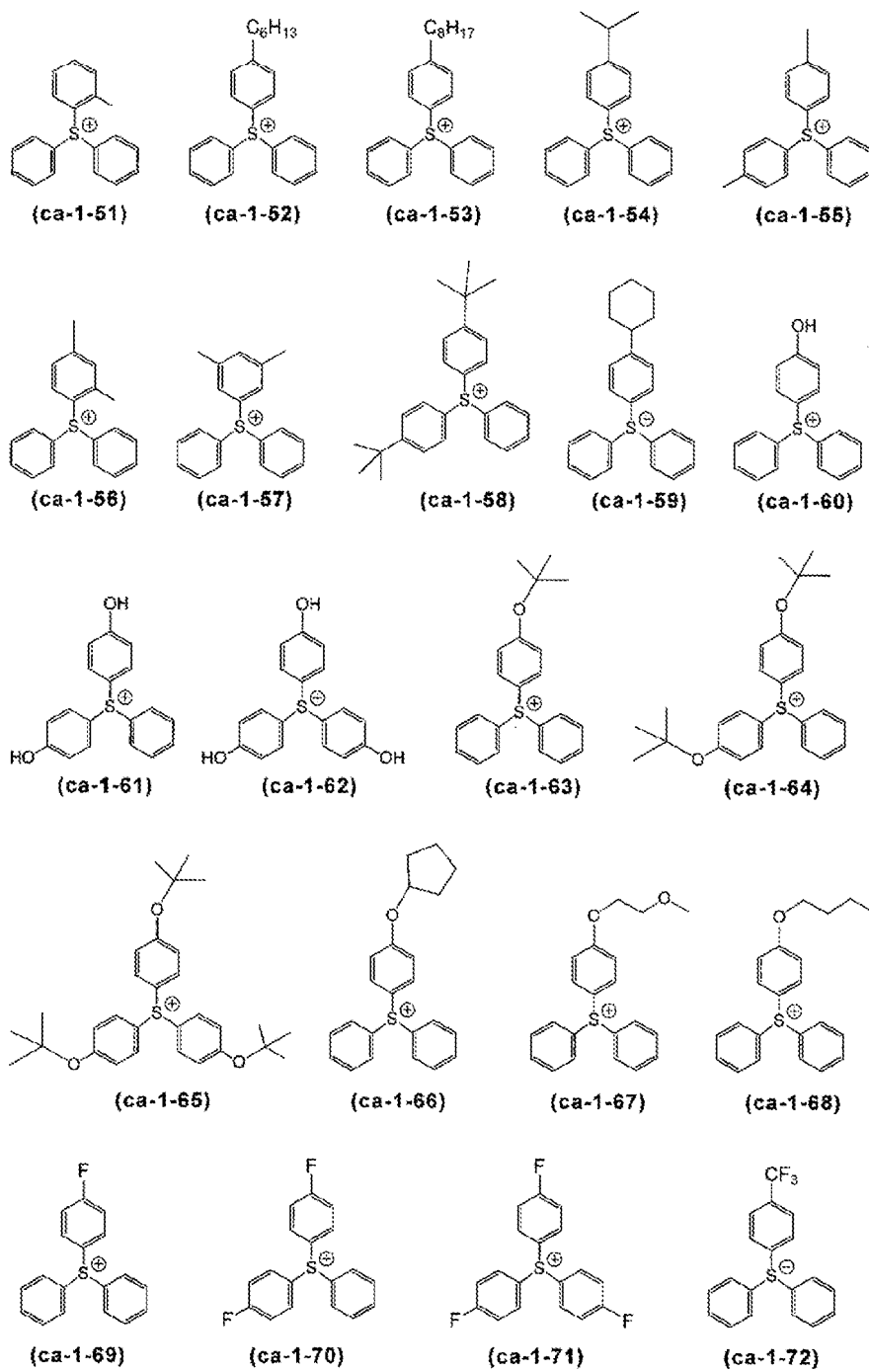


[0214]

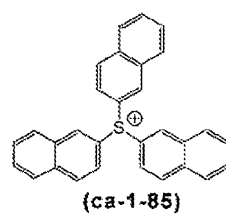
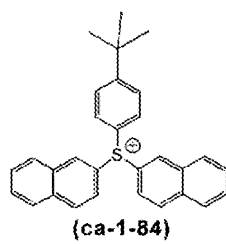
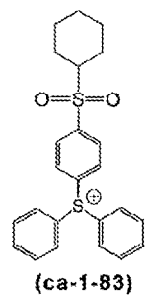
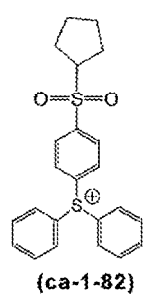
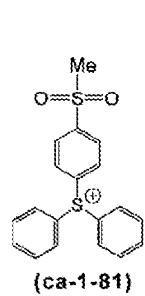
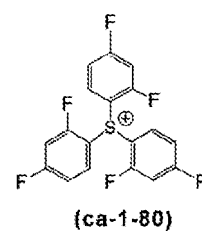
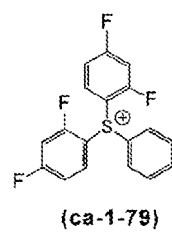
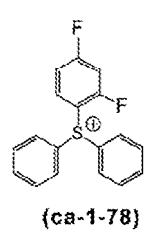
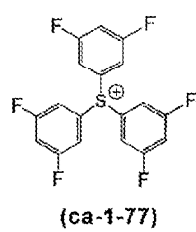
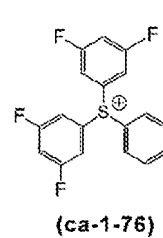
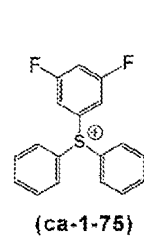
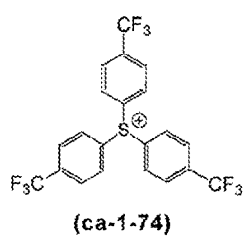
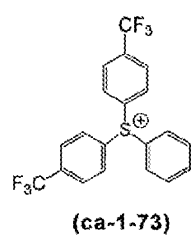


[In the formula, g1, g2, and g3 represent the number of repetitions, g1 is an integer of 1 to 5, g2 is an integer of 0 to 20, and g3 is an integer of 0 to 20.]

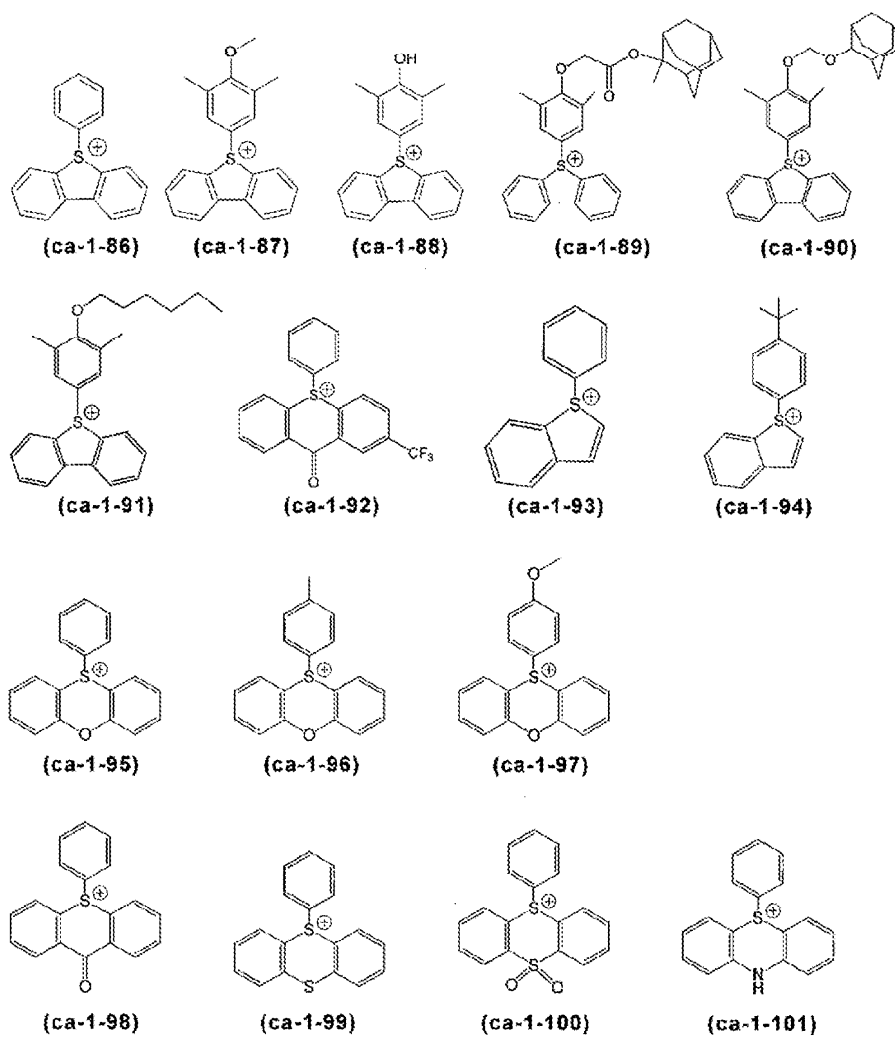
[0215]



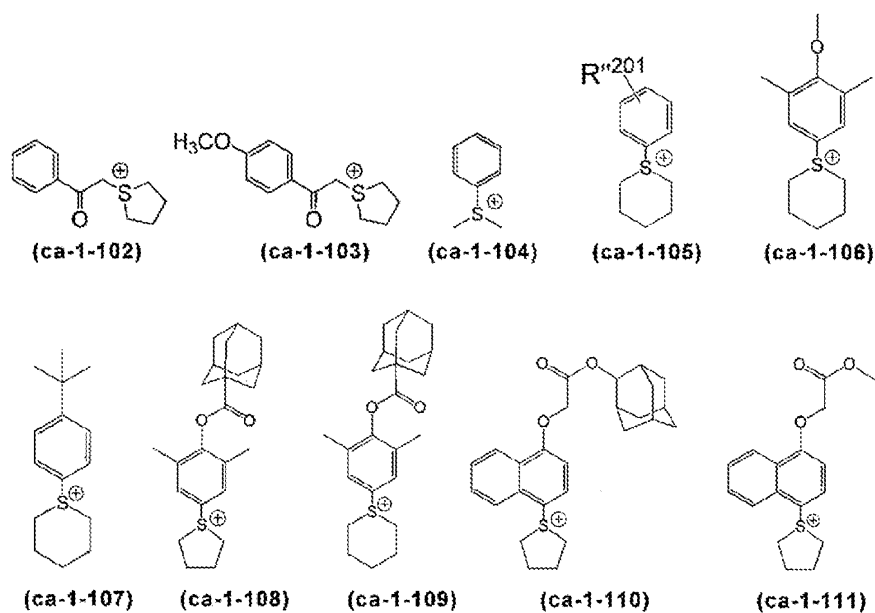
[0216]



[0217]

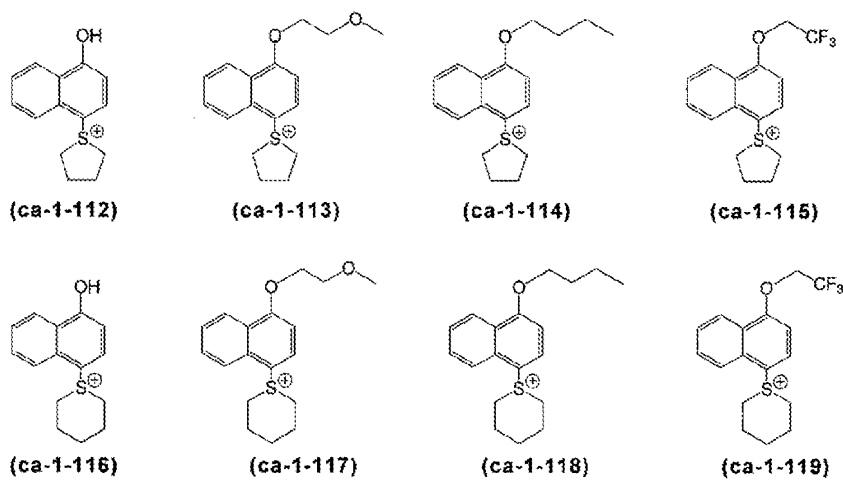


[0218]

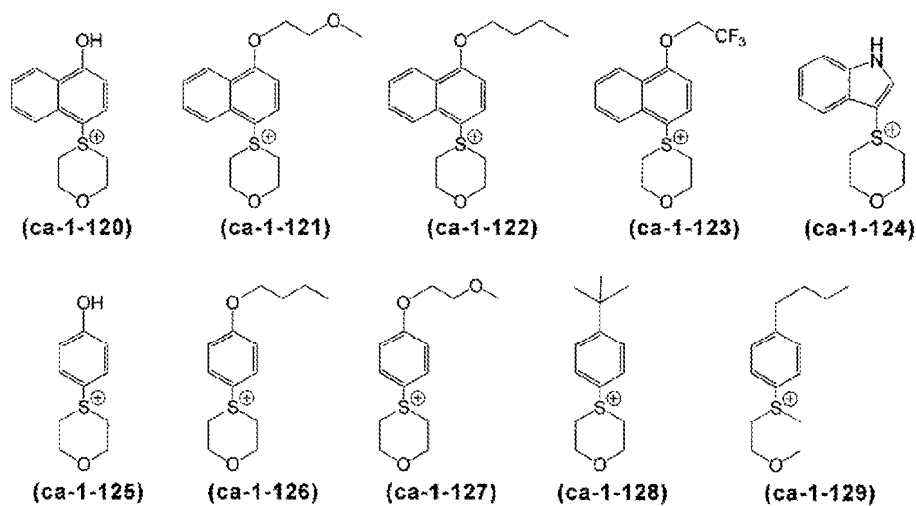


[In the formula, R^{201} represents a hydrogen atom or a substituent, and the substituent is the same as the substituent that R^{201} to R^{207} and R^{210} to R^{212} may have.]

[0219]



[0220]



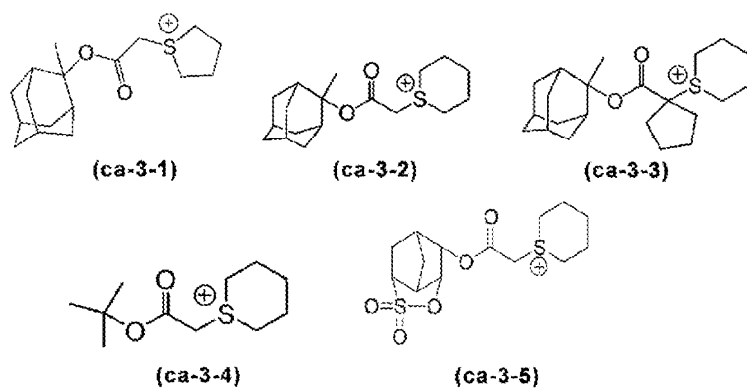
[0221]

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

5 [0222]

Specific examples of suitable cations represented by Formula (ca-3) include cations represented by Formulae (ca-3-1) to (ca-3-5) shown below.

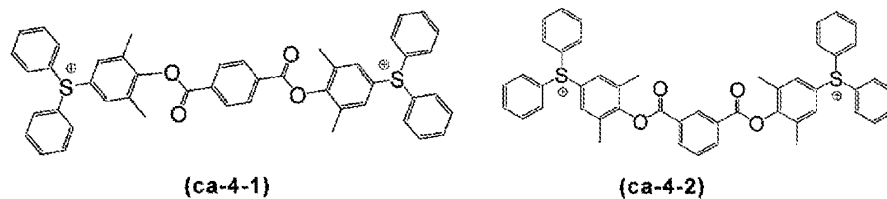
[0223]



10 [0224]

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

[0225]

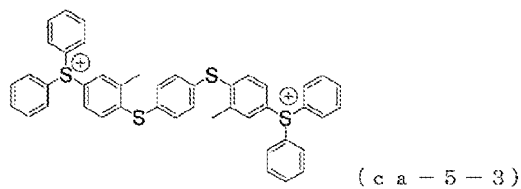
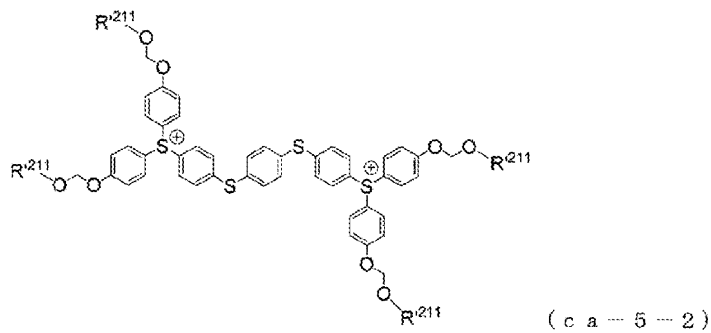
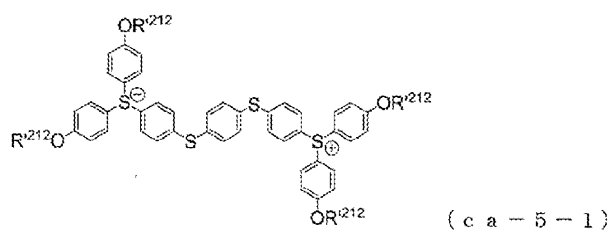


[0226]

In addition, specific examples of suitable cations represented by Formula (ca-5)

5 include cations represented by each of General Formulae (ca-5-1) to (ca-5-3) shown below.

[0227]



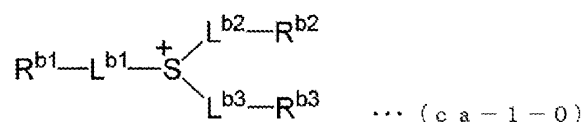
[0228]

10 Among the above cations, as the cation moiety ((M^{m+})_{1/m}), a cation represented

by General Formula (ca-1) is preferable, and a monophenyl-type cation is more preferable.

Further, as the preferred cation moiety $[(M^{m+})_{1/m}]$, a monophenyl-type cation represented by General Formula (ca-1-0) can be mentioned.

5 [0229]



[In the formula, R^{b1} represents an aryl group which may have a substituent.

R^{b2} and R^{b3} are each independently an aliphatic hydrocarbon group. R^{b2} and R^{b3} may be bonded to each other to form a ring structure. L^{b1} , L^{b2} , and L^{b3} are each

10 independently a divalent linking group or a single bond.]

[0230]

In Formula (ca-1-0), R^{b1} is an aryl group which may have a substituent and is the same as the aryl group which may have a substituent in R^{201} to R^{203} . That is, examples of the aryl group as R^{b1} include an aryl group having 6 to 20 carbon atoms, and

15 a phenyl group or a naphthyl group is preferable. Examples of the substituent which may be included in R^{b1} 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 Formulae (ca-r-1) to (ca-r-8) shown above.

[0231]

20 In Formula (ca-1-0), R^{b2} and R^{b3} are each independently an aliphatic hydrocarbon group. The aliphatic hydrocarbon group as R^{b2} and R^{b3} may be chain-like and may be cyclic, and examples thereof include a chain-like or cyclic alkyl group or alkenyl group.

Here, as the alkyl group as R^{b2} and R^{b3} , a chain-like or cyclic alkyl group having 1 to 30 carbon atoms is preferable.

Here, the alkenyl group preferably has 2 to 10 carbon atoms.

[0232]

5 R^{b2} and R^{b3} may be bonded to each other to form a ring structure. In a case of forming a ring with a sulfur atom in the formula, these groups may be bonded to one another via a hetero atom such as a sulfur atom, an oxygen atom or a nitrogen atom, or a functional group such as a carbonyl group, $-SO-$, $-SO_2-$, $-SO_3-$, $-COO-$, $-CONH-$ or $-N(R_N)-$ (here, R_N represents an alkyl group having 1 to 5 carbon atoms). As a ring to be
10 formed, a ring containing the sulfur atom in the formula in the ring skeleton thereof is preferably a 3- to 10-membered ring and most preferably a 5- to 7-membered ring including the sulfur atom. Specific examples of the ring to be formed include a thiophene ring, a thiazole ring, a benzothiophene ring, a thianthrene ring, a benzothiophene ring, a dibenzothiophene ring, a 9H-thioxanthene ring, a thioxanthone
15 ring, a thianthrene ring, a phenoxathiin ring, a tetrahydrothiophenium ring, and a tetrahydrothiopyranium ring.

[0233]

In Formula (ca-1-0), L^{b1} , L^{b2} , and L^{b3} are each independently a divalent linking group or a single bond.

20 As the divalent linking groups, L^{b1} , L^{b2} , and L^{b3} each independently represent $-C(=O)-$, $-C(=O)-O-$, $-OC(=O)-$, an arylene group, an alkylene group or alkenylene group.

[0234]

Examples of the arylene group as L^{b1} , L^{b2} , and L^{b3} include a group in which one hydrogen atom has been further removed from an aryl group exemplified as the aromatic
25 hydrocarbon group represented by R^{101} in Formula (b-1). That is, a group in which two

hydrogen atoms have been further removed from an aromatic ring (benzene, fluorene, naphthalene, anthracene, phenanthrene, biphenyl, or an aromatic hetero ring in which some carbon atoms constituting any of these aromatic rings have been substituted with hetero atoms) is exemplified.

- 5 Examples of the alkylene group and alkenylene group as L^{b1} , L^{b2} , and L^{b3} include a group in which one hydrogen atom has been further removed from the chain-like alkyl group or the chain-like alkenyl group as R^{101} in Formula (b-1). That is, a group obtained by further removing one hydrogen atom from a linear alkyl group having 1 to 20 carbon atoms and a group obtained by further removing one hydrogen atom from
- 10 a branched alkyl group having 3 to 20 carbon atoms are exemplified.

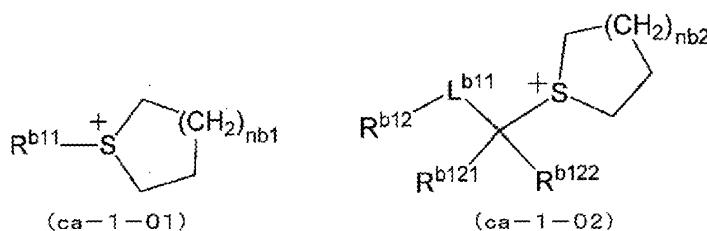
[0235]

L^{b1} is preferably a single bond, since the acid generation efficiency by exposure to light is further increased.

[0236]

- 15 More preferably, the cation moiety of the component (B) is a cation represented by General Formula (ca-1-01) or a cation represented by General Formula (ca-1-02). A cation represented by General Formula (ca-1-01) is particularly preferable.

[0237]



- 20 [In the formulae, R^{b11} and R^{b12} each independently represent an aryl group which may have a substituent. L^{b11} represents $-C(=O)-$ or $-C(=O)-O-$. R^{b121} and R^{b122} each

independently represent a hydrogen atom or an alkyl group having 1 to 5 carbon atoms.

nb1 represents an integer of 1 to 3. nb2 represents an integer of 1 to 3.]

[0238]

In the formula, R^{b11} and R^{b12} each are the same as R^{b1} in Formula (ca-1-0).

- 5 Among these, an unsubstituted aryl group is preferable. The preferred aryl groups include a phenyl group and a naphthyl group.

R^{b121} and R^{b122} each are a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, preferably a hydrogen atom, a methyl group, or an ethyl group, and more preferably a hydrogen atom.

- 10 nb1 is an integer of 1 to 3, preferably 1 or 2, and more preferably 2.

nb2 is an integer of 1 to 3, preferably 1 or 2, and more preferably 1.

[0239]

The cation represented by General Formula (ca-1-01) is preferably a cation represented by Chemical Formulae (ca-1-104) to (ca-1-129). Among these, a cation

- 15 represented by Chemical Formula (ca-1-104) or a cation represented by Chemical Formula (ca-1-105) (in a case where R^{n201} is a hydrogen atom) is more preferable.

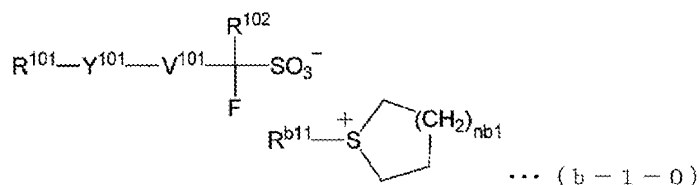
The cation represented by General Formula (ca-1-02) is preferably a cation represented by Chemical Formula (ca-1-102) or a cation represented by Chemical Formula (ca-1-103).

- 20 [0240]

For the component (B), the above-described acid generator may be used alone or in combination of two or more thereof.

As the component (B) in the present embodiment, a compound represented by General Formula (b-1-0) is particularly preferable.

- 25 [0241]



[In the formula, R^{101} , Y^{101} , V^{101} , and R^{102} are respectively the same as R^{101} , Y^{101} , V^{101} , and R^{102} in Formula (b-1). R^{b11} and $nb1$ are respectively the same as R^{b11} and $nb1$ in Formula (ca-1-01).]

5 [0242]

In a case where the resist composition contains the component (B), the content of the component (B) is preferably 0.5 to 7 parts by mass or less, more preferably 1 to 4 parts by mass, and still more preferably 1 to 3 parts by mass with respect to 100 parts by mass of the component (A).

10 In a case where the content of the component (B) is set to be in the above-described range, pattern formation can be satisfactorily performed. Further, in a case where each component of the resist composition is dissolved in an organic solvent, the above range is preferable since a uniform solution is easily obtained and the storage stability of the resist composition is improved. In addition, in a case where the content
15 of the component (B) is equal to or greater than the lower limit of the preferred range, the light transmittance of the resist film is easily increased, and high sensitivity is easily achieved.

[0243]

· In regard to acid diffusion controlling component (D)

20 The resist composition of the present embodiment may further contain an acid diffusion controlling component (hereinafter, referred to as “component (D)”) in addition to the component (A) or the component (A) and the component (B). The component

(D) functions as a quencher (an acid diffusion controlling agent) which traps the acid generated in the resist composition upon light exposure.

The component (D) may a photodecomposable base (D1) which lose acid diffusion controlling activity (hereinafter, referred to as the “component (D1)”) by decomposition by light exposure and a nitrogen-containing organic compound (D2) (hereinafter, referred to as a “component (D2)”) which does not correspond to the component (D1).

[0244]

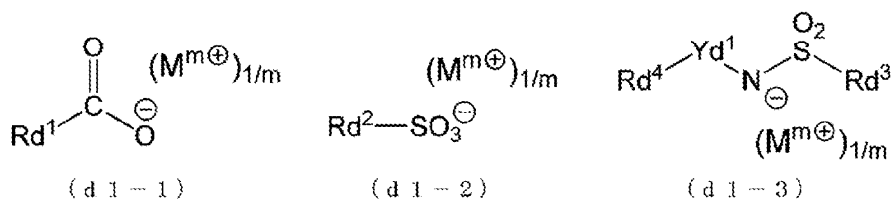
.. In regard to component (D1)

In a case where a resist composition containing the component (D1) is obtained, the contrast between the light-exposed portions and the light-unexposed portions of the resist film can be further improved at the time of the formation of a resist pattern.

The component (D1) is not particularly limited as long as the component is decomposed upon light exposure and loses the acid diffusion controllability, and one or more compounds selected from the group consisting of a compound represented by General Formula (d1-1) (hereinafter, referred to as a “component (d1-1)”), a compound represented by General Formula (d1-2) (hereinafter, referred to as a “component (d1-2)”), and a compound represented by General Formula (d1-3) (hereinafter, referred to as a “component (d1-3)”) are preferable.

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

[0245]



[In the formulae, Rd¹ to Rd⁴ 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. Here, the carbon atom adjacent to the S atom as

5 Rd² in Formula (d1-2) has no fluorine atom bonded thereto. Yd¹ represents a single bond or a divalent linking group. m represents an integer of 1 or greater, and each M^{m+} independently represents an m-valent organic cation.]

[0246]

{ Component (d1-1) }

10 ... Anion moiety

In Formula (d1-1), Rd¹ represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent, and examples thereof are the same as those described above as R¹⁰¹ in Formula (b-1).

15 Among these, as the group as Rd¹, an aromatic hydrocarbon group which may have a substituent, an aliphatic cyclic group which may have a substituent and a chain-like alkyl group which may have a substituent are preferable. Examples of the substituent for these groups include a hydroxyl group, an oxo group, an alkyl group, an aryl group, a fluorine atom, a fluorinated alkyl group, a lactone-containing cyclic group

20 represented by any of General Formulae (a2-r-1) to (a2-r-7), an ether bond, an ester bond, and a combination thereof. In a case where an ether bond or an ester bond is included as the substituent, the substituent may be bonded via an alkylene group, and a linking

group represented by any of Formulae (y-al-1) to (y-al-5) is preferable as the substituent.

The aromatic hydrocarbon group is more preferably a phenyl group or a naphthyl group.

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

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

15 [0247]

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

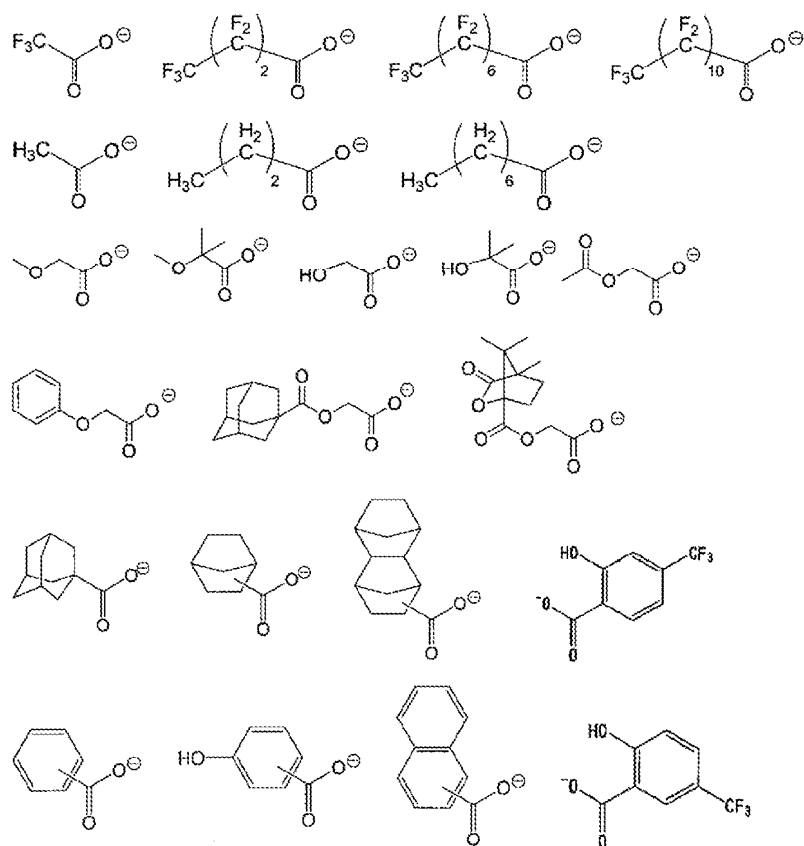
As Rd^1 , a fluorinated alkyl group in which some or all hydrogen atoms constituting a linear alkyl group have been substituted with fluorine atom(s) is preferable, and a fluorinated alkyl group in which all of the hydrogen atoms constituting a linear
25 alkyl group have been substituted with fluorine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

particularly preferable.

[0248]

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

5 [0249]



[0250]

.. Cation moiety

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

10 The organic cations of M^{m+} are preferably the same as those represented by General Formulae (ca-1) to (ca-5), the cations represented by General Formula (ca-1) are preferable, and cations represented by General Formulae (ca-1-1) to (ca-1-129) are more

preferable.

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

[0251]

5 {Component (d1-2)}

... Anion moiety

In Formula (d1-2), Rd^2 represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent, and examples thereof are the same as those described
10 above as R^{101} in Formula (b-1).

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

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 has preferably 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
20 from adamantane, norbornane, isobornane, tricyclodecane, or tetracyclododecane (which may have a substituent) and a group in which one or more hydrogen atoms have been removed from camphor are more preferable.

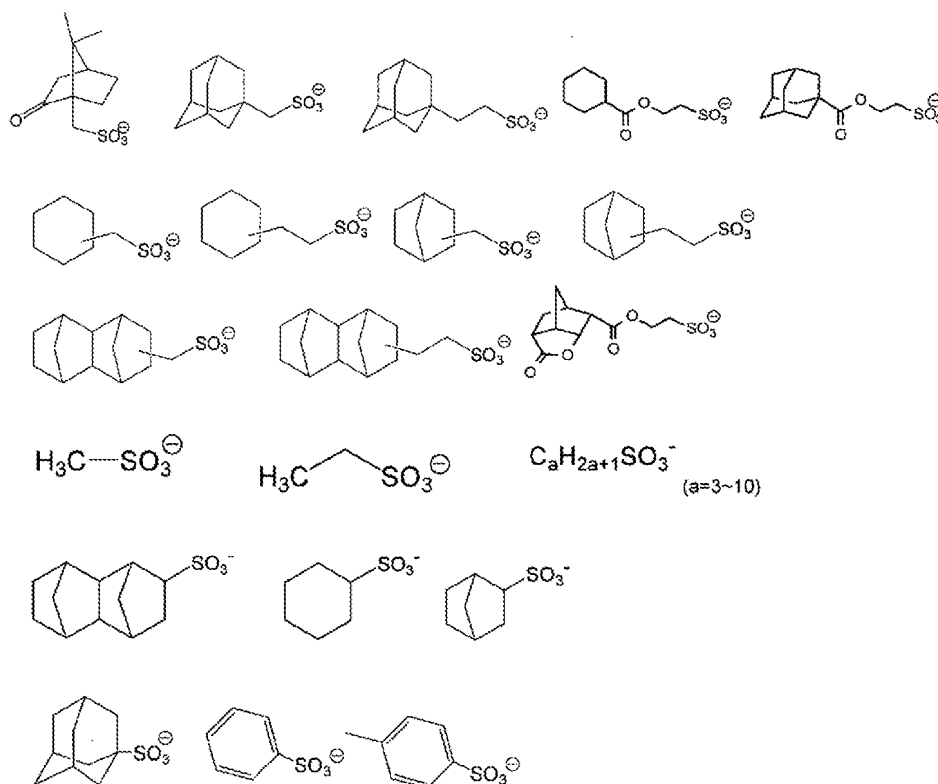
The hydrocarbon group as Rd^2 may have a substituent. As the substituent, the same groups as the substituents which may be included in the hydrocarbon group (such
25 as an aromatic hydrocarbon group, an aliphatic cyclic group, or a chain-like alkyl group)

as Rd^1 in Formula (d1-1) can be exemplified.

[0252]

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

5 [0253]



[0254]

.. Cation moiety

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

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

[0255]

{Component (d1-3)}

... Anion moiety

In Formula (d1-3), Rd^3 represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent, and the same groups as those described above as R^{101} in Formula (b-1) are exemplified, and a cyclic group containing a fluorine atom, a chain-like alkyl group, or a chain-like alkenyl group is preferable. Among these, a fluorinated alkyl group is preferable, and the same fluorinated alkyl groups as those described above as Rd^1 are more preferable.

10 [0256]

In Formula (d1-3), Rd^4 represents a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent, and examples thereof are the same as those described above as R^{101} in Formula (b-1).

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

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

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

25

butoxy group, and a tert-butoxy group. Among these, a methoxy group and an ethoxy group are preferable.

[0257]

As the alkenyl group as Rd^4 , the same groups as those described above as R^{101} in Formula (b-1) can be exemplified, 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 having 1 to 5 carbon atoms or a halogenated alkyl group having 1 to 5 carbon atoms as a substituent.

[0258]

As the cyclic group as Rd^4 , the same groups as those described above as R^{101} in Formula (b-1) can be exemplified. Among these, as the cyclic group, an alicyclic group in which one or more hydrogen atoms have been removed from a cycloalkane such as cyclopentane, cyclohexane, adamantane, norbornane, isobornane, tricyclodecane or tetracyclododecane or an aromatic group such as a phenyl group or a naphthyl group is preferable. In a case where Rd^4 represents an alicyclic group, the resist composition can be satisfactorily dissolved in an organic solvent, thereby improving the lithography characteristics. In a case where Rd^4 is an aromatic group, the resist composition is excellent in light absorption efficiency and thus has good sensitivity and lithography characteristics.

[0259]

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

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

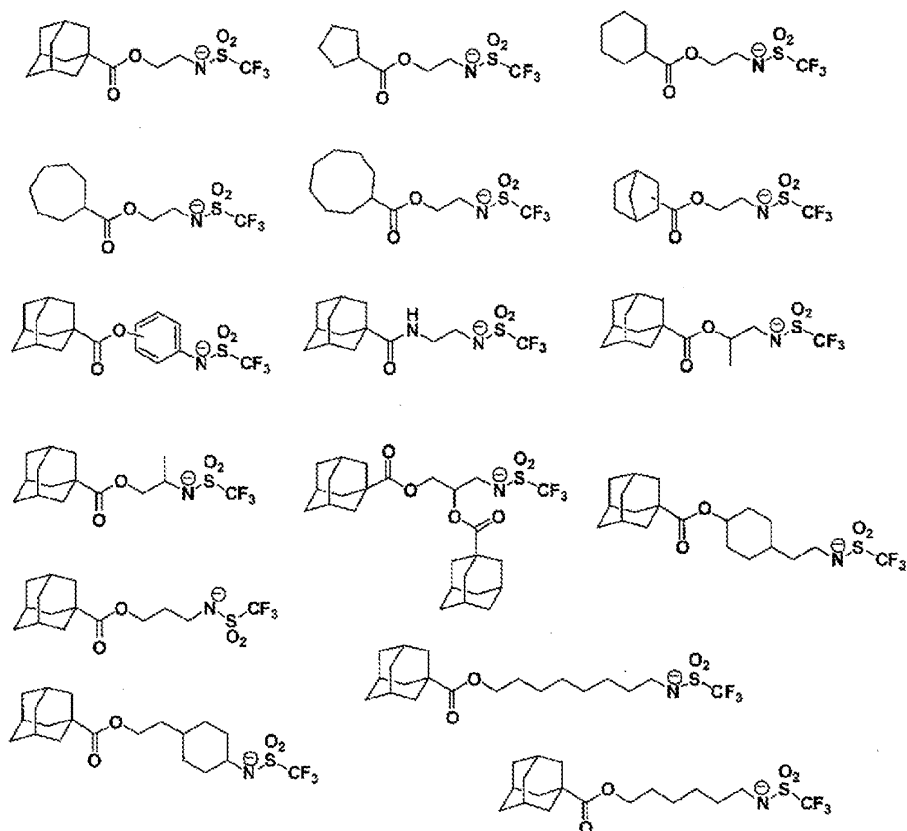
as the divalent hydrocarbon group which may have a substituent and the divalent linking group containing a hetero atom explained above as the divalent linking group as Ya^{21} in Formula (a2-1).

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.

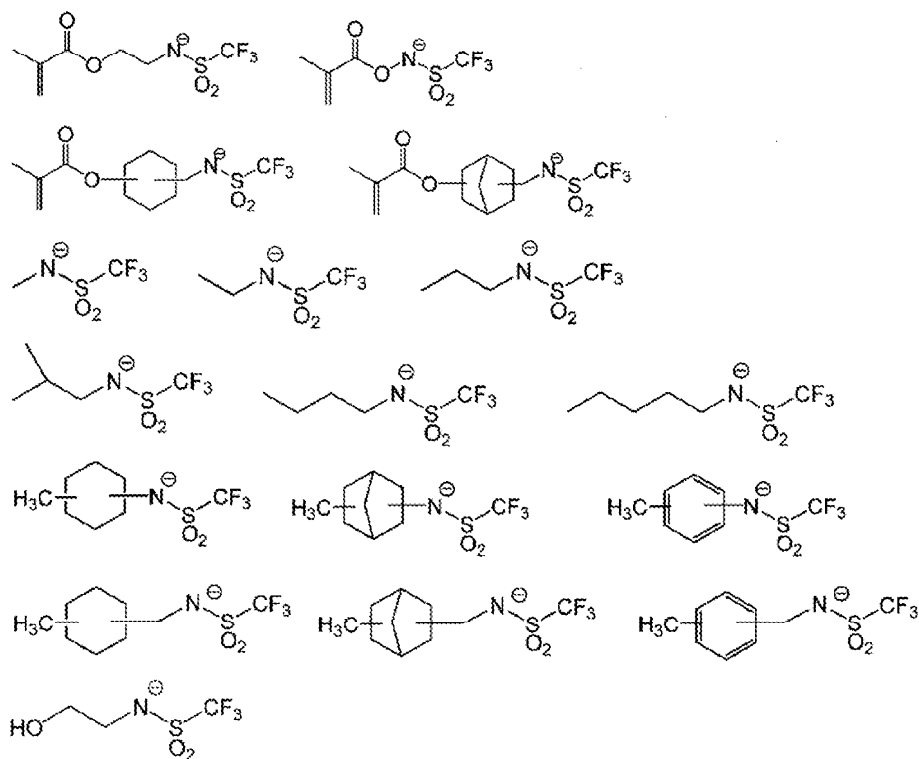
[0260]

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

[0261]



[0262]



[0263]

.. Cation moiety

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

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

[0264]

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

In a case where the resist composition contains the component (D1), the content
 of the component (D1) is preferably 0.5 to 10 parts by mass, more preferably 0.5 to 8
 parts by mass, and still more preferably in a range of 1 to 8 parts by mass with respect to
 100 parts by mass of the component (A).

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

[0265]

Method of producing component (D1):

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

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

[0266]

· In regard to component (D2)

The acid diffusion controlling component may contain a nitrogen-containing organic compound component (hereinafter, referred to as a “component (D2)”) which does not correspond to the above-mentioned component (D1).

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

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

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

- 5 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-
- 10 n-pentylamine, tri-n-heptylamine, tri-n-octylamine, tri-n-nonylamine, tri-n-decylamine, and tri-n-dodecylamine; and alkyl alcohol amines such as diethanolamine, triethanolamine, diisopropanolamine, triisopropanolamine, di-n-octanolamine, and tri-n-octanolamine. Among these, trialkylamines of 5 to 10 carbon atoms are preferable, and tri-n-pentylamine and tri-n-octylamine are particularly preferable.

15 [0267]

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).

- 20 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.

25 [0268]

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

5 triethanolamine triacetate, and triethanolamine triacetate is preferable.

[0269]

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

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

10 N-tert-butoxycarbonylpyrrolidine.

[0270]

The component (D2) may be used alone or in combination of two or more kinds thereof.

In a case where the resist composition contains the component (D2), the content

15 of the component (D2) is typically in a range of 0.01 to 5 parts by mass with respect to 100 parts by mass of the component (A). By setting the content within the above range, the resist pattern shape, the post-exposure temporal stability, and the like are improved.

[0271]

· In regard to at least one compound (E) selected from group consisting of

20 organic carboxylic acids, phosphorus oxo acids, and derivatives thereof

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

25 phosphorus oxo acid and a derivative thereof.

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

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

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

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

10 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.

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

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

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

[0272]

· In regard to fluorine additive component (F)

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

Specific examples of the component (F) include polymers having a constitutional unit (f1) represented by Formula (f1-1) shown below. As the polymer, a polymer (homopolymer) consisting of a constitutional unit (f1) represented by Formula (f1-1) shown below; a copolymer including a constitutional unit (a1) containing an acid decomposable group whose polarity increases due to an action of an acid and the constitutional unit (f1); a copolymer of the constitutional unit (f1), a constitutional unit derived from acrylic acid or methacrylic acid, and the above-described constitutional unit (a1). Preferred examples of the constitutional unit (a1) to be copolymerized with the constitutional unit (f1) include a constitutional unit derived from 1-ethyl-1-cyclooctyl (meth)acrylate and a constitutional unit derived from 1-methyl-1-adamantyl (meth)acrylate.

$$\begin{array}{c} \text{R} \\ | \\ \text{---} \text{C} \text{---} \\ | \\ \text{O} \text{---} \text{C} \text{---} \text{Rf}^{102} \text{---} \text{Rf}^{103} \\ | \\ \text{O} \text{---} \text{C} \text{---} \text{Rf}^{101} \\ | \\ \text{---} \end{array} \quad \text{nf}^1 \quad \dots (f-1)$$

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

[0274]

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

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

Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom and, an iodine atom, and a fluorine atom is particularly preferable. Among these examples, as Rf^{102} and Rf^{103} , a hydrogen atom, a fluorine atom, or an alkyl group having 1 to 5 carbon atoms is preferable, and a hydrogen atom, a fluorine atom, a methyl group, or an ethyl group is more preferable.

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

[0275]

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 has preferably 1 to 20 carbon atoms, more preferably 1 to 15 carbon atoms, and particularly preferably 1 to 10 carbon atoms.

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

10 Among these, as R^{f101}, a fluorinated hydrocarbon group having 1 to 6 carbon atoms is more preferable, and a trifluoromethyl group, -CH₂-CF₃, -CH₂-CF₂-CF₃, -CH(CF₃)₂, -CH₂-CH₂-CF₃, and -CH₂-CH₂-CF₂-CF₂-CF₂-CF₃ are still more preferable.
[0276]

 The weight-average molecular weight (Mw) (in terms of polystyrene determined
15 by gel permeation chromatography) of the component (F) is preferably in a range of 1,000 to 50,000, more preferably in a range of 5,000 to 40,000, and most preferably in a range of 10,000 to 30,000. In a case where the weight-average molecular weight is equal or lower than the upper limit of the above-described range, the resist composition exhibits a satisfactory solubility in a solvent for a resist enough to be used as a resist.
20 On the other hand, in a case where the weight-average molecular weight is equal to or greater than the lower limit of the above-described range, dry etching resistance and the cross-sectional shape of the resist pattern become excellent.

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

[0277]

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

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

[0278]

· In regard to organic solvent component (S)

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

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

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
20 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 (such as
monomethylether, monoethylether, monopropylether or monobutylether) or
monophenylether of any of these polyhydric alcohols or compounds having an ester bond
25 (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).

The component (S) may be used alone or may be used as a mixed solvent of two or more thereof.

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

[0279]

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

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

Further, as the component (S), a mixed solvent of at least one selected from

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

[0280]

5 The amount of the component (S) is not particularly limited and is appropriately set to have a concentration which allows a substrate or the like to be coated with coating solution depending on the film thickness of the coated film. In general, the component (S) is used in an amount such that the solid content of the resist composition becomes in the range of 20% to 55% by mass and preferably in a range of 30% to 45% by mass.

10 [0281]

As desired, other miscible additives can also be added to the resist composition of the present embodiment. The resist composition may contain miscible additives such as additive resins, a surfactant (for example, a fluorine surfactant), dissolution inhibitors, plasticizers, stabilizers, colorants, halation prevention agents, and dyes for improving the performance of the resist film, as appropriate.

15 [0282]

The method of forming a resist pattern according to the present aspect described above is a method useful for forming a resist film of high film thickness having a thickness of 7 μm or more and is performed using a specific resist composition.

20 By using the specific resist composition, that is, a resist composition containing a resin component (A1) having a constitutional unit (a10), a constitutional unit (a4), and a constitutional unit (a1), the light transmittance of a resist film having a high film thickness can be improved. As a result, even in a case where a resist film having a high film thickness of 7 μm or more is formed, high sensitivity can be achieved, resolution can
25 be improved, and a resist pattern having a good shape can be formed.

[0283]

In addition, according to the method of forming a resist pattern of the present embodiment, the use of the specific resist composition improves its solubility in a developing solution. As a result, the occurrence of defects can be suppressed, and the stability of pattern dimensions can be increased. Further, according to the method of forming a resist pattern of the present embodiment, sufficient etching resistance is maintained.

[0284]

The method of forming a resist pattern of the present embodiment is a method useful for manufacturing a three-dimensional structure device and is suitable for use in processing a multi-step staircase structure (overlapping or the like). By applying the method of forming a resist pattern according to the present embodiment, the stacking of memory films (manufacturing of a large-capacity memory having a three-dimensional structure) can be achieved with high accuracy.

15 [Examples]

[0285]

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

[0286]

20 <Preparation of resist composition>

Each component shown in Table 1 was mixed and dissolved to prepare resist compositions (1) to (6) (each component having a solid content of 40% by mass).

[0287]

[Table 1]

	Component (A)	Component (B)	Component (D)	Component (E)	Component (Add)	Component (S)
Resist composition (1)	(A)-1 [100]	(B)-1 [2.28]	(D)-1 [0.020]	(E)-1 [0.015]	(Add)-1 [0.20]	(S)-1 [154]
Resist composition (2)	(A)-2 [100]	(B)-1 [2.28]	(D)-1 [0.020]	(E)-1 [0.015]	(Add)-1 [0.20]	(S)-1 [154]
Resist composition (3)	(A)-3 [100]	(B)-1 [2.28]	(D)-1 [0.020]	(E)-1 [0.015]	(Add)-1 [0.20]	(S)-1 [154]
Resist composition (4)	(A)-4 [100]	(B)-1 [2.28]	(D)-1 [0.020]	(E)-1 [0.015]	(Add)-1 [0.20]	(S)-1 [154]
Resist composition (5)	(A)-5 [100]	(B)-1 [2.28]	(D)-1 [0.020]	(E)-1 [0.015]	(Add)-1 [0.20]	(S)-1 [154]
Resist composition (6)	(A)-6 [100]	(B)-1 [2.28]	(D)-1 [0.020]	(E)-1 [0.015]	(Add)-1 [0.20]	(S)-1 [154]

[0288]

In Tables 1, each abbreviation has the following meaning. The numerical values in the brackets are blending amounts (parts by mass).

(A)-1: a high molecular compound represented by Chemical Formula (A1)-1.

The weight-average molecular weight (Mw) of the polymer compound (A)-1 and the molecular weight dispersity (Mw/Mn) in terms of standard polystyrene acquired by GPC measurement were respectively 10,000 and 2.5. The copolymer compositional ratio (the proportion (molar ratio) between constitutional units in the structural formula) acquired by ¹³C-NMR was the constitutional unit (a101)/the constitutional unit (a41)/the constitutional unit (a11) = 50/35/15.

[0289]

(A)-2: a high molecular compound represented by Chemical Formula (A1)-1.

The weight-average molecular weight (Mw) of the polymer compound (A)-1 and the molecular weight dispersity (Mw/Mn) in terms of standard polystyrene acquired by GPC

measurement were respectively 10,000 and 2.5. The copolymer compositional ratio (the proportion (molar ratio) between constitutional units in the structural formula) acquired by ^{13}C -NMR was the constitutional unit (a101)/the constitutional unit (a41)/the constitutional unit (a11) = 65/20/15.

5 [0290]

(A)-3: a high molecular compound represented by Chemical Formula (A1)-1.

The weight-average molecular weight (Mw) of the polymer compound (A)-1 and the molecular weight dispersity (Mw/Mn) in terms of standard polystyrene acquired by GPC measurement were respectively 10,000 and 2.5. The copolymer compositional ratio (the proportion (molar ratio) between constitutional units in the structural formula) acquired by ^{13}C -NMR was the constitutional unit (a101)/the constitutional unit (a41)/the constitutional unit (a11) = 70/15/15.

[0291]

(A)-4: a high molecular compound represented by Chemical Formula (A1)-1.

15 The weight-average molecular weight (Mw) of the polymer compound (A)-1 and the molecular weight dispersity (Mw/Mn) in terms of standard polystyrene acquired by GPC measurement were respectively 10,000 and 2.5. The copolymer compositional ratio (the proportion (molar ratio) between constitutional units in the structural formula) acquired by ^{13}C -NMR was the constitutional unit (a101)/the constitutional unit (a41)/the constitutional unit (a11) = 40/45/15.

[0292]

(A)-5: a high molecular compound represented by Chemical Formula (A1)-1.

The weight-average molecular weight (Mw) of the polymer compound (A)-1 and the molecular weight dispersity (Mw/Mn) in terms of standard polystyrene acquired by GPC measurement were respectively 10,000 and 2.5. The copolymer compositional ratio

25

(the proportion (molar ratio) between constitutional units in the structural formula)

acquired by ^{13}C -NMR was the constitutional unit (a101)/the constitutional unit (a41)/the constitutional unit (a11) = 80/5/15.

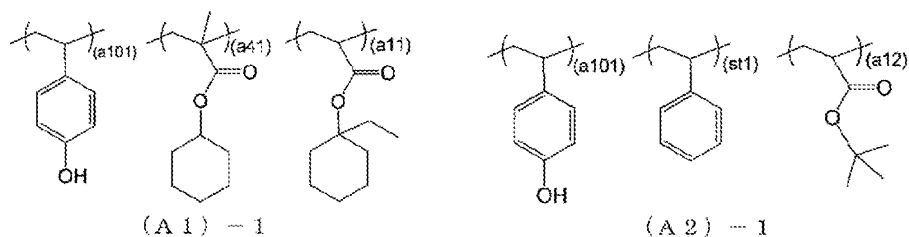
[0293]

5 (A)-6: a high molecular compound represented by Chemical Formula (A2)-1.

The weight-average molecular weight (M_w) of the polymer compound (A)-1 and the molecular weight dispersity (M_w/M_n) in terms of standard polystyrene acquired by GPC measurement were respectively 10,000 and 2.5. The copolymer compositional ratio (the proportion (molar ratio) between constitutional units in the structural formula)

10 acquired by ^{13}C -NMR was the constitutional unit (a101)/the constitutional unit (st1)/the constitutional unit (a12) = 65/20/15.

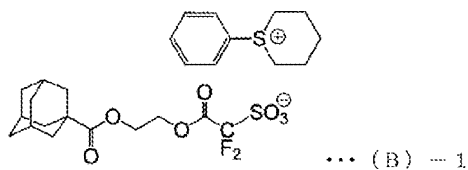
[0294]



[0295]

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

[0296]



[0297]

(D)-1: tri-n-pentylamine

(E)-1: phenylphosphonic acid

(Add)-1: fluorine surfactant, trade name “R-40” manufactured by DIC

5 Corporation.

(S)-1: propylene glycol monomethyl ether acetate and propylene glycol

monomethyl ether at a mass ratio of 5/5

[0298]

<Formation (I) of resist pattern>

10 (Examples 1 to 3)

Step (i):

An 8-inch silicon wafer was coated with each of the resist compositions (1) to
(3) using a coater, and the coated wafer was subjected to a prebake (PAB) treatment on a
hot plate at a temperature of 130°C for 90 seconds so that the coated wafer was dried to
15 form a resist film having a film thickness of 15 μm .

Step (ii):

Next, a KrF excimer laser (248 nm) was selectively applied to the resist film by
a KrF exposure apparatus NSR-S203B (manufactured by Nikon Corporation; numerical
aperture (NA) = 0.68, $\sigma = 0.40$) through a mask pattern (6% halftone).

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

Step (iii):

Subsequently, alkali development was performed under at 23°C for 60 seconds
using a 2.38% by mass tetramethylammonium hydroxide (TMAH) aqueous solution
25 “NMD-3” (trade name, manufactured by TOKYO OHKA KOGYO CO., LTD.) as a

developing solution.

Thereafter, water rinsing was performed for 30 seconds using pure water, and shake-off drying was performed.

[0299]

5 (Comparative Example 1)

A resist pattern was formed in the same manner as in Examples 1 to 3, except that the resist composition (6) was used.

[0300]

As a result of the above-described “Formation (I) of resist pattern”, a pattern of
10 an isolated line having a space width of 5 μm (hereinafter, referred to as an “IS pattern”) was formed in the resist film in all examples.

[0301]

[Sensitivity]

An optimum light exposure amount E_{op} (mJ/cm^2) at which the IS pattern having
15 a target size was formed according to the method in the section of “Formation (I) of resist pattern” was determined and set as the sensitivity. The results are listed in Table 2 as “ E_{op} (mJ/cm^2)”.

[0302]

[Shape of resist pattern]

20 The shape of the IS pattern formed by the above-described “Formation (I) of resist pattern” was observed with a length-measuring scanning electron microscope (SEM, acceleration voltage 800 V, trade name: SU-8000, manufactured by Hitachi High-Tech Corporation), and Table 2 shows the results of the evaluation as “Shape” according to the following evaluation criteria.

25 Evaluation criteria

A: tapered shape

B: top-round shape

[0303]

[Table 2]

		Comparative Example 1	Example 1	Example 2	Example 3
Resist composition		(6)	(1)	(2)	(3)
Component (A)	Constitutional unit (a101)	65	50	65	70
	Constitutional unit (st1)	20	-	-	-
	Constitutional unit (a41)	-	35	20	15
	Constitutional unit (a12)	15	-	-	-
	Constitutional unit (a11)	-	15	15	15
Evaluation	Eop (mJ/cm ²)	81.9	36.8	36.4	33.1
	Shape	B	A	A	A

[0304]

From the results shown in Table 2, it can be seen that according to the method of forming a resist pattern of Examples 1 to 3, even in a case where a resist film having a film thickness of 15 μm is formed, a pattern having high sensitivity and good shape can be formed.

On the other hand, in the method of forming a resist pattern of Comparative Example 1, the sensitivity was low and the shape was bad.

10 [0305]

<Formation (II) of resist pattern>

(Examples 4 to 8)

Step (i):

An 8-inch silicon wafer was coated with each of the resist compositions (1) to (5) using a coater, and the coated wafer was subjected to a prebake (PAB) treatment on a hot plate at a temperature of 130°C for 90 seconds so that the coated wafer was dried to form a resist film having a film thickness of 15 μm .

Step (ii):

Next, a KrF excimer laser (248 nm) was selectively applied to the resist film by a KrF exposure apparatus NSR-S203B (manufactured by Nikon Corporation; numerical aperture (NA) = 0.68, $\sigma = 0.40$) through a mask pattern (6% halftone).

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

Step (iii):

Subsequently, alkali development was performed under at 23°C for 60 seconds using a 2.38% by mass tetramethylammonium hydroxide (TMAH) aqueous solution
10 “NMD-3” (trade name, manufactured by TOKYO OHKA KOGYO CO., LTD.) as a developing solution.

Thereafter, water rinsing was performed for 30 seconds using pure water, and shake-off drying was performed.

[0306]

15 As a result of the above-described “Formation (II) of resist pattern”, a pattern of an isolated line having a space width of 3 μm (hereinafter, referred to as an “IS pattern”) was formed in the resist film in all examples.

[0307]

[Defect (number of defects)]

20 With respect to the IS pattern formed by the above-described “Formation (II) of resist pattern”, the total number of defects in the wafer (the total number of defects) was measured using a surface defect observation apparatus (manufactured by KLA Corporation, product name: KLA2371).

25 Two wafers were used for each measurement in each example, and the average value of the total numbers of defects in the wafer (the total numbers of defects) was

adopted. The evaluation result is shown in Table 3 as “Defect” according to the following evaluation criteria.

Evaluation criteria

A: The number of defects is 200 or lower.

5 B: The number of defects is greater than 200 and lower than 300.

C: The number of defects is 300 or greater.

[0308]

[Critical dimension uniformity (CDU) in wafer surface (Shot)]

With respect to the IS pattern formed by the above-described “Formation (II) of resist pattern”, the IS pattern (7×15 shot) was observed from above, and the space width in the IS pattern (38 points in the shot) was measured with a length-measuring scanning electron microscope (SEM, acceleration voltage 300 V, trade name: S-9380, manufactured by Hitachi High-Tech Corporation). Three times (3σ) the standard deviation (σ) calculated from the measurement result was determined. The lower the value of 3σ obtained as described-above is, the higher the uniformity of the dimension (CD) of space width formed in the resist film is.

10

15

The evaluation result is shown in Table 3 as “CDU” according to the following evaluation criteria.

Evaluation criteria

20 A: The value of 3σ is 60 nm or lower

B: The value of 3σ is greater than 60 nm and lower than 70 nm

C: The value of 3σ is 70 nm or greater

[0309]

[Table 3]

	Resist composition	Constitutional unit (a101)	Defect	CDU
Example 7	(4)	40% by mole	C	A
Example 4	(1)	50% by mole	B	A
Example 5	(2)	65% by mole	A	A
Example 6	(3)	70% by mole	A	B
Example 8	(5)	80% by mole	A	C

[0310]

From the results shown in Table 3, it can be seen that according to the method of forming a resist pattern of Examples 4 to 8, the occurrence of defects is reduced and the uniformity of the dimension (CD) is high. In particular, it can be seen that in a case where the resist compositions (1), (2), and (3) are used (particularly preferably in a case where the resist composition (2) is used), these effects are further enhanced.

[0311]

The preferred Examples of the present invention have been described as above, but the present invention is not limited to these Examples. Additions, omissions, substitutions, and other modifications of the configuration can be made without departing from the spirit of the present invention. The present invention is not limited by the description described above and is limited only by the scope of the attached claims.

[CLAIMS]

[Claim 1]

A method of forming a resist pattern, comprising:

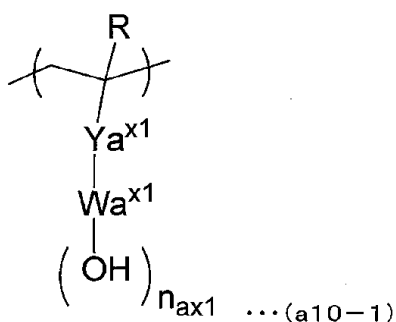
5 a step (i) of forming a resist film having a film thickness of 7 μm or more on a supporting body using a resist composition;

a step (ii) of exposing the resist film to light; and

a step (iii) of developing the exposed resist film to form a resist pattern,

wherein the resist composition exhibits changed solubility in a developing
10 solution due to an action of acid generated upon exposure, and the resist composition comprises a resin component (A1) having:

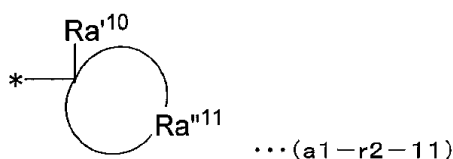
a constitutional unit (a10) represented by General Formula (a10-1):



wherein R represents a hydrogen atom, an alkyl group having 1 to 5 carbon
15 atoms, or a halogenated alkyl group having 1 to 5 carbon atoms, $\text{Y}^{\text{a}^{\text{x}1}}$ represents a single bond or a divalent linking group, $\text{W}^{\text{a}^{\text{x}1}}$ represents an $(n_{\text{ax}1} + 1)$ -valent aromatic hydrocarbon group, and $n_{\text{ax}1}$ represents an integer of 1 to 3,

a constitutional unit (a4) containing an acid non-dissociable aliphatic cyclic group, and

20 a constitutional unit (a1) containing an acid decomposable group represented by General Formula (a1-r2-11):



wherein Ra'^{10} represents a hydrocarbon group having 1 to 10 carbon atoms, Ra''^{11} represents a group that forms a monocyclic aliphatic cyclic group together with a carbon atom to which Ra'^{10} is bonded, and * represents a bond.

5 [Claim 2]

The method of forming a resist pattern according to Claim 1, wherein a content proportion of the constitutional unit (a10) is 45% to 75% by mole with respect to all the constitutional units (100% by mole) constituting the resin component (A1).

10 [Claim 3]

The method of forming a resist pattern according to Claim 1 or 2, wherein a content proportion of the constitutional unit (a1) is 5% to 20% by mole with respect to all the constitutional units (100% by mole) constituting the resin component (A1).

15 [Claim 4]

The method of forming a resist pattern according to any one of Claims 1 to 3, wherein in the step (ii), the resist film is irradiated with KrF excimer laser light.