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Nemoto et al.

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(54) **RADIATION-SENSITIVE RESIN
COMPOSITION, METHOD OF FORMING
RESIST PATTERN, POLYMER, AND
COMPOUND**

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(58) **Field of Classification Search**
None
See application file for complete search history.

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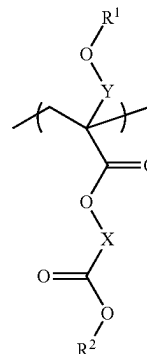
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(57) **ABSTRACT**

A radiation-sensitive resin composition includes: a first
polymer including a structural unit which includes an acid-
labile group; a second polymer including a structural unit
represented by formula (1); and a radiation-sensitive acid
generator. R¹ represents a monovalent organic group having
1 to 20 carbon atoms; R² represents a monovalent organic
group having 1 to 20 carbon atoms; X represents a divalent
organic group having 1 to 20 carbon atoms; and Y represents
a divalent hydrocarbon group having 1 to 20 carbon atoms.
The divalent organic group represented by X, the monova-
lent organic group represented by R², or both has a fluorine
atom.

(1)



20 Claims, No Drawings

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RADIATION-SENSITIVE RESIN COMPOSITION, METHOD OF FORMING RESIST PATTERN, POLYMER, AND COMPOUND

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a continuation application of International Application No. PCT/JP2020/032006, filed Aug. 25, 2020, which claims priority to Japanese Patent Application No. 2019-185551 filed Oct. 8, 2019. The contents of these applications are incorporated herein by reference in their entirety.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a radiation-sensitive resin composition, a method of forming a resist pattern, a polymer, and a compound.

Description of the Related Art

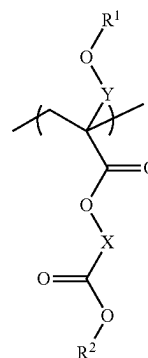
A radiation-sensitive resin composition for use in micro-fabrication by lithography generates an acid at a light-exposed region upon an irradiation with a radioactive ray, e.g., an electromagnetic wave such as a far ultraviolet ray such as an ArF excimer laser beam (wavelength of 193 nm), a KrF excimer laser beam (wavelength of 248 nm), etc., an extreme ultraviolet ray (EUV), or a charged particle ray such as an electron beam. A chemical reaction in which the acid serves as a catalyst causes a difference in rates of dissolution in a developer solution between light-exposed regions and light-unexposed regions, whereby a resist pattern is formed on a substrate.

Such a radiation-sensitive resin composition is required not only to have favorable sensitivity to exposure light, but also to have superiority with regard to each of LWR (Line Width Roughness) performance, which indicates line width uniformity, and CDU (Critical Dimension Uniformity) performance, which indicates variance of line widths in greater ranges. To meet such requirements, types, molecular structures, and the like of polymers, acid generating agents, and other components which may be used in radiation-sensitive resin compositions have been investigated (see Japanese Unexamined Patent Publication, Publication Nos. 2009-14815 and 2013-200560).

SUMMARY OF THE INVENTION

According to an aspect of the present invention, a radiation-sensitive resin composition includes: a first polymer including a structural unit which includes an acid-labile group; a second polymer including a structural unit represented by formula (1); and a radiation-sensitive acid generator. R^1 represents a monovalent organic group having 1 to 20 carbon atoms; R^2 represents a monovalent organic group having 1 to 20 carbon atoms; X represents a divalent organic group having 1 to 20 carbon atoms; and Y represents a divalent hydrocarbon group having 1 to 20 carbon atoms. The divalent organic group represented by X, the monovalent organic group represented by R^2 , or both has a fluorine atom.

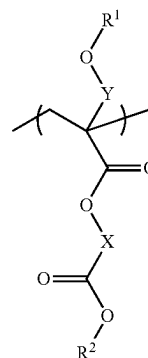
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(1)

According to another aspect of the present invention, a method of forming a resist pattern, includes forming a resist film directly or indirectly on a substrate by applying the above-mentioned radiation-sensitive resin composition. The resist film is exposed. The resist film exposed is developed.

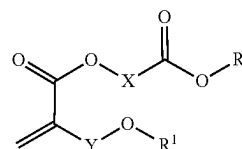
According to a further aspect of the present invention, a polymer includes a structural unit represented by formula (1).



(1)

In the formula (1), R^1 represents a monovalent organic group having 1 to 20 carbon atoms; R^2 represents a monovalent organic group having 1 to 20 carbon atoms; X represents a divalent organic group having 1 to 20 carbon atoms; and Y represents a divalent hydrocarbon group having 1 to 20 carbon atoms. The divalent organic group represented by X, the monovalent organic group represented by R^2 , or both has a fluorine atom.

According to a further aspect of the present invention, a compound is represented by formula (i).



(i)

In the formula (i), R^1 represents a monovalent organic group having 1 to 20 carbon atoms; R^2 represents a monovalent organic group having 1 to 20 carbon atoms; X represents a divalent organic group having 1 to 20 carbon atoms; and Y

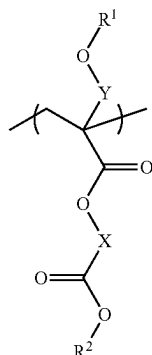
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represents a divalent hydrocarbon group having 1 to 20 carbon atoms. The divalent organic group represented by X, the monovalent organic group represented by R², or both has a fluorine atom.

DESCRIPTION OF EMBODIMENTS

Under current circumstances in which miniaturization of resist patterns has proceeded to a level in which line widths are 40 nm or less, in addition to the aforementioned types of performance, radiation-sensitive resin compositions are required to enable forming a resist pattern with superior water repellency and few defects.

One embodiment of the invention is a radiation-sensitive resin composition containing: a first polymer (hereinafter, may be also referred to as “(A) polymer” or “polymer (A)”) having a structural unit (hereinafter, may be also referred to as “structural unit (I)”) which includes an acid labile group; and a second polymer (hereinafter, may be also referred to as “(E) polymer” or “polymer (E)”) having a second structural unit (hereinafter, may be also referred to as “structural unit (W)”) represented by the following formula (1); and a radiation-sensitive acid generator (hereinafter, may be also referred to as “(B) acid generator” or “acid generator (B)”).



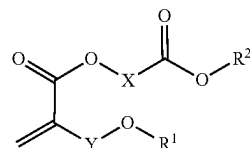
wherein, in the formula (1), R¹ represents a monovalent organic group having 1 to 20 carbon atoms; R² represents a monovalent organic group having 1 to 20 carbon atoms; X represents a divalent organic group having 1 to 20 carbon atoms; and Y represents a divalent hydrocarbon group having 1 to 20 carbon atoms, wherein at least one of the divalent organic group represented by X and the monovalent organic group represented by R² has a fluorine atom.

According to an other embodiment of the invention, a method of forming a resist pattern includes: applying a radiation-sensitive resin composition directly or indirectly on a substrate; exposing a resist film formed by the applying; and developing the resist film exposed, wherein the radiation-sensitive resin composition contains: the polymer (A), the polymer (E), and the acid generator (B).

Still another embodiment of the invention is the polymer (E) having the structural unit (W).

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Yet another embodiment of the invention is a compound (hereinafter, may be also referred to as “compound (F)”) represented by the following formula (i):



wherein, in the formula (1), R¹ represents a monovalent organic group having 1 to 20 carbon atoms; R² represents a monovalent organic group having 1 to 20 carbon atoms; X represents a divalent organic group having 1 to 20 carbon atoms; and Y represents a divalent hydrocarbon group having 1 to 20 carbon atoms, wherein at least one of the divalent organic group represented by X and the monovalent organic group represented by R² has a fluorine atom.

The radiation-sensitive resin composition, the method of forming a resist pattern, the polymer, and the compound of the embodiments of the present invention enable forming a resist pattern with superior water repellency and few defects. Thus, these can be suitably used in manufacturing of a semiconductor device and the like, in which further progress of miniaturization is expected in the future.

Radiation-Sensitive Resin Composition

The radiation-sensitive resin composition of one embodiment of the present invention contains the polymer (A), the polymer (E), and the acid generator (B). The radiation-sensitive resin composition may contain, as favorable components, an acid diffusion controller (C) and a solvent (D), and may contain, within a range not leading to impairment of the effects of the present invention, other optional component(s).

Due to containing the polymer (A), the polymer (E), and the acid generator (B), the radiation-sensitive resin composition has favorable sensitivity to exposure light, and enables a resist pattern to be formed with superior water repellency and few defects. Although not necessarily clarified and without wishing to be bound by any theory, the reason for achieving the aforementioned effects by the radiation-sensitive resin composition due to involving such a constitution may be presumed, for example, as in the following. It is considered that owing to the structural unit (W) in the polymer (E) contained in the radiation-sensitive resin composition, the sensitivity improves, and in addition, a highly water repellent property and the defect-inhibiting property can be exhibited. Hereinafter, each component of the radiation-sensitive resin composition will be described.

(A) Polymer

The polymer (A) is a polymer having the structural unit (I). The polymer (A) preferably has, in addition to the structural unit (I), a structural unit (hereinafter, may be also referred to as "structural unit (II)") including a lactone structure, a cyclic carbonate structure, a sultone structure, or a combination thereof; a structural unit (hereinafter, may be also referred to as "structural unit (III)") including an alcoholic hydroxyl group; and/or a structural unit (hereinafter, may be also referred to as "structural unit (IV)")

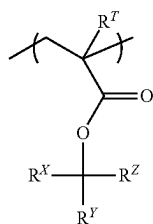
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including a phenolic hydroxyl group, and may have an other structural unit aside from the structural units (I) to (IV). The polymer (A) may have one, or two or more types of each structural unit. Each structural unit will be described below.

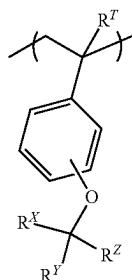
Structural Unit (I)

The structural unit (I) is a structural unit including an acid-labile group. The "acid-labile group" as referred to herein means a group that substitutes for a hydrogen atom of a carboxy group or a phenolic hydroxyl group, and is dissociable by an action of an acid. When the polymer (A) has the acid-labile group in the structural unit (I), the acid-labile group is dissociated in light-exposed regions by an action of an acid generated in the exposing, and a difference in solubility in a developer solution emerges between the light-exposed regions and the light-unexposed regions, thereby enabling forming the resist pattern.

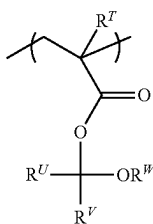
The structural unit (I) is exemplified by structural units (hereinafter, may be also referred to as "structural units (I-1A), (I-1B), (I-2A), and (I-2B)") represented by the following formulae (2-1A), (2-1B), (2-2A), and (2-2B), and the like. It is to be noted that in the structural units (I-1A) to (I-2B), $-\text{CR}^X\text{R}^Y\text{R}^Z$ or $-\text{CR}^U\text{R}^V(\text{OR}^W)$ bonding to an oxyoxygen atom derived from the carboxy group or the phenolic hydroxyl group corresponds to the acid-labile group.



(2-1A)



(2-1B)

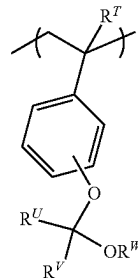


(2-2A)

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-continued

(2-2B)



In the above formulae (2-1A) and (2-1B), R^T represents a hydrogen atom, a fluorine atom, a methyl group, or a trifluoromethyl group; R^X represents a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms; and R^Y and R^Z each independently represent a monovalent hydrocarbon group having 1 to 20 carbon atoms, or R^Y and R^Z taken together represent an alicyclic structure having 3 to 20 ring atoms, together with the carbon atom to which R^Y and R^Z bond.

In the above formulae (2-2A) and (2-2B), R^T represents a hydrogen atom, a fluorine atom, a methyl group, or a trifluoromethyl group; R^U represents a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms; and R^V and R^W each independently represent a monovalent hydrocarbon group having 1 to 20 carbon atoms, or R^V and R^W taken together represent an alicyclic structure having 4 to 20 ring atoms, together with the carbon atom to which R^U bonds and the oxygen atom adjacent to this carbon atom.

Examples of the monovalent hydrocarbon group having 1 to 20 carbon atoms which may be represented by R^X , R^Y , R^Z , R^U , R^V , or R^W include a monovalent chain hydrocarbon group having 1 to 20 carbon atoms, a monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, a monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, and the like.

Examples of the monovalent chain hydrocarbon group having 1 to 20 carbon atoms include: alkyl groups such as a methyl group, an ethyl group, an n-propyl group, and an i-propyl group; alkenyl groups such as an ethenyl group and a propenyl group; alkynyl groups such as an ethynyl group and a propynyl group; and the like. Examples of the monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms include: alicyclic saturated hydrocarbon groups such as a cyclopropyl group, a cyclobutyl group, cyclopentyl group, a cyclohexyl group, a norbornyl group, and an adamantyl group; alicyclic unsaturated hydrocarbon groups such as a cyclopropenyl group, a cyclobutenyl group, cyclopentenyl group, a cyclohexenyl group, and a norbornenyl group; and the like. Examples of the monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms include: aryl groups such as a phenyl group, a tolyl group, a xylyl group, a naphthyl group, and an anthryl group; aralkyl groups such as a benzyl group, a phenethyl group, a naphthylmethyl group, and an anthrylmethyl group; and the like.

Examples of the alicyclic structure having 3 to 20 ring atoms which may be constituted by R^Y and R^Z taken together include: saturated alicyclic structures such as a cyclopropane structure, a cyclobutane structure, a cyclopentane structure, a cyclohexane structure, a norbornane structure, and an adamantane structure; unsaturated alicyclic structures such as a cyclopropene structure, a cyclobutene structure, a

cyclopentene structure, a cyclohexene structure, and a norbornene structure; and the like.

Examples of the aliphatic heterocyclic structure having 4 to 20 ring atoms which may be constituted by R^V and R^W taken together include saturated oxygen-containing heterocyclic structures such as an oxacyclobutane structure, an oxacyclopentane structure, and an oxacyclohexane structure; unsaturated oxygen-containing heterocyclic structures such as an oxacyclobutene structure, an oxacyclopentene structure, and an oxacyclohexene structure; and the like.

In light of copolymerizability of a monomer that gives the structural unit (I), R^T represents preferably a hydrogen atom or a methyl group. R^X represents preferably a hydrogen atom, an alkyl group, or an aryl group. R^Y and R^Z represent preferably an alkyl group or an alicyclic saturated hydrocarbon group. The structural unit (I) is preferably the structural unit (I-1A).

Examples of the structural unit (I) include structural units which use as monomers, compounds represented by the formulae (m-1) to (m-4) and (m-20) disclosed in EXAMPLES, described later, and the like. In addition, examples of the structural unit (I) include, of structural units exemplified as the structural unit (I) in Japanese Unexamined Patent Application, Publication No. 2018-013744, structural units corresponding to the above formulae (2-1A), (2-1B), (2-2A), and (2-2B), and the like.

The lower limit of a proportion of the structural unit (I) with respect to total structural units constituting the polymer (A) is preferably 5 mol %, more preferably 10 mol %, still more preferably 20 mol %, and particularly preferably 30 mol %. The upper limit of the proportion is preferably 80 mol %, more preferably 70 mol %, and still more preferably 60 mol %. This proportion is particularly preferred in a case in which the exposure light is an ArF excimer laser beam. In a case in which the exposure light is EUV, the lower limit of the proportion with respect to total structural units is preferably 10 mol %, and more preferably 20 mol %. The upper limit of the proportion is preferably 70 mol %, and more preferably 60 mol %. When the proportion of the structural unit (I) falls within the above ranges, the sensitivity of the radiation-sensitive resin composition to exposure light can be further improved, and moreover, the highly water repellent property and the defect-inhibiting property can be further improved.

Structural Unit (II)

The structural unit (II) is a structural unit other than the structural unit (I), and includes a lactone structure, a cyclic carbonate structure, a sultone structure, or a combination thereof. When the polymer (A) has the structural unit (II), the solubility of the polymer (A) in a developer solution becomes easy to adjust in a more appropriate manner, and as a result, the sensitivity of the radiation-sensitive resin composition to exposure light can be further improved, and the highly water repellent property and the defect-inhibiting property can be further improved.

Examples of the structural unit (II) include structural units which use as monomers, compounds represented by the formulae (m-5) to (m-11) and (m-13) disclosed in EXAMPLES, described later, and the like. In addition, examples of the structural unit (II) include structural units exemplified as the structural unit (III) in Japanese Unexamined Patent Application, Publication No. 2018-013744, and the like.

The lower limit of a proportion of the structural unit (II) with respect to total structural units in the polymer (A) is

preferably 5 mol %, more preferably 10 mol %, still more preferably 20 mol %, and particularly preferably 30 mol %. The upper limit of the proportion is preferably 80 mol %, and more preferably 70 mol %. When the proportion of the structural unit (II) falls within the above range, the solubility of the polymer (A) in a developer solution becomes easy to adjust in a still more appropriate manner, and as a result, the highly water repellent property and the defect-inhibiting property can be still further improved.

Structural Unit (III)

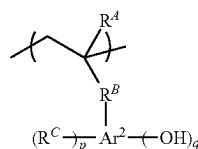
The structural unit (III) is a structural unit other than the structural unit (I) and the structural unit (II), and includes an alcoholic hydroxyl group. When the polymer (A) has the structural unit (III), the solubility of the polymer (A) in a developer solution becomes easy to adjust in a more appropriate manner, and as a result, the highly water repellent property and the defect-inhibiting property of the radiation-sensitive resin composition can be further improved.

Examples of the structural unit (III) include structural units which use as monomers, compounds represented by the formulae (m-12) and (m-14) disclosed in EXAMPLES, described later, and the like. In addition, examples of the structural unit (III) include structural units exemplified as the structural unit (IV) in Japanese Unexamined Patent Application, Publication No. 2018-028574, and the like.

The lower limit of a proportion of the structural unit (III) with respect to total structural units constituting the polymer (A) is preferably 5 mol %, and more preferably 10 mol %. The upper limit of the proportion is preferably 40 mol %, and more preferably 30 mol %. This proportion is particularly preferred in a case in which the exposure light is an ArF excimer laser beam. In a case in which the exposure light is EUV, the lower limit of the proportion with respect to total structural units is preferably 5 mol %, more preferably 10 mol %, and still more preferably 20 mol %. The upper limit of the proportion is preferably 60 mol %, more preferably 50 mol %, and still more preferably 40 mol %. When the proportion of the structural unit (III) falls within the above ranges, the solubility of the polymer (A) in a developer solution becomes easy to adjust in an even more appropriate manner, and as a result, the highly water repellent property and the defect-inhibiting property of the radiation-sensitive resin composition can be still further improved.

Structural Unit (IV)

The structural unit (IV) is a structural unit other than the structural unit (I), the structural unit (II), and the structural unit (III), and includes a phenolic hydroxyl group. The "phenolic hydroxyl group" as referred to herein is not limited to a hydroxy group directly bonding to a benzene ring, and means any hydroxy group directly bonding to an aromatic ring. In the case of using an ArF excimer laser beam, a KrF excimer laser beam, EUV, an electron beam, or the like as the radioactive ray, when the polymer (A) has the structural unit (IV), the sensitivity to exposure light can be further improved, and as a result, the LWR performance and the CDU performance of the radiation-sensitive resin composition can be further improved. Examples of the structural unit (IV) include structural units represented by the following formula (P), and the like.



In the above formula (P), R^{A} represents a hydrogen atom, a fluorine atom, a methyl group, or a trifluoromethyl group; R^{B} represents a single bond, --O-- , --COO-- , or --CONH-- ; Ar^2 represents a group obtained by removing $(p+q+1)$ hydrogen atoms on an aromatic ring from an arene having 6 to 20 ring atoms; p is an integer of 0 to 10, wherein in a case in which p is 1, R^{C} represents a halogen atom or a monovalent organic group having 1 to 20 carbon atoms, in a case in which p is no less than 2, a plurality of R^{C} s are identical or different from each other and each R^{C} represents a halogen atom or a monovalent organic group having 1 to 20 carbon atoms, or no less than two of the plurality of R^{C} s taken together represent a ring structure having 4 to 20 ring atoms together with the carbon chain to which the no less than two R^{C} s bond; and q is an integer of 1 to 11, wherein a sum of p and q is no greater than 11.

In light of copolymerizability of a monomer that gives the structural unit (IV), R^{A} represents preferably a hydrogen atom or a methyl group, and more preferably a hydrogen atom. R^{B} represents preferably a single bond or --COO-- , and more preferably a single bond. Examples of the arene having 6 to 20 ring atoms which gives Ar^2 include benzene, naphthalene, anthracene, phenanthrene, tetracene, pyrene, and the like. Of these, benzene or naphthalene is preferred, and benzene is further preferred.

The monovalent organic group having 1 to 20 carbon atoms which may be represented by R^{C} is exemplified by: a monovalent hydrocarbon group having 1 to 20 carbon atoms; a group which includes a divalent hetero atom-containing group between two adjacent carbon atoms or at the end of the atomic bonding side of the hydrocarbon group; a group obtained by substituting with a monovalent hetero atom-containing group, a part or all of hydrogen atoms included in the hydrocarbon group or the divalent hetero atom-containing group; and the like. R^{C} represents preferably a hydrocarbon group, and more preferably an alkyl group. Examples of the ring structure having 4 to 20 ring atoms which may be constituted by the no less than 2 of the plurality of R^{C} s taken together include an alicyclic structure such as a cyclohexane structure, and the like. p is preferably 0 to 2, more preferably 0 or 1, and more preferably 0. q is preferably 1 to 3, and more preferably 1 or 2.

Examples of the structural unit (IV) include structural units which use as monomers, compounds represented by the formulae (m-15) and (m-16) disclosed in EXAMPLES, described later, and the like. In addition, examples of the structural unit (IV) include structural units exemplified as the structural unit (II) in Japanese Unexamined Patent Application, Publication No. 2018-013744, and the like.

The lower limit of a proportion of the structural unit (IV) with respect to total structural units constituting the polymer (A) is preferably 5 mol %, more preferably 10 mol %, and particularly preferably 20 mol %. The upper limit of the proportion is preferably 80 mol %, more preferably 70 mol %, and particularly preferably 60 mol %. When the proportion of the structural unit (IV) falls within the above range, the highly water repellent property and the defect-inhibiting property can be further improved.

The other structural unit is exemplified by a structural unit including an acid-nonlabile hydrocarbon group, and the like.

Examples of the acid-nonlabile hydrocarbon group include a monovalent chain hydrocarbon group which bonds to the oxy group of --COO-- , a monovalent alicyclic hydrocarbon group, and the like. In the case in which the polymer (A) has the other structural unit, the upper limit of a proportion of the other structural unit is preferably 30 mol %, and more preferably 20 mol %. The lower limit of the proportion is, for example, 1 mol %.

The lower limit of a polystyrene-equivalent weight average molecular weight (Mw) of the polymer (A) as determined by gel permeation chromatography (GPC) is preferably 2,000, more preferably 3,000, still more preferably 4,000, and particularly preferably 5,000. The upper limit of the Mw is preferably 30,000, more preferably 20,000, still more preferably 15,000, and particularly preferably 10,000. When the Mw of the polymer (A) falls within the above range, coating characteristics of the radiation-sensitive resin composition can be improved, and as a result, the highly water repellent property and the defect-inhibiting property can be further improved.

The upper limit of a ratio (Mw/Mn) of the Mw to a polystyrene-equivalent number average molecular weight (Mn) of the polymer (A) as determined by GPC is preferably 3.00, more preferably 2.50, still more preferably 2.00, and particularly preferably 1.85. The lower limit of the ratio is typically 1.00, and preferably 1.10.

It is to be noted that the Mw and the Mn of the polymer as referred to herein are values determined using gel permeation chromatography (GPC) under the following conditions.

GPC columns: "G2000 HXL"×2, "G3000 HXL"×1, and "G4000 HXL"×1, available from Tosoh Corporation;
elution solvent: tetrahydrofuran
flow rate: 1.0 mL/minute
sample concentration: 1.0% by mass
amount of injected sample: 100 μL
column temperature: 40° C.
detector: differential refractometer
standard substance: mono-dispersed polystyrene

The lower limit of a proportion of the polymer (A) with respect to total components other than the solvent (D) in the radiation-sensitive resin composition is preferably 50% by mass, more preferably 70% by mass, and still more preferably 80% by mass. Either one, or two or more types of the polymer (A) can be used.

Method of Synthesizing Polymer (A)

The polymer (A) can be synthesized by, for example, polymerizing a monomer that gives each structural unit according to a well-known procedure.

(E) Polymer

The polymer (E) is a polymer which has the structural unit (W). The polymer (E) is a polymer having a higher total proportion by mass of fluorine atoms being greater than that of the polymer (A). A polymer having higher hydrophobicity than that of a polymer acting as a base polymer tends to be localized in the surface layer of a resist film; thus, since the polymer (E) has the higher total proportion by mass of fluorine atoms being greater than that of the polymer (A), the polymer (E) tends to be localized in the surface layer of the

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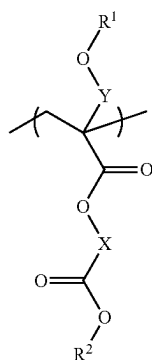
resist film due to the characteristics that result from the hydrophobicity. In addition, due to the characteristics that result from the hydrophobicity, a receding contact angle between the resist film and a liquid immersion medium becomes higher. Thus, due containing the polymer (E), the radiation-sensitive resin composition is suitable for a liquid immersion lithography process, and in addition, forming a resist pattern having superior water repellency and inhibited occurrence of defects is enabled.

The lower limit of the proportion of fluorine atoms in the polymer (E) is preferably 1% by mass, more preferably 2% by mass, and still more preferably 3% by mass. The upper limit of the proportion is preferably 60% by mass, more preferably 50% by mass, and still more preferably 40% by mass. When the total proportion by mass of fluorine atoms falls within the above range, localization of the polymer (E) in the resist film can be more appropriately adjusted. It is to be noted that the total proportion by mass of fluorine atoms in the polymer may be calculated based on the structure of the polymer determined by ^{13}C -NMR spectroscopy.

In addition to the structural unit (W), the polymer (E) preferably has the structural unit (I), the structural unit (II), the structural unit (III), and/or the structural unit (IV), each described above, and may have the other structural unit aside from the structural units (I) to (IV). For example, the polymer (E) preferably has a structural unit (hereinafter, may be also referred to as "structural unit (F)") which has a fluorine atom, the structure unit (F) being a structure unit other than the structural unit (W). The polymer (E) may have one, or two or more types of each structural unit. Each structural unit will be described below.

Structural Unit (W)

The structural unit (W) is a structural unit represented by the following formula (1). Due to the polymer (E) having the structural unit (W), the sensitivity to exposure light is favorable, and forming a resist pattern with superior water repellency and few defects is enabled.



In the formula (1), R^1 represents a monovalent organic group having 1 to 20 carbon atoms; R^2 represents a monovalent organic group having 1 to 20 carbon atoms; X represents a divalent organic group having 1 to 20 carbon atoms; and Y represents a divalent hydrocarbon group having 1 to 20 carbon atoms, wherein at least one of the divalent organic group represented by X and the monovalent organic group represented by R^2 has a fluorine atom.

The monovalent organic group having 1 to 20 carbon atoms represented by R^1 or R^2 is exemplified by a substi-

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tuted or unsubstituted monovalent hydrocarbon group having 1 to 20 carbon atoms, and the like. Examples of the monovalent hydrocarbon group having 1 to 20 carbon atoms include groups similar to the monovalent hydrocarbon groups having 1 to 20 carbon atoms which may be represented by R^X in the above formula (2-1A), and the like. Further, examples of a substituent in the case in which R^1 or R^2 represents the substituted hydrocarbon group include a halogen atom, a hydroxy group, an alkoxy group, an acetoxy group, an alkoxyalkoxy group, and the like, and the substituent of R^2 is preferably a halogen atom, and particularly preferably a fluorine atom. It is to be noted that in the case in which R^1 or R^2 represents the monovalent hydrocarbon group, a methylene group which constitutes the monovalent hydrocarbon group may be replaced with an ester group or an ether group. As described above, in the case in which R^1 or R^2 represents the substituted hydrocarbon group, a plurality of hydrogen atoms included in the hydrocarbon group may be substituted with different types of substituents or the same type of substituent; together with such substitution, a methylene group may be replaced with an ester group as described above; a methylene group may be replaced with an ether group; or a plurality of methylene groups may each be replaced with an ester group or an ether group.

In the case in which the monovalent organic group represented by R^2 has a fluorine atom, the monovalent organic group may be exemplified by a monovalent fluorinated hydrocarbon group having 1 to 20 carbon atoms, and the like. Examples of the monovalent fluorinated hydrocarbon group preferably include a monovalent fluorinated hydrocarbon group having 2 to 10 carbon atoms, and specifically, a group in which an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group, an n-pentyl group, an i-pentyl group, an s-pentyl group, an n-hexyl group, or an n-heptane group has been partially fluorinated can be preferably exemplified. These groups may be substituted with a substituent other than a fluorine atom.

The divalent organic group having 1 to 20 carbon atoms represented by X is exemplified by a substituted or unsubstituted divalent hydrocarbon group having 1 to 20 carbon atoms, and the like. Examples of the divalent hydrocarbon group having 1 to 20 carbon atoms include groups obtained by removing one hydrogen atom from the monovalent hydrocarbon group having 1 to 20 carbon atoms which may be represented by R^X in the above formula (2-1A), and the like.

In the case in which the monovalent organic group represented by X has a fluorine atom, the monovalent organic group may be exemplified by a monovalent fluorinated hydrocarbon group having 1 to 20 carbon atoms, and the like.

X represents preferably the substituted or unsubstituted divalent hydrocarbon group having 1 to 20 carbon atoms, $\text{---X}^1\text{---O---}$, or $\text{---X}^2\text{---NH---}$. X^1 and X^2 each independently represent a substituted or unsubstituted divalent hydrocarbon group having 1 to 20 carbon atoms. Examples of the substituent include a fluorine atom, an alkoxy group, an acetoxy group, and the like. In the case in which X represents the substituted hydrocarbon group, a plurality of hydrogen atoms included in the hydrocarbon group may be substituted with a plurality of the same type of substituent or with different substituents.

The divalent hydrocarbon group having 1 to 20 carbon atoms represented by X^1 and the divalent hydrocarbon group having 1 to 20 carbon atoms represented by X^2 preferably

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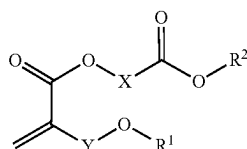
each independently represent a divalent aliphatic hydrocarbon group having 1 to 4 carbon atoms.

The divalent aliphatic hydrocarbon group having 1 to 4 carbon atoms may be exemplified by a divalent chain hydrocarbon group having 1 to 4 carbon atoms. Examples of the divalent chain hydrocarbon group having 1 to 4 carbon atoms include alkanediyl groups such as a methanediyl group, an ethanediyl group, an n-propanediyl group, and an i-propanediyl group; alkenediyl groups such as an ethenediyl group and a propenediyl group; alkynediyl groups such as an ethynediyl group and a propynediyl group; and the like.

The divalent hydrocarbon group having 1 to 20 carbon atoms represented by Y is exemplified by groups obtained by removing one hydrogen atom from the monovalent hydrocarbon group having 1 to 20 carbons which may be represented by R^X in the above formula (2-1A), and the like. Of these, Y represents preferably a divalent aliphatic hydrocarbon group having 1 to 4 carbon atoms. Examples of the divalent aliphatic hydrocarbon group having 1 to 4 carbon atoms include the divalent aliphatic hydrocarbon group having 1 to 4 carbon atoms represented by X^1 , and the like.

Compound (F)

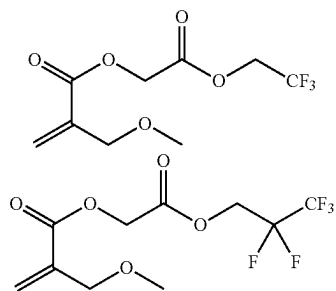
The monomer which gives the structural unit (W) may be exemplified by a compound (F) represented by the following formula (i), and the like.



In the above formula (i), R^1 represents a monovalent organic group having 1 to 20 carbon atoms; X represents a divalent organic group having 1 to 20 carbon atoms; R^2 represents a monovalent organic group having 1 to 20 carbon atoms; and Y represents a divalent hydrocarbon group having 1 to 20 carbon atoms, wherein at least one of the divalent organic group represented by X and the monovalent organic group represented by R^2 has a fluorine atom.

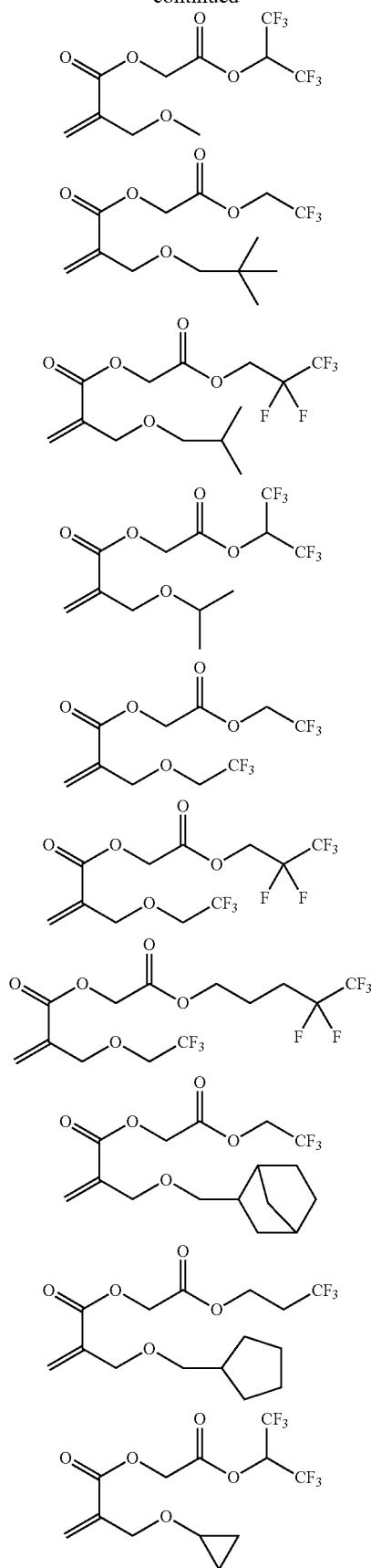
X, R^1 , R^2 , and Y in the above formula (i) are described in the above formula (1).

Specific examples of the compound (F) include compounds represented by the following formulae, and the like. More specifically, the structural unit (W) is exemplified by structural units which use these compounds as monomers, and the like.



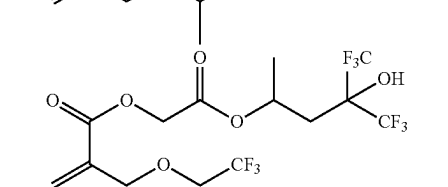
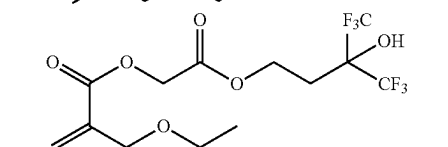
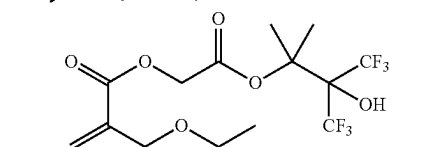
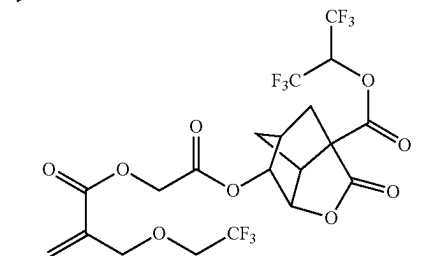
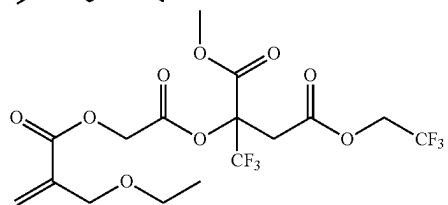
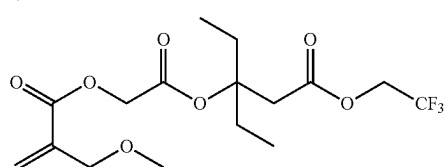
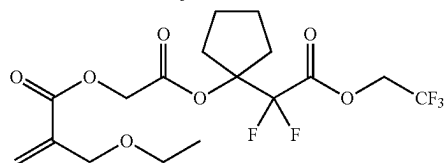
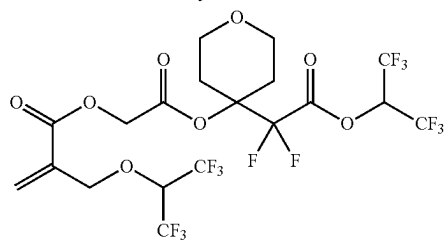
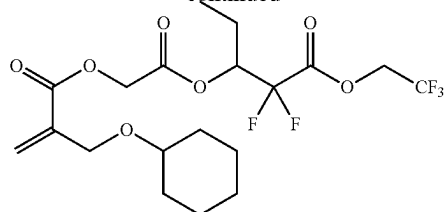
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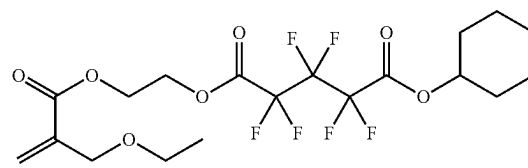
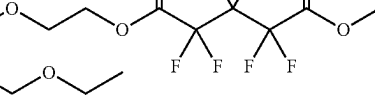
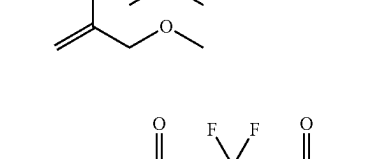
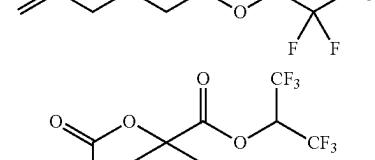
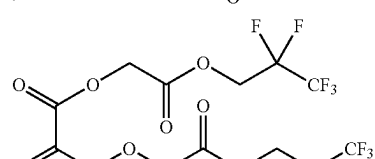
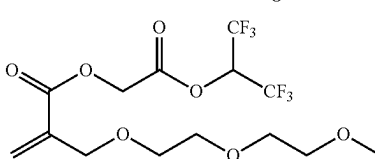
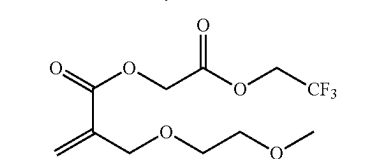
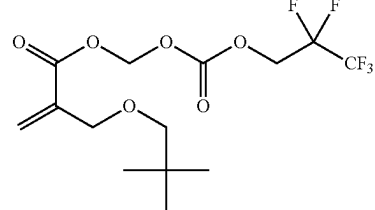
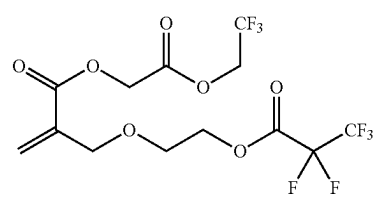
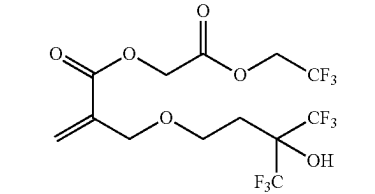
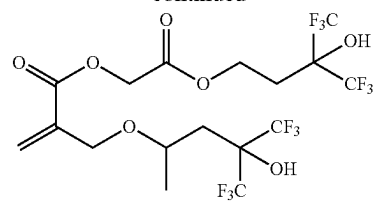


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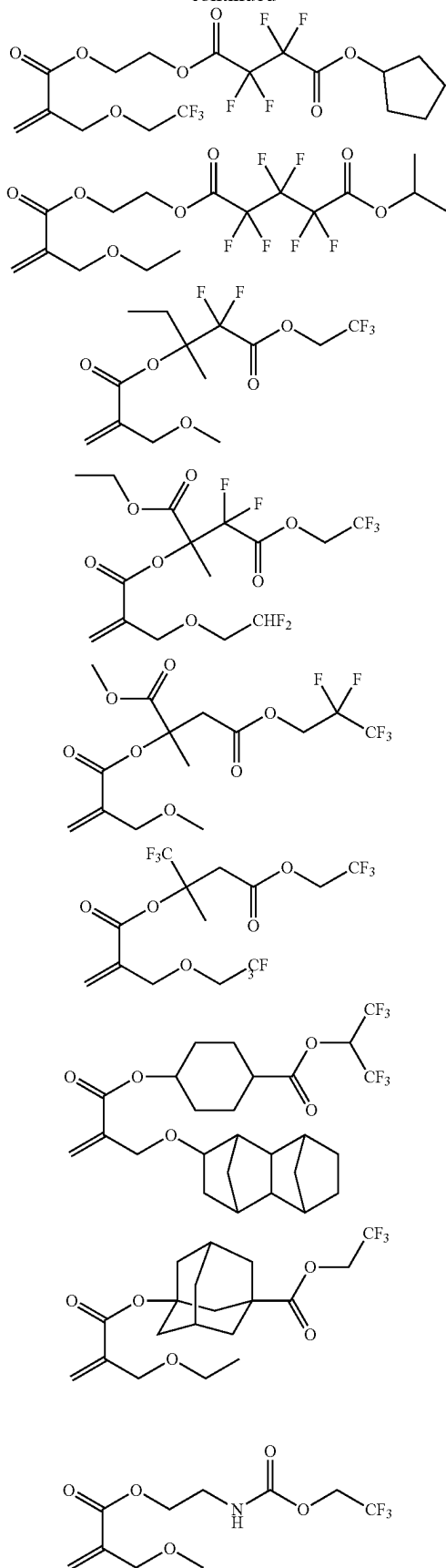
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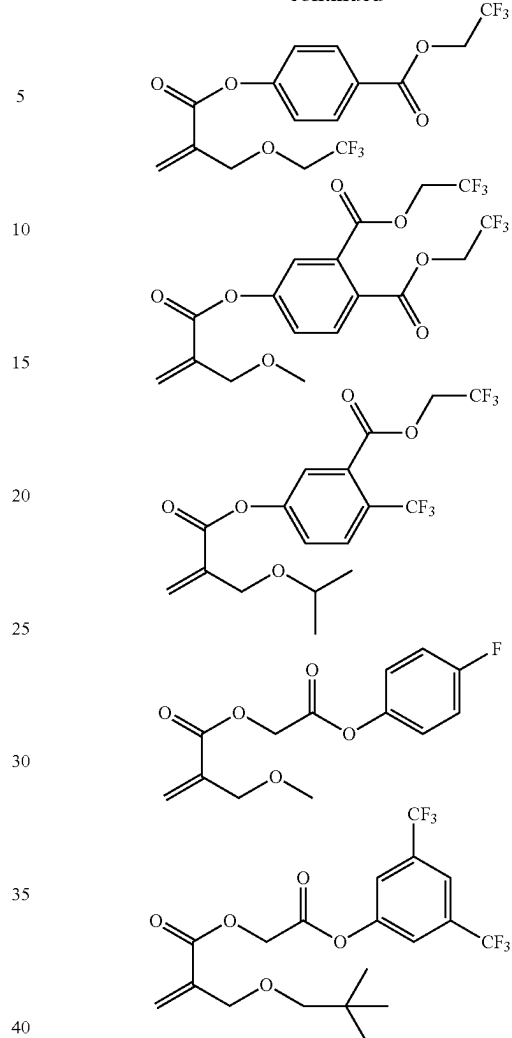
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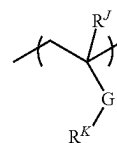
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The lower limit of a proportion of the structural unit (W) with respect to total structural units constituting the polymer (E) is preferably 1 mol %, more preferably 5 mol %, still more preferably 20 mol %, and particularly preferably 40 mol %. The upper limit of the proportion is preferably 100 mol %, more preferably 95 mol %, and still more preferably 90 mol %. When the proportion of the structural unit (W) falls within the above range, the sensitivity of the radiation-sensitive resin composition to exposure light can be further improved, and moreover, the highly water repellent property and the defect-inhibiting property can be further improved.

Structural Unit (F)

Examples of the structural unit (F) include a structural unit represented by the following formula (f-1), and the like.



(f-1)

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In the above formula (f-1), R^J represents a hydrogen atom, a fluorine atom, a methyl group, or a trifluoromethyl group; G represents a single bond, an oxygen atom, a sulfur atom, $-\text{COO}-$, $-\text{SO}_2-\text{NH}-$, $-\text{CONH}-$, or $-\text{OCONH}-$; and R^K represents a monovalent organic group having 1 to 8 carbon atoms which has a fluorine atom.

In light of copolymerizability of a monomer that gives the structural unit (F), R^J represents preferably a hydrogen atom or a methyl group, and more preferably a methyl group. G represents preferably $-\text{COO}-$, $-\text{SO}_2-\text{NH}-$, $-\text{CONH}-$, or $-\text{OCONH}-$, and more preferably $-\text{COO}-$.

Examples of the structural unit (F) include structural units which use as monomers, compounds represented by the formulae (m-17) to (m-19) and (m-21) to (m-23) disclosed in EXAMPLES, described later, and the like.

The lower limit of a proportion of the structural unit (F) with respect to total structural units constituting the polymer (E) is preferably 1 mol %, more preferably 5 mol %, and still more preferably 10 mol %. The upper limit of the proportion is preferably 90 mol %, more preferably 80 mol %, and still more preferably 70 mol %. When the proportion of the structural unit (F) falls within the above range, the proportion by mass of fluorine atoms contained in the polymer (E) can be still more appropriately adjusted.

The polymer (E) preferably has a structural unit including an acid-labile group and/or a structural unit including an alcoholic hydroxyl group. The structural unit including the acid-labile group is exemplified by the structural units exemplified as the structural unit (I) in the polymer (A), and the like. The structural unit including the alcoholic hydroxyl group is exemplified by the structural units exemplified as the structural unit (III) in the polymer (A), and the like.

The lower limit of a proportion of the structural unit which includes the acid-labile group with respect to total structural units constituting the polymer (E) is preferably 1 mol %, and more preferably 5 mol %. The upper limit of the proportion is preferably 70 mol %, more preferably 60 mol %, and still more preferably 50 mol %.

The lower limit of a proportion of the structural unit which includes the alcoholic hydroxyl group with respect to total structural units constituting the polymer (E) is preferably 1 mol %, and more preferably 5 mol %. The upper limit of the proportion is preferably 50 mol %, more preferably 40 mol %, and still more preferably 30 mol %.

Other Structural Unit

The polymer (E) may have the other structural unit within a range not leading to impairment of the effects of the present invention. The proportion of the other structural unit may be appropriately determined in accordance with a purpose thereof.

The lower limit of a polystyrene-equivalent weight average molecular weight (M_w) of the polymer (E) as determined by gel permeation chromatography (GPC) is preferably 2,000, more preferably 3,000, still more preferably 4,000, and particularly preferably 5,000. The upper limit of the M_w is preferably 30,000, more preferably 20,000, still more preferably 15,000, and particularly preferably 10,000. When the M_w of the polymer (E) falls within the above range, coating characteristics of the radiation-sensitive resin composition can be improved, and as a result, the LWR performance and the CDU performance can be further improved.

The upper limit of a ratio (M_w/M_n) of the M_w to a polystyrene-equivalent number average molecular weight (M_n) of the polymer (E) as determined by GPC is preferably

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3.00, more preferably 2.50, still more preferably 2.00, and particularly preferably 1.85. The lower limit of the ratio is typically 1.00, and preferably 1.10.

The lower limit of a content of the polymer (E) with respect to 100 parts by mass of the polymer (A) is preferably 0.1 parts by mass, more preferably 0.5 parts by mass, and still more preferably 1 part by mass. The upper limit of the content is preferably 30 parts by mass, more preferably 25 parts by mass, and still more preferably 20 parts by mass. The radiation-sensitive resin composition may contain one, or two or more types of the polymer (E).

Method of Synthesizing Polymer (E)

The polymer (E) can be synthesized by, for example, polymerizing a monomer that gives each structural unit in accordance with a well-known procedure.

(B) Acid Generator

The acid generator (B) is a component which generates an acid by irradiation with a radioactive ray. Examples of the radioactive ray include electromagnetic waves such as a visible light ray, an ultraviolet ray, a far ultraviolet ray, EUV, an X-ray, and a γ -ray; charged particle rays such as an electron beam and an α -ray, and the like. A change in solubility in a developer solution and the like of the polymer (A) in the radiation-sensitive resin composition is promoted by an action of an acid generated from the acid generator (B), and as a result, the resolution and the LWR performance can be further improved. The acid generator (B) may be contained in the radiation-sensitive resin composition either in the form of a low-molecular-weight compound (hereinafter, may be also referred to as "(B) acid generating agent" or "acid generating agent (B)") or in the form of an acid generator incorporated as a part of a polymer such as the polymer (A) or the like, or may be in a combination of both these forms.

The acid generating agent (B) is exemplified by an onium salt compound, an N-sulfonyloxyimide compound, a halogen-containing compound, a diazoketone compound, and the like.

Examples of the onium salt compound include a sulfonium salt, a tetrahydrothiophenium salt, an iodonium salt, a phosphonium salt, a diazonium salt, a pyridinium salt, and the like.

Examples of the sulfonium salt include triphenylsulfonium trifluoromethanesulfonate, triphenylsulfonium nonafluoro-n-butanesulfonate, triphenylsulfonium perfluoro-n-octanesulfonate, triphenylsulfonium 2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethanesulfonate, triphenylsulfonium camphorsulfonate, 4-cyclohexylphenyldiphenylsulfonium nonafluoro-n-butanesulfonate, 4-methanesulfonylphenyldiphenylsulfonium nonafluoro-n-butanesulfonate, triphenylsulfonium 1,1,2,2-tetrafluoro-6-(1-adamantanecarbonyloxy)-hexane-1-sulfonate (a compound represented by the formula (B-4) in EXAMPLES, described later), triphenylsulfonium 2-(1-adamanty)-1,1-difluoroethanesulfonate, triphenylsulfonium 2-(adamantane-1-ylcarbonyloxy)-1,1,3,3,3-pentafluoropropane-1-sulfonate (a compound represented by the formula (B-3) in EXAMPLES, described later), triphenylsulfonium maleate, and the like. Other examples of the sulfonium salt include compounds represented by the formulae (B-1), (B-5), and (B-6) in EXAMPLES, described later, and the like.

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Examples of the tetrahydrothiophenium salt include 1-(4-n-butoxynaphthalen-1-yl)tetrahydrothiophenium trifluoromethanesulfonate, 1-(4-n-butoxynaphthalen-1-yl)tetrahydrothiophenium nonafluoro-n-butanesulfonate, 1-(4-n-butoxynaphthalen-1-yl)tetrahydrothiophenium perfluoro-n-octanesulfonate, 1-(4-n-butoxynaphthalen-1-yl)tetrahydrothiophenium 2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethanesulfonate (a compound represented by formula (B-2) in EXAMPLES, described later), 1-(4-n-butoxynaphthalen-1-yl)tetrahydrothiophenium camphorsulfonate, 1-(6-n-butoxynaphthalen-2-yl)tetrahydrothiophenium nonafluoro-n-butanesulfonate, 1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium nonafluoro-n-butanesulfonate, and the like.

Examples of the iodonium salt include diphenyliodonium trifluoromethanesulfonate, diphenyliodonium nonafluoro-n-butanesulfonate, diphenyliodonium perfluoro-n-octanesulfonate, diphenyliodonium 2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethanesulfonate, diphenyliodonium camphorsulfonate, bis(4-t-butylphenyl)iodonium nonafluoro-n-butanesulfonate, and the like.

Examples of the N-sulfonyloxyimide compound include N-trifluoromethylsulfonyloxy phthalimide, N-(trifluoromethylsulfonyloxy)-1,8-naphthalimide, N-(trifluoromethylsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(nonafluoro-n-butylsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(perfluoro-n-octylsulfonyloxy)-1,8-naphthalimide, N-(perfluoro-n-octylsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(2-bicyclo[2.2.1]hept-2-yl-1,1,2,2-tetrafluoroethylsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(2-(3-tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodecanyl)-1,1-difluoroethylsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, N-(camphorsulfonyloxy)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide, and the like.

Of these, the acid generating agent (B) is preferably the sulfonium salt or the tetrahydrothiophenium salt, and more preferably a compound represented by the following formulae (B-1) to (B-6). Other examples of the acid generating agent (B) include compounds exemplified as the acid generator (B) in Japanese Unexamined Patent Application, Publication No. 2018-013744, and the like.

In the case in which the acid generator (B) is the acid generating agent (B), the lower limit of a content of the acid generating agent (B) with respect to 100 parts by mass of the polymer (A) is preferably 0.1 parts by mass, more preferably 1 part by mass, still more preferably 2 parts by mass, and particularly preferably 5 parts by mass. The upper limit of the content is preferably 100 parts by mass, more preferably 60 parts by mass, still more preferably 40 parts by mass, and particularly preferably 30 parts by mass. When the content of the acid generating agent (B) falls within the above range, the sensitivity of the radiation-sensitive resin composition to exposure light can be further improved, and moreover, the highly water repellent property and the defect-inhibiting property can be further improved. The radiation-sensitive resin composition may contain one, or two or more types of the acid generator (B).

Furthermore, the acid generator (B) may be exemplified by a polymer in which the structure of the acid generator is incorporated as a part of the polymer (A).

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(C) Acid Diffusion Controller

The radiation-sensitive resin composition may contain the acid diffusion controller (C) as an optional component. The acid diffusion controller (C) controls a diffusion phenomenon, in the resist film, of the acid generated from the acid generating agent (B) and the like upon exposure, thereby achieving an effect of controlling unwanted chemical reactions in a light-unexposed region. The acid diffusion controller (C) may be contained in the radiation-sensitive resin composition in the form of a low-molecular weight compound (hereinafter, may be also appropriately referred to as "(C) acid diffusion control agent" or "acid diffusion control agent (C)") or in the form of an acid diffusion controller incorporated as a part of a polymer such as the polymer (A) or the like, or may be in a combination of both these forms.

The acid diffusion control agent (C) is exemplified by a photodegradable base that is photosensitized by an exposure to generate a weak acid, and the like. An exemplary photodegradable base includes a compound containing a radiation-sensitive onium cation which degrades upon exposure and an anion of a weak acid, and the like. In a light-exposed region, the photodegradable base generates a weak acid from: a proton generated upon degradation of the radiation-sensitive onium cation; and the anion of the weak acid, whereby acid diffusion controllability decreases. Examples of the photodegradable base include compounds represented by the formulae (C-1) to (C-4) disclosed in EXAMPLES, described later, and the like. Alternatively, the acid diffusion control agent (C) is exemplified by a nitrogen-containing compound. Specific examples of the nitrogen-containing compound include a compound represented by the formula (C-5) disclosed in EXAMPLES, described later, and the like. Other specific examples of the acid diffusion control agent (C) include compounds exemplified as the acid diffusion control agent (D) in Japanese Unexamined Patent Application, Publication No. 2018-013744.

In the case in which the radiation-sensitive resin composition contains the acid diffusion control agent (C), the lower limit of a content of the acid diffusion control agent (C) with respect to 100 parts by mass of the polymer (A) is preferably 0.1 parts by mass, more preferably 0.5 parts by mass, and still more preferably 1 part by mass. The upper limit of the content is preferably 20 parts by mass, more preferably 10 parts by mass, and still more preferably 5 parts by mass.

The lower limit of a proportion of the acid diffusion control agent (C) with respect to 100 mol % of the acid generating agent (B) is preferably 1 mol %, more preferably 5 mol %, and still more preferably 10 mol %. The upper limit of the proportion is preferably 250 mol %, more preferably 150 mol %, and still more preferably 100 mol %.

When the content and the proportion of the acid diffusion control agent (C) fall within the above ranges, the sensitivity of the radiation-sensitive resin composition to exposure light, the highly water repellent property, and the defect-inhibiting property can be further improved. The radiation-sensitive resin composition may contain one, or two or more types of the acid diffusion controller (C).

(D) Solvent

The radiation-sensitive resin composition typically contains the solvent (D). The solvent (D) is not particularly limited as long as it is a solvent capable of dissolving or dispersing at least the polymer (A), the polymer (E), the acid generator (B), and the optional component(s), which is/are contained as desired.

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The solvent (D) is exemplified by an alcohol solvent, an ether solvent, a ketone solvent, an amide solvent, an ester solvent, a hydrocarbon solvent, and the like.

Examples of the alcohol solvent include:
 aliphatic monohydric alcohol solvents having 1 to 18 carbon atoms such as 4-methyl-2-pentanol;
 alicyclic monohydric alcohol solvents having 3 to 18 carbon atoms such as cyclohexanol;
 polyhydric alcohol solvents having 2 to 18 carbon atoms such as 1,2-propylene glycol;
 polyhydric alcohol partial ether solvents having 3 to 19 carbon atoms such as propylene glycol-1-monomethyl ether; and the like.

Examples of the ether solvent include:
 dialkyl ether solvents such as diethyl ether;
 cyclic ether solvents such as tetrahydrofuran;
 aromatic ring-containing ether solvents such as diphenyl ether; and the like.

Examples of the ketone solvent include:
 chain ketone solvents such as acetone;
 cyclic ketone solvents such as cyclohexanone;
 2,4-pentanedione, acetonylacetone, and acetophenone; and the like.

Examples of the amide solvent include:
 cyclic amide solvents such as N,N'-dimethylimidazolidinone;
 chain amide solvents such as N-methylformamide; and the like.

Examples of the ester solvent include:
 monocarboxylic acid ester solvents such as ethyl lactate;
 polyhydric alcohol carboxylate solvents such as propylene glycol acetate;
 polyhydric alcohol partial ether carboxylate solvents such as propylene glycol monomethyl ether acetate;
 polyhydric carboxylic acid diester solvents such as diethyl oxalate;
 lactone solvents such as γ -butyrolactone;
 carbonate solvents such as dimethyl carbonate; and the like.

Examples of the hydrocarbon solvent include:
 aliphatic hydrocarbon solvents having 5 to 12 carbon atoms such as n-pentane;
 aromatic hydrocarbon solvents having 6 to 16 carbon atoms such as toluene; and the like.

Of these, the ketone solvent or the ester solvent is preferred; the cyclic ketone solvent, the monocarboxylic acid ester solvent, the polyhydric alcohol partial ether carboxylate solvent, or the lactone solvent is more preferred; and cyclohexanone, ethyl lactate, propylene glycol monomethyl ether acetate, or γ -butyrolactone is still more preferred. The radiation-sensitive resin composition may contain one, or two or more types of the solvent (D).

The lower limit of a proportion of the solvent (D) in the radiation-sensitive resin composition is preferably 50% by mass, more preferably 60% by mass, and still more preferably 70% by mass. The upper limit of the proportion is preferably 99.9% by mass, more preferably 99.5% by mass, and still more preferably 99% by mass.

The lower limit of a content of the solvent (D) with respect to 100 parts by mass of the polymer (A) is preferably 100 parts by mass, more preferably 500 parts by mass, and still more preferably 1,000 parts by mass. The upper limit of the content is preferably 20,000 parts by mass, more preferably 15,000 parts by mass, and still more preferably 10,000 parts by mass.

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Other Optional Component(s)

Examples of the other optional component(s) include a surfactant, and the like. The radiation-sensitive resin composition may contain one, or two or more types of the other optional component(s).

Method of Preparing Radiation-Sensitive Resin Composition

The radiation-sensitive resin composition may be prepared, for example, by mixing the polymer (A), the polymer (E), and the acid generator (B), as well as the optional components such as the acid diffusion controller (C), the solvent (D), and the like, which are added as needed, in a certain ratio, and preferably filtering a thus resulting mixture through a membrane filter having a pore size of no greater than 0.2 μm .

The radiation-sensitive resin composition may be used either for positive-tone pattern formation conducted using an alkaline developer solution, or for negative-tone pattern formation conducted using an organic solvent-containing developer solution. The radiation-sensitive resin composition may be suitably used for ArF exposure, involving exposure with an ArF excimer laser beam, or for EUV exposure, involving exposure with an extreme ultraviolet ray (EUV).

Method of Forming Resist Pattern

The method of forming a resist pattern according to an other embodiment of the present invention includes: a step (hereinafter, may be also referred to as "applying step") of applying the radiation-sensitive resin composition of the one embodiment of the invention directly or indirectly on a substrate; a step (hereinafter, may be also referred to as "exposing step") of exposing a resist film formed by the applying step; and a step (hereinafter, may be also referred to as "developing step") of developing the resist film exposed.

Due to using the radiation-sensitive resin composition according to the one embodiment of the present invention, the method of forming a resist pattern of the other embodiment of the present invention enables forming a resist pattern with favorable sensitivity to exposure light, and having superior water repellency and few defects. Each step will be described below.

Applying Step

In this step, the radiation-sensitive resin composition is applied directly or indirectly on a substrate. Accordingly, a resist film is formed. The substrate is exemplified by a conventionally well-known substrate such as a silicon wafer, a wafer coated with silicon dioxide or aluminum, and the like. In addition, an organic or inorganic antireflective film disclosed in, for example, Japanese Examined Patent Application, Publication No. H6-12452, Japanese Unexamined Patent Application, Publication No. S59-93448, or the like may be provided on the substrate. An application procedure is exemplified by spin-coating, cast coating, roll-coating, and the like. After the application, prebaking (PB) may be carried out as needed for evaporating the solvent remaining in the coating film. The lower limit of a PB temperature is preferably 60° C., and more preferably 80° C. The upper limit of the PB temperature is preferably 150° C., and more preferably 140° C. The lower limit of a PB time period is

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preferably 5 seconds, and more preferably 10 seconds. The upper limit of the PB time period is preferably 600 seconds, and more preferably 300 seconds. The lower limit of an average thickness of the resist film formed is preferably 10 nm, and more preferably 20 nm. The upper limit of the average thickness is preferably 1,000 nm, and more preferably 500 nm.

Exposing Step

In this step, the resist film formed by the applying step is exposed. This exposure is carried out by irradiation with an exposure light through a photomask (as the case may be, through a liquid immersion medium such as water). Examples of the exposure light include electromagnetic waves such as visible light rays, ultraviolet rays, far ultraviolet rays, EUV (13.5 nm), X-rays, and γ -rays; charged particle rays such as electron beams and α -rays; and the like, which may be selected in accordance with a line width and the like of the intended pattern. Of these, far ultraviolet rays, EUV, or electron beams are preferred; an ArF excimer laser beam (wavelength: 193 nm), a KrF excimer laser beam (wavelength: 248 nm), EUV, or an electron beam is more preferred; and an ArF excimer laser beam or EUV is still more preferred. It is to be noted that exposure conditions such as exposure dose and the like may be appropriately selected in accordance with a formulation of the radiation-sensitive resin composition, type(s) of additive(s), the type of exposure light, and the like.

It is preferred that post exposure baking (PEB) is carried out after the exposure to promote dissociation of the acid-labile group included in the polymer (A) caused by the acid generated upon the exposure in exposed regions of the resist film. This PEB enables an increase in a difference in solubility of the resist film in a developer solution between the light-exposed regions and light-unexposed regions. The lower limit of a PEB temperature is preferably 50° C., more preferably 80° C., and still more preferably 90° C. The upper limit of the PEB temperature is preferably 180° C., and more preferably 130° C. The lower limit of a PEB time period is preferably 5 seconds, more preferably 10 seconds, and still more preferably 30 seconds. The upper limit of the PEB time period is preferably 600 seconds, more preferably 300 seconds, and still more preferably 100 seconds.

Developing Step

In this step, the resist film exposed is developed. Accordingly, formation of a predetermined resist pattern is enabled. The development is typically followed by washing with a rinse agent such as water or an alcohol and then drying. The development procedure in the developing step may be carried out by either development with an alkali, using an alkaline developer solution, or development with an organic solvent, using an organic solvent-containing developer solution.

In the case of the development with an alkali, the alkaline developer solution for use in the development is exemplified by: alkaline aqueous solutions prepared by dissolving at least one alkaline compound such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, aqueous ammonia, ethylamine, n-propylamine, diethylamine, di-n-propylamine, triethylamine, methyldiethylamine, ethyldimethylamine, triethanolamine, tetramethylammonium hydroxide (TMAH), pyrrole, piperidine, choline, 1,8-diazabicyclo-[5.4.0]-7-undecene, and 1,5-diazabicyclo-[4.3.0]-5-nonene; and the like. Of these, an

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aqueous TMAH solution is preferred, and a 2.38% by mass aqueous TMAH solution is more preferred.

In the case of the development with an organic solvent, the organic solvent-containing developer solution is exemplified by: an organic solvent such as an alcohol solvent, an ether solvent, a ketone solvent, an ester solvent, and a hydrocarbon solvent; a solvent containing the organic solvent; and the like. An exemplary organic solvent includes one, or two or more types of the solvents exemplified as the solvent (D), described above, and the like. Of these, the ester solvent or the ketone solvent is preferred. The ester solvent is preferably an acetic acid ester solvent, and more preferably n-butyl acetate. The ketone solvent is preferably the chain ketone, and more preferably 2-heptanone. The lower limit of a proportion of the organic solvent in the developer solution is preferably 80% by mass, more preferably 90% by mass, still more preferably 95% by mass, and particularly preferably 99% by mass. Examples of components other than the organic solvent in the developer solution are exemplified by water, silicone oil, and the like.

Examples of the development procedure include: a dipping procedure in which the substrate is immersed for a given time period in the developer solution charged in a container; a puddle procedure in which the developer solution is placed to form a dome-shaped bead by way of the surface tension on the surface of the substrate for a given time period to conduct a development; a spraying procedure in which the developer solution is sprayed onto the surface of the substrate; a dynamic dispensing procedure in which the developer solution is continuously applied onto the substrate, which is rotated at a constant speed, while scanning with a developer solution-application nozzle at a constant speed; and the like.

The resist pattern to be formed according to the method of forming a resist pattern is exemplified by a line and space pattern, a hole pattern, and the like.

Polymer

The polymer of still another embodiment of the present invention is the polymer (E) having the structural unit (W) represented by the above formula (1). The polymer can be suitably used as a component of the radiation-sensitive resin composition of the one embodiment of the present invention, described above. The polymer is described as the polymer (E), described above.

Compound

The compound of yet another embodiment of the present invention is the compound (F) represented by the above formula (i). The compound is described as the compound (F), described above.

EXAMPLES

Hereinafter, the present invention is explained in detail by way of Examples, but the present invention is not in any way limited to these Examples. Measuring methods for various types of physical properties are shown below.

Weight Average Molecular Weight (Mw) and
Number Average Molecular Weight (Mn)

Measurements of the Mw and the Mn of the polymer were carried out by gel permeation chromatography (GPC) using GPC columns available from Tosoh Corporation ("G2000

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HXL"×2, "G3000 HXL"×1, and "G4000 HXL"×1) under the following conditions. Furthermore, a dispersity index (Mw/Mn) was calculated according to measurement results of the Mw and the Mn.

elution solvent: tetrahydrofuran

flow rate: 1.0 mL/minute

sample concentration: 1.0% by mass

amount of injected sample: 100 uL

column temperature: 40° C.

detector: differential refractometer

standard substance: mono-dispersed polystyrene

¹³C-NMR Analysis

A ¹³C-NMR analysis was performed using a nuclear magnetic resonance apparatus ("JNM-Delta 400," available from JEOL, Ltd.).

Synthesis of Compound (F) (Monomer)

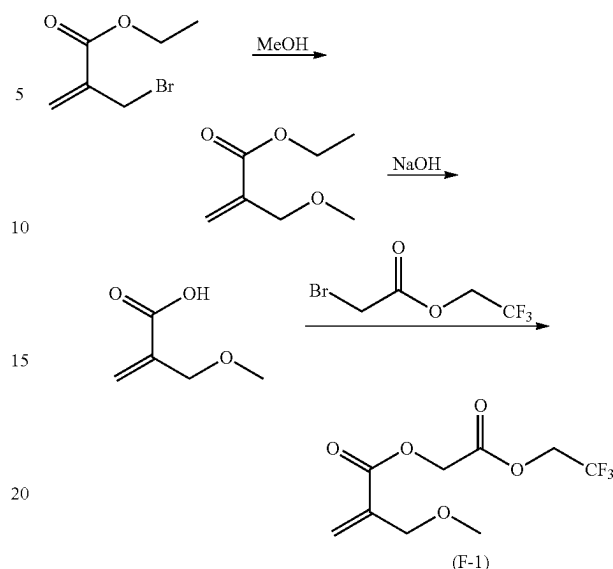
Synthesis Example 1: Synthesis of Compound (F-1)

Step 1: Into a reaction vessel were charged 20.0 mmol of ethyl 2-(bromomethyl)acrylate, 40.0 mmol of triethylamine, 60.0 mmol of methanol, and 50 g of tetrahydrofuran, and a resulting mixture was stirred at 50° C. for 5 hours. Thereafter, the reaction solution was cooled to no greater than 30° C. and water was added for dilution. Ethyl acetate was added and extraction was performed, whereby an organic layer was separated. The organic layer thus obtained was washed with a saturated aqueous sodium chloride solution, and then with water. After drying with sodium sulfate, a solvent was distilled away. Purification was carried out with column chromatography to give an alkoxy derivative with a favorable yield.

Step 2: To the above-described alkoxy derivative was added a mixture of methanol: water (1:1 (mass ratio)) to give a 1 M solvent, and then 20.0 mmol of sodium hydroxide was added thereto, and a reaction was permitted at 70° C. for 3 hours. After that, the reaction solution was cooled to no greater than 30° C. and 1 M hydrochloric acid was added to acidify an inside of the system. Ethyl acetate was added and extraction was performed, whereby an organic layer was separated. The organic layer thus obtained was washed with a saturated aqueous sodium chloride solution, and then with water. After drying this with sodium sulfate, a solvent was distilled away to give a carboxylic acid derivative with a favorable yield.

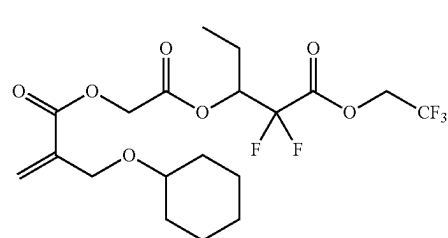
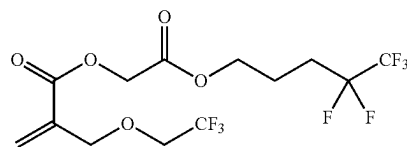
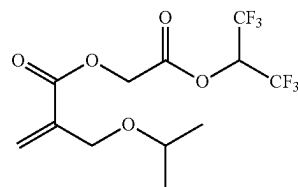
Step 3: To the above-described carboxylic acid derivative were added 30.0 mmol of potassium carbonate, 30.0 mmol of 2-bromoacetic acid 2,2,2-trifluoroethyl, and 50 g of dimethyl formamide, and a resulting mixture was stirred at 50° C. for 4 hours. After that, the reaction solution was cooled to no greater than 30° C. and water was added for dilution. Ethyl acetate was added and extraction was performed, whereby an organic layer was separated. The organic layer thus obtained was washed with a saturated aqueous sodium chloride solution, and then with water. After drying this with sodium sulfate, a solvent was distilled away, and purification was carried out with column chromatography to give a compound represented by the following formula (F-1) (hereinafter, may be also referred to as "compound (F-1)" or "monomer (F-1)") with a favorable yield. A synthesis scheme of the compound (F-1) is shown below.

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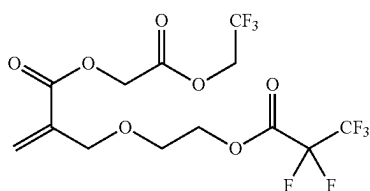
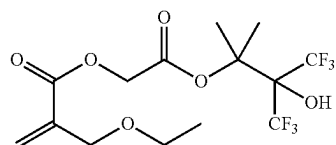
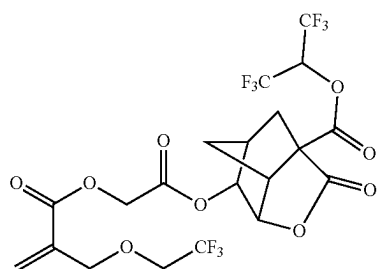
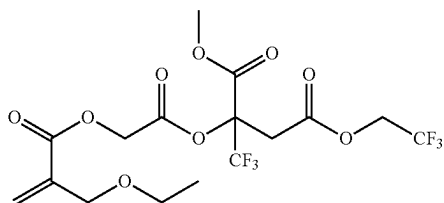
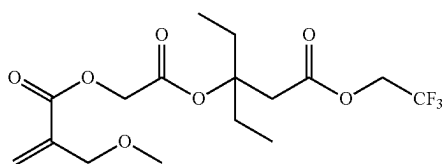
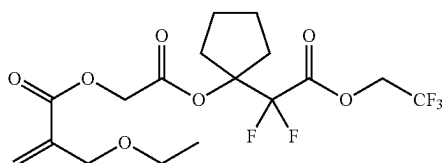
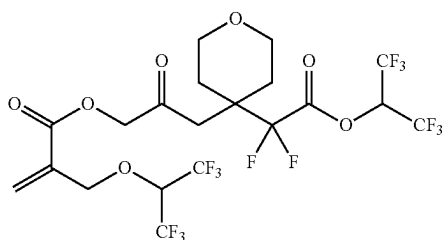
Synthesis Examples 2 to 18: Synthesis of Monomer (F-2) to Monomer (F-18)

Compounds represented by the following formulae (F-2) to (F-18) were synthesized by an operation similar to that of Synthesis Example 1, except that instead of methanol in Step 1 and 2-bromoacetic acid 2,2,2-trifluoroethyl in Step 3 of Synthesis Example 1, corresponding materials were used (hereinafter, compounds represented by each of the formulae (F-2) to (F-18) may be referred to as "compound (F-2)" to "(compound (F-18))" or "monomer (F-2)" to "monomer (F-18)").



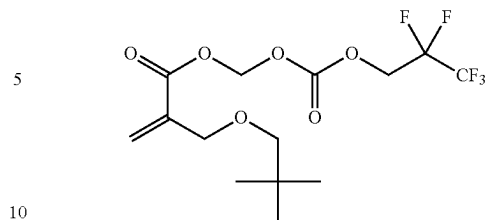
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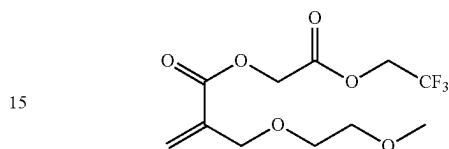
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(F-5)



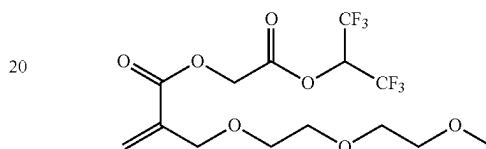
(F-12)

(F-6)



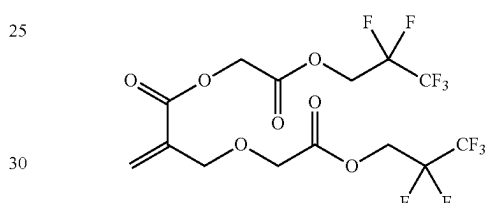
(F-13)

(F-7)



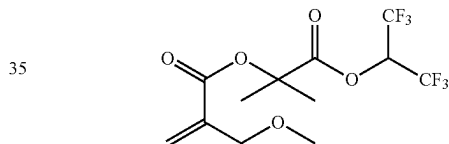
(F-14)

(F-8)

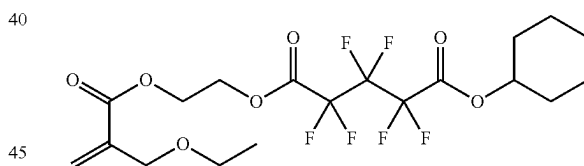


(F-15)

(F-9)

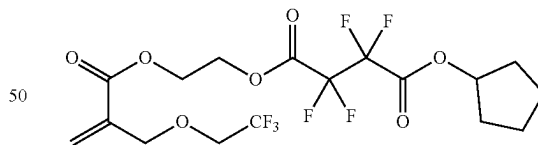


(F-16)



(F-17)

(F-10)



(F-18)

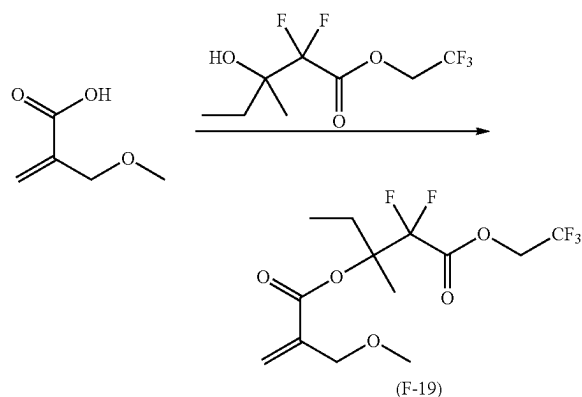
Synthesis Example 19: Synthesis of Compound (F-19)

(F-11)

To 25.0 mmol of the carboxylic acid derivative obtained in Step 2 of Synthesis Example 1 were added 30.0 mmol of oxalyl chloride and 50 g of acetonitrile, and a resulting mixture was stirred at room temperature for 1 hour. Thereafter, to a thus resulting reaction solution were added 30.0 mmol of 2,2-difluoro-3-hydroxy-3-methylpentanoic acid 2,2,2-trifluoroethyl, 30.0 mmol of triethylamine, and 15 g of acetonitrile, and a resulting mixture was further stirred at 50° C. for 4 hours. Next, the reaction solution was cooled to no greater than 30° C., and water was added for dilution. Ethyl

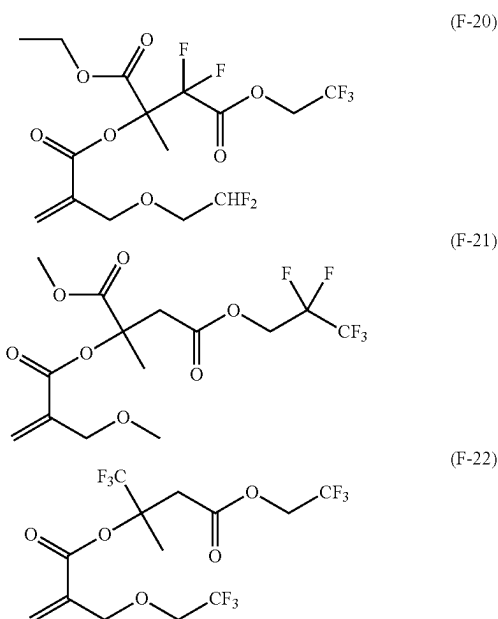
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acetate was added thereto to perform extraction, whereby an organic layer was separated. The organic layer thus obtained was washed with a saturated aqueous sodium chloride solution, and then with water. After drying this with sodium sulfate, a solvent was distilled away, and purification was carried out with column chromatography to give a compound represented by the following formula (F-19) (hereinafter, may be also referred to as “compound (F-19)” or “monomer (F-19)”) with a favorable yield. A synthesis scheme of the compound (F-19) is shown below.



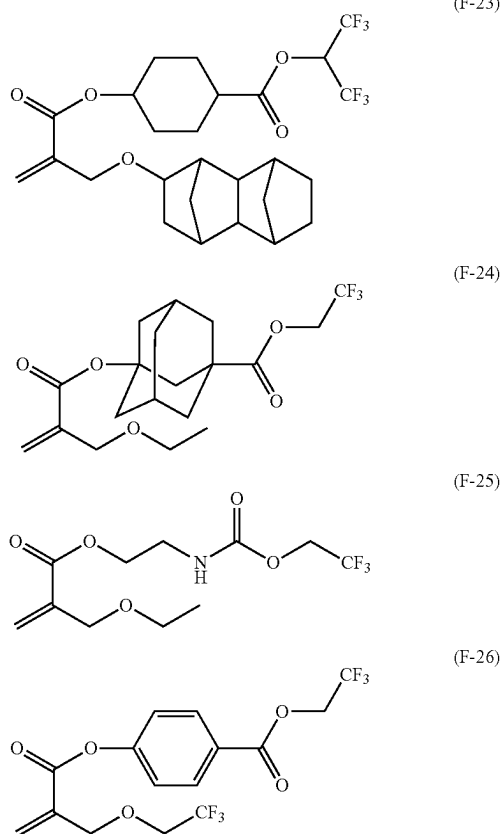
Synthesis Examples 20 to 26: Synthesis of Monomer (F-20) to Monomer (F-26)

Compounds represented by the following formulae (F-20) to (F-26) were synthesized by an operation similar to that of Synthesis Example 19, except that instead of the carboxylic acid derivative and 2,2-difluoro-3-hydroxy-3-methylpentanoic acid 2,2,2-trifluoroethyl of Synthesis Example 19, corresponding materials were used (hereinafter, compounds represented by each of the formulae (F-20) to (F-26) may be referred to as “compound (F-20)” to “compound (F-26)” or “monomer (F-20)” to “monomer (F-26)”).



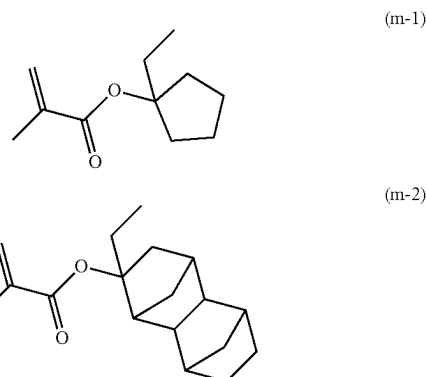
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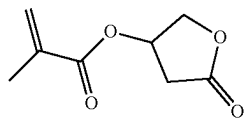
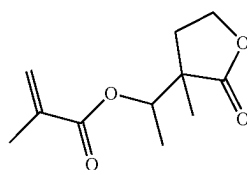
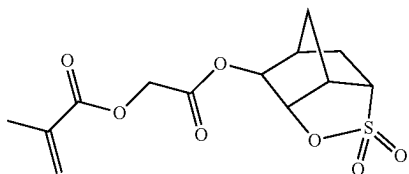
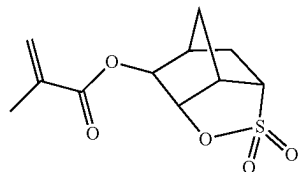
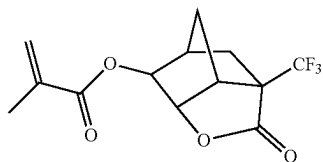
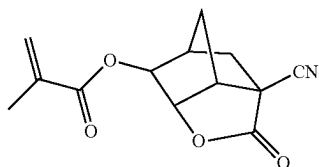
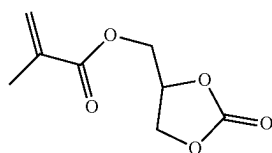
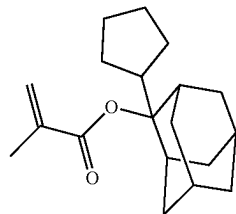
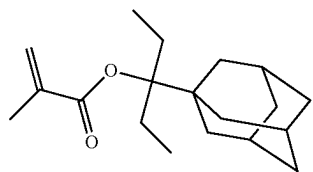
Synthesis of Polymer (A) and Polymer (E)

Of the monomers used for synthesizing each polymer in the Examples and the Comparative Examples, monomers other than the monomers (F-1) to (F-26) are shown below. It is to be noted that in the following Synthesis Examples, unless otherwise specified particularly, the term “parts by mass” means a value, provided that the total mass of the monomers used was 100 parts by mass, and the term “mol %” means a value, provided that the total mol number of the monomers used was 100 mol %.



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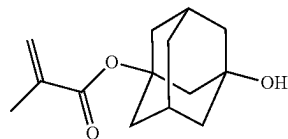
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(m-3)

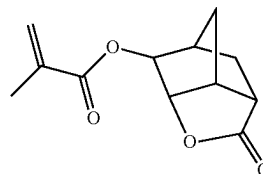
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(m-12)

(m-4)

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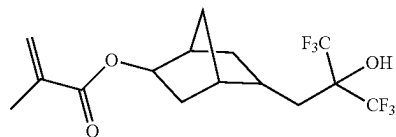


(m-13)

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(m-5)

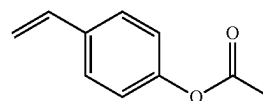
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(m-14)

(m-6)

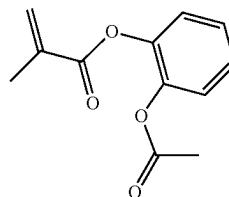
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(m-15)

(m-7)

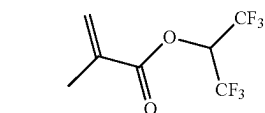
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(m-16)

(m-8)

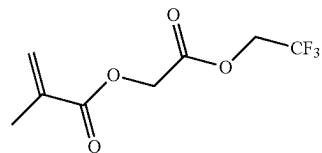
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(m-17)

(m-9)

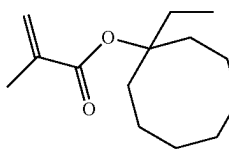
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(m-18)

(m-10)

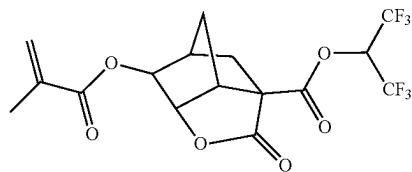
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(m-20)

(m-11)

60

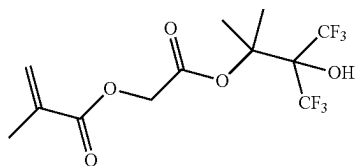


(m-21)

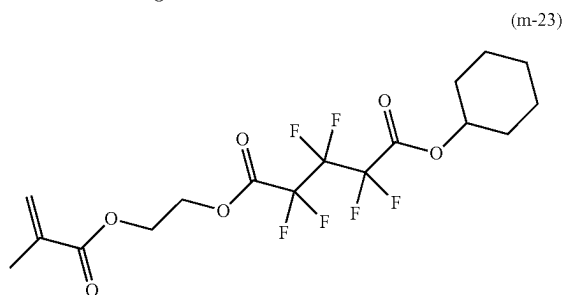
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(m-22)



(m-23)

Synthesis Example 27: Synthesis of Polymer (A-1)

The monomer (m-1), the monomer (m-2), and the monomer (m-1) were dissolved in 2-butanone (200 parts by mass) such that the molar ratio became 40/15/45 (mol %), and a monomer solution was prepared by adding AIBN (azobisisobutyronitrile) (3 mol % with respect to 100 mol % total of the monomers used) as an initiator. Into an empty reaction vessel was charged 2-butanone (100 parts by mass), and

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after purging with nitrogen for 30 minutes, a temperature inside the reaction vessel was brought to 80° C., and the monomer solution was added dropwise over 3 hours with stirring. The time of starting the dropwise addition was regarded as the time of starting the polymerization reaction, and the polymerization reaction was allowed to proceed for 6 hours. After completion of the polymerization reaction, the polymerization solution was cooled to no greater than 30° C. by water cooling. The thus cooled polymerization solution was charged into methanol (2,000 parts by mass), and a thus precipitated white powder was filtered off. The white powder obtained by the filtration was washed twice with methanol and filtered off, followed by drying at 50° C. for 17 hours to give a white powdery polymer (A-1) (yield: 80%). The Mw of the polymer (A-1) was 8,700, and the Mw/Mn was 1.49. Furthermore, as a result of the ¹³C-NMR analysis, the proportions of the structural units derived from (m-1), (m-2), and (m-10) were, respectively, 39.9 mol %, 14.3 mol %, and 45.8 mol %.

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Synthesis Examples 28 to 34: Synthesis of Polymers (A-2) to (A-8)

Polymers (A-2) to (A-8) were synthesized by a similar operation to that of Synthesis Example 27 except that each monomer of the type and in the proportion shown in Table 1 below was used. The proportion (mol %) and the physical property values (the Mw and the Mw/Mn) of each structural unit of each polymer thus obtained are shown together in Table 1 below. It is to be noted that in Table 1, “—” indicates that the corresponding monomer was not used.

TABLE 1

[illegible]

Synthesis Example 35: Synthesis of Polymer (A-9)

The monomer (m-1) and the monomer (m-15) were dissolved in 1-methoxy-2-propanol (200 parts by mass) such that the molar ratio became 50/50 (mol %), and a monomer solution was prepared by adding AIBN (3 mol %) as an initiator. Into an empty reaction vessel was charged 1-methoxy-2-propanol (100 parts by mass), and after purging with nitrogen for 30 minutes, a temperature inside the reaction vessel was brought to 80° C., and the monomer solution was added dropwise over 3 hours with stirring. The time of starting the dropwise addition was regarded as the time of starting the polymerization reaction, and the polymerization reaction was allowed to proceed for 6 hours. After completion of the polymerization reaction, the polymerization solution was cooled to no greater than 30° C. by water cooling. The thus cooled polymerization solution was charged into hexane (2,000 parts by mass), and a thus precipitated white powder was filtered off. The white powder obtained by the filtration was washed twice with hexane and filtered off, and dissolved in 1-methoxy-2-propanol (300 parts by mass). Next, methanol (500 parts by mass), triethylamine (50 parts by mass), and ultra-pure water (10 parts by mass) were added thereto, and a hydrolysis reaction was performed at 70° C. for 6 hours with stirring. After completion of the reaction, the remaining solvent was distilled away. A solid thus obtained was dissolved in acetone (100 parts by mass), followed by adding dropwise to water (500 parts by mass) to permit coagulation of the polymer. A solid thus obtained was filtered off, and drying at 50° C. for 13 hours gave a white powdery polymer (A-9) (yield: 78%). The Mw of the polymer (A-9) was 7,700, and the Mw/Mn was 1.77. Furthermore, as a result of the ¹³C-NMR analysis, the proportions of the structural units derived from (m-1) and (m-15) were, respectively, 50.3 mol % and 49.7 mol %.

Synthesis Examples 36 to 37: Synthesis of Polymers (A-10) to (A-11)

Polymers (A-10) to (A-11) were synthesized by a similar operation to that of Synthesis Example 35 except that each monomer of the type and in the proportion shown in Table 2 below was used. The proportion (mol %) and the physical property values (the Mw and the Mw/Mn) of each structural unit of each polymer thus obtained are shown together in Table 2 below.

Synthesis Example 38: Synthesis of Polymer (E-1)

The monomer (F-1) and the monomer (m-2) were dissolved in 2-butanone (200 parts by mass) such that the molar ratio became 80/20 (mol %), and a monomer solution was prepared by adding AIBN (3 mol %) as an initiator. Into an empty reaction vessel was charged 2-butanone (100 parts by mass), and after purging with nitrogen for 30 minutes, a temperature inside the reaction vessel was brought to 80° C., and the monomer solution was added dropwise over 3 hours with stirring. The time of starting the dropwise addition was regarded as the time of starting the polymerization reaction, and the polymerization reaction was allowed to proceed for 6 hours. After completion of the polymerization reaction, the polymerization solution was cooled to no greater than 30° C. by water cooling. The solvent was substituted with acetonitrile (400 parts by mass), and then an operation of adding hexane (100 parts by mass) and stirring to collect an acetonitrile layer was repeated three times. The solvent was substituted with propylene glycol monomethyl ether acetate to give a solution of the polymer (E-1) (yield: 70%). The Mw of the polymer (E-1) was 6,600, and the Mw/Mn was 1.54. Furthermore, as a result of the ¹³C-NMR analysis, the proportions of the structural units derived from (F-1) and (m-2) were, respectively, 78.1 mol % and 21.9 mol %.

Synthesis Examples 39 to 66: Synthesis of Polymers (E-2) to (E-29)

Polymers (E-2) to (E-29) were synthesized by a similar operation to that of Synthesis Example 38 except that each monomer of the type and in the proportion shown in Table 3 below was used. The proportion (mol %) and the physical property values (the Mw and the Mw/Mn) of each structural unit of each polymer thus obtained are shown together in Table 3 below.

TABLE 2

(A) Polymer	type	Monomer that gives structural unit (I)			Monomer that gives structural unit (III)			Monomer that gives structural unit (IV)			Mw	Mw/Mn
		proportion (mol%)	proportion structural unit (mol%)	proportion (mol%)	proportion of structural unit (mol%)	proportion (mol%)	proportion of structural unit (mol%)					
Synthesis Example 35	A-9	m-1	50	50.3	—	—	—	m-15	50	49.7	7,700	1.77
Synthesis Example 36	A-10	m-1	50	50.7	—	—	—	m-16	50	49.3	7,100	1.67
Synthesis Example 37	A-11	m-1	40	41.2	m-14	30	31.2	m-15	30	27.6	7,000	1.59

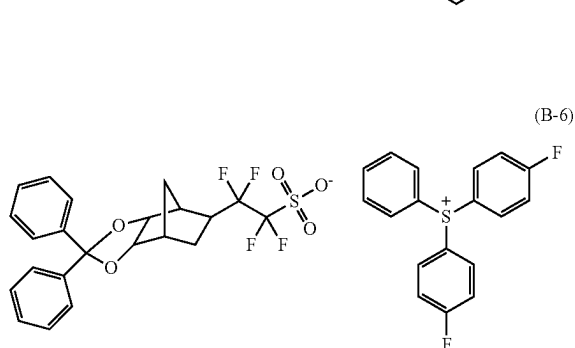
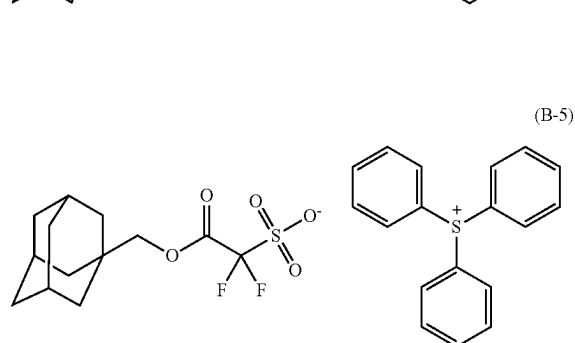
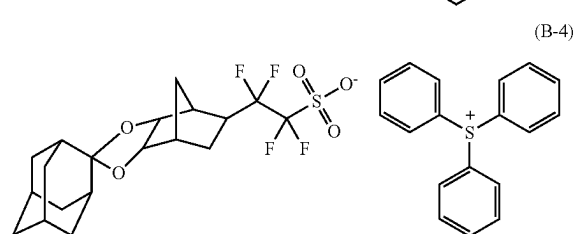
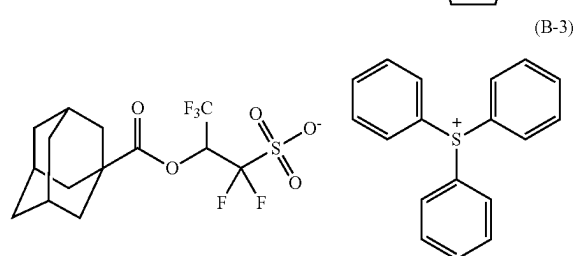
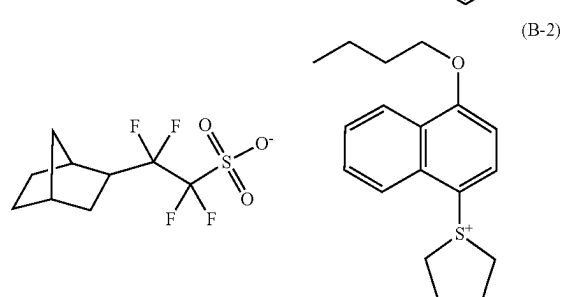
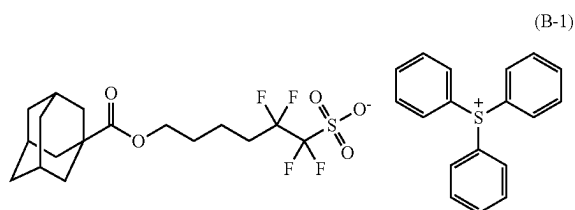
TABLE 3

	(E) Poly- mer	Monomer that gives structural unit(W)			Monomer that gives structural unit (I)			Monomer that gives structural unit unit (III)			Monomer that gives structural (F)			Mw	Mw/ Mn
		type	pro- portion (mol%)	pro- portion of struc- tural unit (mol%)	type	pro- portion (mol%)	pro- portion of struc- tural unit (mol%)	type	pro- portion (mol%)	pro- portion of struc- tural unit (mol%)	type	pro- portion (mol%)	pro- portion of struc- tural unit (mol%)		
Synthesis Example 38	E-1	F-1	80	78.1	m-2	20	21.9	—	—	—	—	—	—	6,600	1.54
Synthesis Example 39	E-2	F-2	80	76.3	m-20	20	23.7	—	—	—	—	—	—	8,000	1.61
Synthesis Example 40	E-3	F-3	100	100	—	—	—	—	—	—	—	—	—	6,000	1.69
Synthesis Example 41	E-4	F-1	80	77.5	—	—	—	m-14	20	22.5	—	—	—	8,100	1.55
Synthesis Example 42	E-5	F-2	80	78.2	—	—	—	—	—	—	m-19	20	21.8	6,900	1.61
Synthesis Example 43	E-6	F-3	60	58.7	m-20	20	20.8	—	—	—	m-18	20	20.5	6,800	1.59
Synthesis Example 44	E-7	F-4	80	79.4	m-1	20	20.6	—	—	—	—	—	—	8,100	1.54
Synthesis Example 45	E-8	F-5	70	67.9	m-20	30	32.1	—	—	—	—	—	—	8,000	1.61
Synthesis Example 46	E-9	F-6	90	87.9	—	—	—	—	—	—	m-18	10	12.1	7,100	1.57
Synthesis Example 47	E-10	F-7	80	78.9	m-20	10	9.8	m-14	10	11.3	—	—	—	7,200	1.55
Synthesis Example 48	E-11	F-8	70	66.1	m-2	30	33.9	—	—	—	—	—	—	6,600	1.54
Synthesis Example 49	E-12	F-9	70	66.8	m-4	15	15.0	m-14	15	18.2	—	—	—	8,000	1.61
Synthesis Example 50	E-13	F-10	40	39.0	m-3	25	22.5	—	—	—	m-19	35	38.5	7,000	1.53
Synthesis Example 51	E-14	F-11	70	67.0	m-2	15	16.7	—	—	—	m-19	15	16.3	7,300	1.67
Synthesis Example 52	E-15	F-12	50	48.6	m-20	15	14.2	—	—	—	m-19	35	37.2	6,900	1.61
Synthesis Example 53	E-16	F-13	60	58.9	m-4	20	21.2	—	—	—	m-17	20	19.9	7,100	1.57
Synthesis Example 54	E-17	F-14	60	57.8	m-20	10	9.8	m-14	10	11.2	m-18	20	21.2	8,200	1.51
Synthesis Example 55	E-18	F-15	20	17.8	m-20	30	30.7	—	—	—	m-18	50	51.5	7,900	1.61
Synthesis Example 56	E-19	F-16	10	8.4	m-2	30	30.1	—	—	—	m-18	60	61.5	7,700	1.66
Synthesis Example 57	E-20	F-17	70	71.0	m-4	10	9.1	m-14	10	9.2	m-19	10	10.7	7,100	1.52
Synthesis Example 58	E-21	F-18	80	79.6	m-20	10	9.9	—	—	—	m-17	10	10.5	6,800	1.59
Synthesis Example 59	E-22	F-19	50	48.0	m-4	50	52	—	—	—	—	—	—	8,000	1.61
Synthesis Example 60	E-23	F-20	50	48.3	m-20	25	24.1	—	—	—	m-18	25	27.6	7,400	1.69

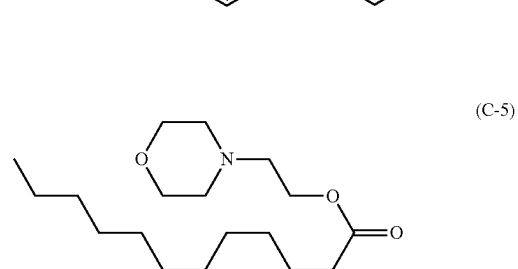
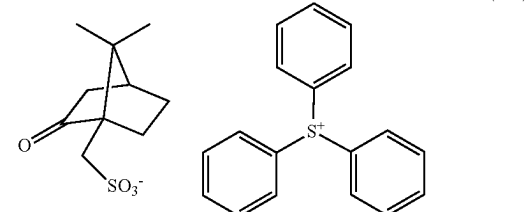
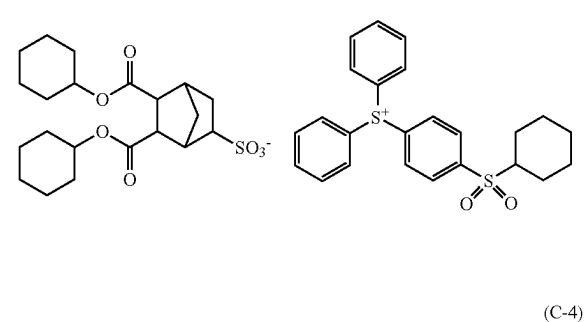
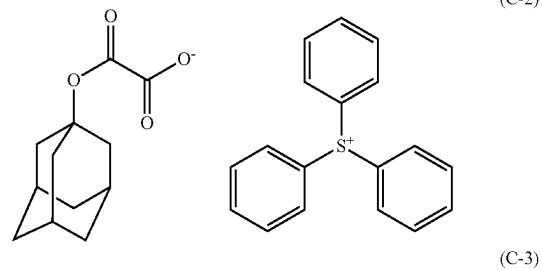
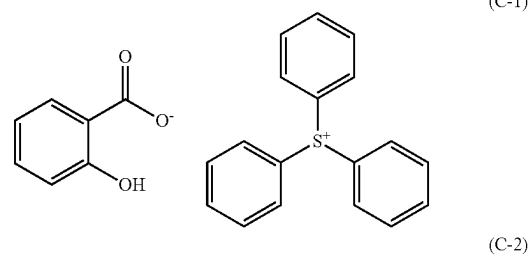
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(C) Acid Diffusion Control Agent



C-1 to C-5: Compounds represented by the following formulae (C-1) to (C-5)



(D) Solvent

- D-1: propylene glycol monomethyl ether acetate
 D-2: propylene glycol monomethyl ether
 D-3: γ -butyrolactone
 D-4: ethyl lactate

Preparation of Positive-Tone Radiation-Sensitive
Resin Composition for ArF Exposure

Example 1

A radiation-sensitive resin composition (J-1) was prepared by: mixing 100 parts by mass of (A-1) as the polymer (A), 14.0 parts by mass of (B-4) as the acid generating agent (B), 2.3 parts by mass of (C-1) as the acid diffusion control agent (C), 3.0 parts by mass (solid content) of (E-1) as the polymer (E), and 3,230 parts by mass of a mixed solvent of

(D-1)/(D-2)/(D-3) as the solvent (D), and filtering a resulting mixture through a membrane filter having a pore size of 0.2 μm .

5 Examples 2 to 53 and Comparative Examples 1 to 11

Radiation-sensitive resin compositions (J-2) to (J-53) and (CR-1) to (CR-11) were prepared in a similar manner to Example 1, except that for each component, the type and content shown in Table 5 below were used.

TABLE 5

Radiation-sensitive resin composition	type	(A) Polymer		(B) Acid generating agent		(C) Acid diffusion control agent		(E) Polymer		(D) Organic solvent	
		type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)
Example 1	J-1	A-1	100	B-4	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 2	J-2	A-1	100	B-4	14.0	C-1	2.3	E-2	3.0	D-1/D-2/D-3	2,240/960/30
Example 3	J-3	A-1	100	B-4	14.0	C-1	2.3	E-3	3.0	D-1/D-2/D-3	2,240/960/30
Example 4	J-4	A-1	100	B-4	14.0	C-1	2.3	E-4	3.0	D-1/D-2/D-3	2,240/960/30
Example 5	J-5	A-1	100	B-4	14.0	C-1	2.3	E-5	3.0	D-1/D-2/D-3	2,240/960/30
Example 6	J-6	A-1	100	B-4	14.0	C-1	2.3	E-6	3.0	D-1/D-2/D-3	2,240/960/30
Example 7	J-7	A-1	100	B-4	14.0	C-1	2.3	E-7	3.0	D-1/D-2/D-3	2,240/960/30
Example 8	J-8	A-1	100	B-4	14.0	C-1	2.3	E-8	3.0	D-1/D-2/D-3	2,240/960/30
Example 9	J-9	A-1	100	B-4	14.0	C-1	2.3	E-9	3.0	D-1/D-2/D-3	2,240/960/30
Example 10	J-10	A-1	100	B-4	14.0	C-1	2.3	E-10	3.0	D-1/D-2/D-3	2,240/960/30
Example 11	J-11	A-1	100	B-4	14.0	C-1	2.3	E-11	3.0	D-1/D-2/D-3	2,240/960/30
Example 12	J-12	A-1	100	B-4	14.0	C-1	2.3	E-12	3.0	D-1/D-2/D-3	2,240/960/30
Example 13	J-13	A-1	100	B-4	14.0	C-1	2.3	E-13	3.0	D-1/D-2/D-3	2,240/960/30
Example 14	J-14	A-1	100	B-4	14.0	C-1	2.3	E-14	3.0	D-1/D-2/D-3	2,240/960/30
Example 15	J-15	A-1	100	B-4	14.0	C-1	2.3	E-15	3.0	D-1/D-2/D-3	2,240/960/30
Example 16	J-16	A-1	100	B-4	14.0	C-1	2.3	E-16	3.0	D-1/D-2/D-3	2,240/960/30
Example 17	J-17	A-1	100	B-4	14.0	C-1	2.3	E-17	3.0	D-1/D-2/D-3	2,240/960/30
Example 18	J-18	A-1	100	B-4	14.0	C-1	2.3	E-18	3.0	D-1/D-2/D-3	2,240/960/30
Example 19	J-19	A-1	100	B-4	14.0	C-1	2.3	E-19	3.0	D-1/D-2/D-3	2,240/960/30
Example 20	J-20	A-1	100	B-4	14.0	C-1	2.3	E-20	3.0	D-1/D-2/D-3	2,240/960/30
Example 21	J-21	A-1	100	B-4	14.0	C-1	2.3	E-21	3.0	D-1/D-2/D-3	2,240/960/30
Example 22	J-22	A-1	100	B-4	14.0	C-1	2.3	E-22	3.0	D-1/D-2/D-3	2,240/960/30
Example 23	J-23	A-1	100	B-4	14.0	C-1	2.3	E-23	3.0	D-1/D-2/D-3	2,240/960/30
Example 24	J-24	A-1	100	B-4	14.0	C-1	2.3	E-24	3.0	D-1/D-2/D-3	2,240/960/30
Example 25	J-25	A-1	100	B-4	14.0	C-1	2.3	E-25	3.0	D-1/D-2/D-3	2,240/960/30
Example 26	J-26	A-1	100	B-4	14.0	C-1	2.3	E-26	3.0	D-1/D-2/D-4	2,240/960/31
Example 27	J-27	A-1	100	B-4	14.0	C-1	2.3	E-27	3.0	D-1/D-2/D-5	2,240/960/32
Example 28	J-28	A-1	100	B-4	14.0	C-1	2.3	E-28	3.0	D-1/D-2/D-6	2,240/960/33
Example 29	J-29	A-1	100	B-4	14.0	C-1	2.3	E-29	3.0	D-1/D-2/D-7	2,240/960/34
Example 30	J-30	A-2	100	B-4	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 31	J-31	A-3	100	B-4	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 32	J-32	A-4	100	B-4	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 33	J-33	A-5	100	B-4	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 34	J-34	A-6	100	B-4	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 35	J-35	A-7	100	B-4	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 36	J-36	A-8	100	B-4	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 37	J-37	A-1	100	B-1	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 38	J-38	A-1	100	B-2	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 39	J-39	A-1	100	B-3	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 40	J-40	A-1	100	B-5	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 41	J-41	A-1	100	B-6	14.0	C-1	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 42	J-42	A-1	100	B-4	14.0	C-2	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 43	J-43	A-1	100	B-4	14.0	C-3	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 44	J-44	A-1	100	B-4	14.0	C-4	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 45	J-45	A-1	100	B-4	14.0	C-5	2.3	E-1	3.0	D-1/D-2/D-3	2,240/960/30
Example 46	J-46	A-1	100	B-4	14.0	C-1	2.3	E-1	0.3	D-1/D-2/D-3	2,240/960/30
Example 47	J-47	A-1	100	B-4	14.0	C-1	2.3	E-1	1.5	D-1/D-2/D-3	2,240/960/30
Example 48	J-48	A-1	100	B-4	14.0	C-1	2.3	E-1	6.0	D-1/D-2/D-3	2,240/960/30
Example 49	J-49	A-1	100	B-4	14.0	C-1	2.3	E-1	10.0	D-1/D-2/D-3	2,240/960/30
Example 50	J-50	A-1	100	B-4	14.0	C-1	2.3	E-1	25.0	D-1/D-2/D-3	2,240/960/30
Example 51	J-51	A-1	100	B-4	14.0	C-1	2.3	E-1/E-30	0.01/1.0	D-1/D-2/D-3	2,240/960/30
Example 52	J-52	A-1	100	B-4	14.0	C-1	2.3	E-1/E-30	1.0/1.0	D-1/D-2/D-3	2,240/960/30
Example 53	J-53	A-1	100	B-4	14.0	C-1	2.3	E-1/E-30	10.0/1.0	D-1/D-2/D-3	2,240/960/30
Comparative Example 1	CJ-1	A-1	100	B-4	14.0	C-1	2.3	E-30	3.0	D-1/D-2/D-3	2,240/960/30
Comparative Example 2	CJ-2	A-1	100	B-4	14.0	C-1	2.3	E-31	3.0	D-1/D-2/D-3	2,240/960/30

TABLE 5-continued

	Radiation-sensitive resin composition	(A) Polymer		(B) Acid generating agent		(C) Acid diffusion control agent		(E) Polymer		(D) Organic solvent	
		type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)
Comparative Example 3	CJ-3	A-1	100	B-4	14.0	C-1	2.3	E-32	3.0	D-1/D-2/D-3	2,240/960/30
Comparative Example 4	CJ-4	A-1	100	B-4	14.0	C-1	2.3	E-33	3.0	D-1/D-2/D-3	2,240/960/30
Comparative Example 5	CJ-5	A-1	100	B-4	14.0	C-1	2.3	E-34	3.0	D-1/D-2/D-3	2,240/960/30
Comparative Example 6	CJ-6	A-1	100	B-4	14.0	C-1	2.3	E-35	3.0	D-1/D-2/D-3	2,240/960/30
Comparative Example 7	CJ-7	A-1	100	B-4	14.0	C-1	2.3	E-36	3.0	D-1/D-2/D-3	2,240/960/30
Comparative Example 8	CJ-8	A-1	100	B-4	14.0	C-1	2.3	E-37	3.0	D-1/D-2/D-3	2,240/960/30
Comparative Example 9	CJ-9	A-1	100	B-4	14.0	C-1	2.3	E-38	3.0	D-1/D-2/D-3	2,240/960/30
Comparative Example 10	CJ-10	A-1	100	B-4	14.0	C-1	2.3	E-39	3.0	D-1/D-2/D-3	2,240/960/30
Comparative Example 11	CJ-11	A-1	100	B-4	14.0	C-1	2.3	E-40	3.0	D-1/D-2/D-3	2,240/960/30

Formation of Resist Pattern Using Positive-Tone Radiation-Sensitive Resin Composition for ArF Exposure

An underlayer antireflective film having an average thickness of 105 nm was formed by applying a composition for underlayer antireflective film formation ("ARC66," available from Brewer Science, Inc.) on the surface of a 12-inch silicon wafer using a spin-coater ("CLEAN TRACK ACT 12," available from Tokyo Electron Limited), and thereafter baking the composition at 205° C. for 60 seconds. Each positive-tone radiation-sensitive resin composition for ArF exposure prepared as described above was applied on the underlayer antireflective film using the spin-coater, and subjected to PB (prebaking) at 90° C. for 60 seconds. Thereafter, by cooling at 23° C. for 30 seconds, a resist film having an average thickness of 90 nm was formed. Next, the resist pattern was exposed using an ArF excimer laser immersion exposure system ("TWINSCAN XT-1900i," available from ASML Co.) through a mask pattern having spaces of 40 nm and pitches of 105 nm at optical conditions involving: NA of 1.35, and Annular ($\sigma=0.8/0.6$). After the exposure, PEB (post-exposure baking) was carried out at 90° C. for 60 seconds. Thereafter, the resist film was subjected to development with an alkali using a 2.38% by mass aqueous TMAH solution. After the development, washing with water was carried out, followed by drying, to form a positive-tone resist pattern (40 nm line and space pattern).

Evaluations

The resist patterns formed using the radiation-sensitive resin compositions for ArF exposure were evaluated on the sensitivity and the number of post-development defects in accordance with the below methods. Furthermore, the resist films before the ArF exposure were evaluated on the receding contact angle in accordance with the below method. The results are shown in Table 6 below. It is to be noted that line width measurement of the resist patterns was performed using a scanning electron microscope ("CG-5000," available from Hitachi High-Technologies Corporation).

Sensitivity

An exposure dose at which a 40 nm line and space pattern was formed in the aforementioned resist pattern formation using the radiation-sensitive resin composition for ArF exposure was defined as an optimum exposure dose, and this optimum exposure dose was adopted as sensitivity (mJ/cm²). The sensitivity was evaluated to be: "favorable" in a case of being no greater than 26 mJ/cm²; and "unfavorable" in a case of being greater than 26 mJ/cm².

Post-PB Advancing Contact Angle

With regard to the resist film before the ArF exposure in the method of forming a resist pattern, the receding contact angle was measured by the following procedure using DSA-10, available from KRUSS Scientific, in an environment having a room temperature of 23° C., a relative humidity of 40% RH, and normal pressure.

Water was discharged from the needle of the DSA-10 to form a 25 μ l drop of water on the resist film. The drop of water was sucked through the needle for 90 seconds at a rate of 10 μ l/min, and the contact angle was measured every second (90 times in total). In the measurement, the average value of 20 contact angles after the contact angle became stable was calculated, and taken as the post-PB receding contact angle (°). The post-PB receding contact angle was evaluated to be: "favorable" in a case of being no less than 70°; and "unfavorable" in a case of being less than 70°.

Number of Development Defects

The resist film was exposed at the optimum radiation dose to form a line and space pattern having a line width of 40 nm, and used as a wafer for defect inspection. The number of defects on the wafer for defect inspection was measured using a defect inspection device ("KLA2810," available from KLA-Tencor). The number of post-development defects was evaluated to be: "favorable" in a case of the number of defects judged to be derived from the resist film being no greater than 15; and "unfavorable" in a case of the number of such defects being greater than 15.

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TABLE 6

	Radiation-sensitive resin composition	Sensitivity (mJ/cm ²)	Receding contact angle/ post-PB (°)	Number of develop- ment defects	
Example 1	J-1	24	83	0	5
Example 2	J-2	24	85	2	
Example 3	J-3	25	78	1	
Example 4	J-4	25	80	0	
Example 5	J-5	25	81	1	
Example 6	J-6	24	78	0	10
Example 7	J-7	24	85	8	
Example 8	J-8	25	86	9	
Example 9	J-9	24	81	5	
Example 10	J-10	25	78	1	
Example 11	J-11	25	79	4	15
Example 12	J-12	24	77	0	
Example 13	J-13	24	78	5	
Example 14	J-14	25	83	0	
Example 15	J-15	25	84	3	
Example 16	J-16	23	77	9	20
Example 17	J-17	24	77	8	
Example 18	J-18	25	80	0	
Example 19	J-19	25	87	9	
Example 20	J-20	24	82	1	
Example 21	J-21	24	81	2	25
Example 22	J-22	24	85	3	
Example 23	J-23	24	82	0	
Example 24	J-24	25	80	4	
Example 25	J-25	25	86	7	
Example 26	J-26	24	86	6	30
Example 27	J-27	24	84	8	
Example 28	J-28	24	78	2	
Example 29	J-29	24	85	4	
Example 30	J-30	24	80	1	
Example 31	J-31	24	81	2	35
Example 32	J-32	25	83	0	
Example 33	J-33	25	82	0	
Example 34	J-34	24	79	2	
Example 35	J-35	24	85	1	
Example 36	J-36	25	80	0	40
Example 37	J-37	23	83	0	
Example 38	J-38	23	81	0	
Example 39	J-39	25	83	2	
Example 40	J-40	25	84	6	
Example 41	J-41	24	83	1	45
Example 42	J-42	24	82	8	
Example 43	J-43	21	83	8	
Example 44	J-44	23	83	0	
Example 45	J-45	23	84	0	
Example 46	J-46	24	77	1	50
Example 47	J-47	25	80	0	
Example 48	J-48	25	83	2	
Example 49	J-49	25	82	2	
Example 50	J-50	25	80	10	
Example 51	J-51	25	76	9	50
Example 52	J-52	25	83	0	
Example 53	J-53	25	84	0	
Comparative Example 1	CJ-1	28	64	189	
Comparative Example 2	CJ-2	27	67	145	

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TABLE 6-continued

	Radiation-sensitive resin composition	Sensitivity (mJ/cm ²)	Receding contact angle/ post-PB (°)	Number of develop- ment defects
Comparative Example 3	CJ-3	28	60	330
Comparative Example 4	CJ-4	27	64	122
Comparative Example 5	CJ-5	30	66	321
Comparative Example 6	CJ-6	27	62	90
Comparative Example 7	CJ-7	29	61	98
Comparative Example 8	CJ-8	29	60	245
Comparative Example 9	CJ-9	28	66	119
Comparative Example 10	CJ-10	29	64	198
Comparative Example 11	CJ-11	30	66	132

As can be understood from the results in Table 6, when the radiation-sensitive resin compositions of the Examples were used for ArF exposure, the sensitivity, the post-PB receding contact angle performance, and the post-development defect performance were favorable. In contrast, in the case of the Comparative Examples, each characteristic was inferior compared to the Examples. Thus, in the case of using the radiation-sensitive resin compositions of the Examples for ArF exposure, a resist pattern can be formed with high sensitivity, superior water repellency, and few defects.

Preparation of Radiation-Sensitive Resin Composition for Exposure to Extreme Ultraviolet Ray (EUV)

Example 54

A radiation-sensitive resin composition (J-54) was prepared by: mixing 100 parts by mass of (A-9) as the polymer (A), 14.0 parts by mass of (B-6) as the acid generating agent (B), 2.3 parts by mass of (C-1) as the acid diffusion control agent (C), 3.0 parts by mass of (E-2) as the polymer (E), and 6,110 parts by mass of a mixed solvent of (D-1)/(D-4) as the solvent (D), and filtering a resulting mixture through a membrane filter having a pore size of 0.2 μm.

Examples 55 to 81 and Comparative Examples 12 to 18

Radiation-sensitive resin compositions (J-55) to (J-81) and (CR-12) to (CR-18) were prepared in a similar manner to Example 54, except that for each component, the type and content shown in Table 7 below were used.

TABLE 7

	Radiation-sensitive resin composition	(A) Polymer		(B) Acid generating agent		(C) Acid diffusion control agent		(E) Polymer		(D) Organic solvent	
		type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)
Example 54	J-54	A-9	100	B-6	14.0	C-1	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 55	J-55	A-9	100	B-6	14.0	C-1	2.3	E-3	3.0	D-1/D-4	4,280/1,830
Example 56	J-56	A-9	100	B-6	14.0	C-1	2.3	E-4	3.0	D-1/D-4	4,280/1,830
Example 57	J-57	A-9	100	B-6	14.0	C-1	2.3	E-10	3.0	D-1/D-4	4,280/1,830
Example 58	J-58	A-9	100	B-6	14.0	C-1	2.3	E-12	3.0	D-1/D-4	4,280/1,830

TABLE 7-continued

	Radiation-sensitive resin composition	(A) Polymer		(B) Acid generating agent		(C) Acid diffusion control agent		(E) Polymer		(D) Organic solvent	
		type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)	type	content (parts by mass)
Example 59	J-59	A-9	100	B-6	14.0	C-1	2.3	E-13	3.0	D-1/D-4	4,280/1,830
Example 60	J-60	A-9	100	B-6	14.0	C-1	2.3	E-17	3.0	D-1/D-4	4,280/1,830
Example 61	J-61	A-9	100	B-6	14.0	C-1	2.3	E-20	3.0	D-1/D-4	4,280/1,830
Example 62	J-62	A-9	100	B-6	14.0	C-1	2.3	E-23	3.0	D-1/D-4	4,280/1,830
Example 63	J-63	A-9	100	B-6	14.0	C-1	2.3	E-29	3.0	D-1/D-4	4,280/1,830
Example 64	J-64	A-10	100	B-6	14.0	C-1	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 65	J-65	A-11	100	B-6	14.0	C-1	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 66	J-66	A-9	100	B-1	14.0	C-1	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 67	J-67	A-9	100	B-3	14.0	C-1	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 68	J-68	A-9	100	B-4	14.0	C-1	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 69	J-69	A-9	100	B-5	14.0	C-1	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 70	J-70	A-9	100	B-6	14.0	C-2	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 71	J-71	A-9	100	B-6	14.0	C-3	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 72	J-72	A-9	100	B-6	14.0	C-4	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 73	J-73	A-9	100	B-6	14.0	C-5	2.3	E-2	3.0	D-1/D-4	4,280/1,830
Example 74	J-74	A-9	100	B-6	14.0	C-1	2.3	E-2	0.3	D-1/D-4	4,280/1,830
Example 75	J-75	A-9	100	B-6	14.0	C-1	2.3	E-2	1.5	D-1/D-4	4,280/1,830
Example 76	J-76	A-9	100	B-6	14.0	C-1	2.3	E-2	6.0	D-1/D-4	4,280/1,830
Example 77	J-77	A-9	100	B-6	14.0	C-1	2.3	E-2	10.0	D-1/D-4	4,280/1,830
Example 78	J-78	A-9	100	B-6	14.0	C-1	2.3	E-2	25.0	D-1/D-4	4,280/1,830
Example 79	J-79	A-9	100	B-6	14.0	C-1	2.3	E-2/E-27	0.01/1.0	D-1/D-4	4,280/1,830
Example 80	J-80	A-9	100	B-6	14.0	C-1	2.3	E-2/E-27	1.0/1.0	D-1/D-4	4,280/1,830
Example 81	J-81	A-9	100	B-6	14.0	C-1	2.3	E-2/E-27	10.0/1.0	D-1/D-4	4,280/1,830
Comparative Example 12	CJ-12	A-9	100	B-6	14.0	C-1	2.3	E-31	3.0	D-1/D-4	4,280/1,830
Comparative Example 13	CJ-13	A-9	100	B-6	14.0	C-1	2.3	E-32	3.0	D-1/D-4	4,280/1,830
Comparative Example 14	CJ-14	A-9	100	B-6	14.0	C-1	2.3	E-33	3.0	D-1/D-4	4,280/1,830
Comparative Example 15	CJ-15	A-9	100	B-6	14.0	C-1	2.3	E-36	3.0	D-1/D-4	4,280/1,830
Comparative Example 16	CJ-16	A-9	100	B-6	14.0	C-1	2.3	E-37	3.0	D-1/D-4	4,280/1,830
Comparative Example 17	CJ-17	A-9	100	B-6	14.0	C-1	2.3	E-38	3.0	D-1/D-4	4,280/1,830
Comparative Example 18	CJ-18	A-9	100	B-6	14.0	C-1	2.3	E-39	3.0	D-1/D-4	4,280/1,830

Formation of Resist Pattern Using Positive-Tone Radiation-Sensitive Resin Composition for EUV Exposure

An underlayer antireflective film having an average thickness of 105 nm was formed by applying a composition for underlayer antireflective film formation ("ARC66," available from Brewer Science, Inc.) on the surface of a 12-inch silicon wafer using a spin-coater ("CLEAN TRACK ACT 12," available from Tokyo Electron Limited), and thereafter baking the composition at 205° C. for 60 seconds. Each radiation-sensitive resin composition for EUV exposure prepared as described above was applied on the underlayer antireflective film using the spin-coater, and subjected to PB at 130° C. for 60 seconds. Thereafter, by cooling at 23° C. for 30 seconds, a resist film having an average thickness of 55 nm was formed. Next, the resist pattern was exposed using an EUV exposure system ("NXE3300," available from ASML Co.) with NA of 0.33 under an illumination condition of Conventional s=0.89, and with a mask of imecDEFECT32FFR02. After the exposure, the resist film was subjected to PEB at 120° C. for 60 seconds. Thereafter, the resist film was subjected to development with an alkali by using a 2.38% by mass aqueous TMAH solution. After the development, washing with water was carried out, followed by drying, to form a positive-tone resist pattern (32 nm line and space pattern).

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Evaluations

The resist patterns formed using the radiation-sensitive resin compositions for EUV exposure were evaluated on the sensitivity and the number of post-development defects in accordance with the following methods. The results are shown in Table 8 below. It is to be noted that line width measurement of the resist patterns was performed using a scanning electron microscope ("CG-5000," available from Hitachi High-Technologies Corporation).

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Sensitivity

An exposure dose at which a 32 nm line and space pattern was formed in the aforementioned resist pattern formation using the radiation-sensitive resin composition for EUV exposure was defined as an optimum exposure dose, and this optimum exposure dose was adopted as sensitivity (mJ/cm²). The sensitivity was evaluated to be: "favorable" in a case of being no greater than 22 mJ/cm²; and "unfavorable" in a case of being greater than 22 mJ/cm².

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Number of Development Defects

The resist film was exposed at the optimum radiation dose to form a line and space pattern having a line width of 32 nm, and used as a wafer for defect inspection. The number

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of defects on the wafer for defect inspection was measured using a defect inspection device ("KLA2810," available from KLA-Tencor). The number of post-exposure defects was evaluated to be: "favorable" in a case of the number of defects judged to be derived from the resist film being no greater than 15; and "unfavorable" in a case of the number of such defects being greater than 15.

TABLE 8

	Radiation-sensitive resin composition	Sensitivity (mJ/cm ²)	Number of development defects
Example 54	J-54	19	0
Example 55	J-55	19	0
Example 56	J-56	18	5
Example 57	J-57	21	2
Example 58	J-58	18	4
Example 59	J-59	19	0
Example 60	J-60	18	8
Example 61	J-61	20	0
Example 62	J-62	19	7
Example 63	J-63	19	1
Example 64	J-64	19	1
Example 65	J-65	18	0
Example 66	J-66	20	0
Example 67	J-67	19	1
Example 68	J-68	20	0
Example 69	J-69	20	0
Example 70	J-70	19	1
Example 71	J-71	18	1
Example 72	J-72	17	1
Example 73	J-73	19	9
Example 74	J-74	18	8
Example 75	J-75	19	0
Example 76	J-76	19	0
Example 77	J-77	19	2
Example 78	J-78	19	10
Example 79	J-79	21	11
Example 80	J-80	20	3
Example 81	J-81	19	1
Comparative Example 11	CJ-12	26	161
Comparative Example 12	CJ-13	28	221
Comparative Example 13	CJ-14	26	257
Comparative Example 14	CJ-15	25	198
Comparative Example 15	CJ-16	27	132
Comparative Example 16	CJ-17	24	290
Comparative Example 17	CJ-18	25	319
Example 18			

As can be understood from the results in Table 8, when the radiation-sensitive resin compositions of the Examples were used for EUV exposure, the sensitivity and the post-development defect performance were favorable. In contrast, in the case of the Comparative Examples, each characteristic was inferior compared to the Examples. Thus, in the case of using the radiation-sensitive resin compositions of the Examples for EUV exposure, a resist pattern can be formed with high sensitivity, superior water repellency, and few defects.

Preparation of Negative-Tone Radiation-Sensitive Resin Composition for ArF Exposure, Resist Pattern Using Composition, and Evaluation Thereof

Example 82

A radiation-sensitive resin composition (J-82) was prepared by: mixing 100 parts by mass of (A-1) as the polymer

(A), 14.0 parts by mass of (B-5) as the acid generating agent (B), 2.3 parts by mass of (C-3) as the acid diffusion control agent (C), 3.0 parts by mass of (E-7) (solid content) as the polymer (E), and 3,230 parts by mass of a mixed solvent of (D-1)/(D-2)/(D-3) as the solvent (D), and filtering a resulting mixture through a membrane filter having a pore size of 0.2 μ m.

In the resist pattern formation using the negative-tone radiation-sensitive resin composition for ArF exposure, a resist film was formed, ArF exposure was carried out, and PEB was conducted by a similar operation except that the negative-tone radiation-sensitive resin composition for ArF exposure (J-82) was used as the radiation-sensitive resist composition. Thereafter, a negative-tone resist pattern (40 nm line and space pattern) was formed by: subjecting the resist film to development with an organic solvent using n-butyl acetate as an organic solvent developer solution, and drying.

The resist pattern using the negative-tone radiation-sensitive resin composition for ArF exposure and the resist film before ArF exposure were evaluated similarly to the evaluations of the resist patterns using the positive-tone radiation-sensitive resin compositions for ArF exposure. As a result, the radiation-sensitive resin composition of Example 82 was favorable in terms of the sensitivity, the post-PB receding contact angle performance, and the post-development defect performance, even in the case of forming the negative-tone resist pattern by ArF exposure.

According to the radiation-sensitive resin composition and the method of forming a resist pattern of the embodiments of the present invention, a resist pattern can be formed with favorable sensitivity to exposure light, superior water repellency, and few defects. The polymer of the still another embodiment of the present invention can be suitably used as a polymer component of the radiation-sensitive resin composition of the one embodiment of the present invention. The compound of the yet another embodiment of the present invention can be suitably used as a monomer of the polymer of the still another embodiment of the present invention. Thus, these can be suitably used in manufacturing of a semiconductor device and the like, in which further progress of miniaturization is expected in the future.

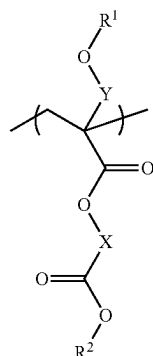
Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

What is claimed is:

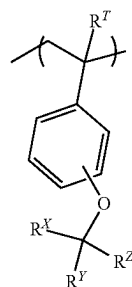
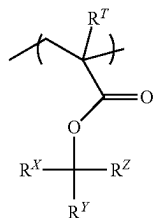
1. A radiation-sensitive resin composition comprising:
 - a first polymer comprising a structural unit which comprises an acid-labile group;
 - a second polymer comprising:
 - a structural unit represented by formula (1); and
 - a structural unit which comprises an acid-labile group and which is represented by at least one formula selected from the group consisting of formula (2-1A), formula (2-1B), formula (2-2A), and formula (2-2B); and

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a radiation-sensitive acid generator,

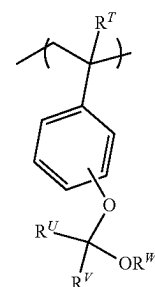
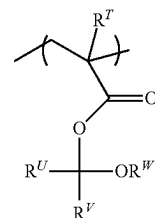


wherein, in the formula (1), one of R¹ and R² represents a substituted or unsubstituted hydrocarbon group which is a substituted or unsubstituted monovalent chain hydrocarbon group having 1 to 20 carbon atoms, a substituted or unsubstituted monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, a substituted or unsubstituted monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, or combinations thereof; the other one of R¹ and R² represents a substituted or unsubstituted hydrocarbon group which is a substituted or unsubstituted monovalent chain hydrocarbon group having 1 to 20 carbon atoms, a substituted or unsubstituted monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, or combinations thereof; provided that in a case where R¹ or R² comprises a methylene group, the methylene group is optionally replaced with an ester group, an ether group, or both; X represents a divalent organic group having 1 to 20 carbon atoms; and Y represents a divalent hydrocarbon group having 1 to 20 carbon atoms, wherein the divalent organic group represented by X, the monovalent organic group represented by R², or both has a fluorine atom,



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-continued



wherein R^T represents a hydrogen atom, a fluorine atom, a methyl group, or a trifluoromethyl group; R^X represents a monovalent hydrocarbon group having 1 to 20 carbon atoms; R^Y and R^Z each independently represent a monovalent hydrocarbon group having 1 to 20 carbon atoms, or R^Y and R^Z taken together represent an alicyclic structure having 3 to 20 ring atoms, together with the carbon atom to which R^Y and R^Z bond; R^U represents a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms; and R^V and R^W each independently represent a monovalent hydrocarbon group having 1 to 20 carbon atoms, or R^V and R^W taken together represent an aliphatic heterocyclic structure having 4 to 20 ring atoms, together with the carbon atom to which R^V bonds and the oxygen atom adjacent to the carbon atom.

2. The radiation-sensitive resin composition according to claim 1, wherein

X represents a substituted or unsubstituted divalent hydrocarbon group having 1 to 20 carbon atoms, —X¹—O—, or —X²—NH—, wherein

X¹ and X² each independently represent a substituted or unsubstituted divalent hydrocarbon group having 1 to 20 carbon atoms.

3. The radiation-sensitive resin composition according to claim 2, wherein the divalent hydrocarbon group having 1 to 20 carbon atoms represented by X¹ and the divalent hydrocarbon group having 1 to 20 atoms represented by X² are each independently a divalent aliphatic hydrocarbon group having 1 to 4 carbon atoms.

4. The radiation-sensitive resin composition according to claim 1, wherein in the formula (1), condition (a), condition (b), or both is satisfied:

(a) X represents —X¹—O—, or —X²—NH—, wherein X¹ and X² each independently represent a substituted or unsubstituted divalent hydrocarbon group having 1 to 20 carbon atoms;

(b) R¹, R², or both represents a group in which at least one methylene group in a substituted or unsubstituted hydrocarbon group having at least 2 carbon atoms is replaced with an ester group, an ether group, or both.

5. The radiation-sensitive resin composition according to claim 1, wherein in the formula (1), X represents —X¹—

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O— or —X²—NH—, wherein X¹ and X² each independently represent a substituted or unsubstituted divalent hydrocarbon group having 1 to 20 carbon atoms.

6. The radiation-sensitive resin composition according to claim 1, wherein in the formula (1), R¹ represents a group in which at least one methylene group in a substituted or unsubstituted hydrocarbon group having at least 2 carbon atoms is replaced with an ester group, an ether group, or both.

7. The radiation-sensitive resin composition according to claim 1, wherein in the formula (1), R² represents a group in which at least one methylene group in a substituted or unsubstituted hydrocarbon group having at least 2 carbon atoms is replaced with an ester group.

8. A method of forming a resist pattern, the method comprising:

forming a resist film directly or indirectly on a substrate

by applying the radiation-sensitive resin composition according to claim 1;

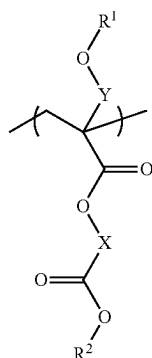
exposing the resist film; and

developing the resist film exposed.

9. A polymer comprising:

a structural unit represented by formula (1); and

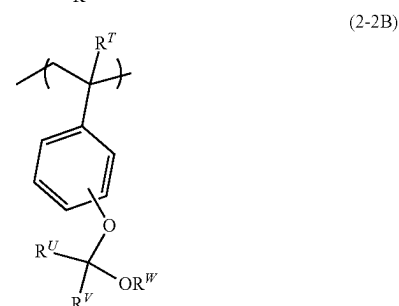
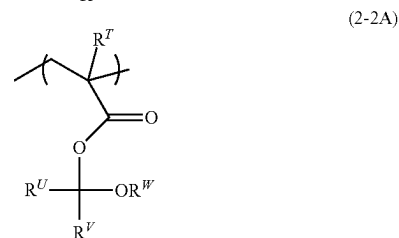
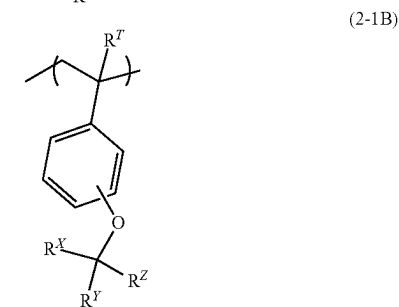
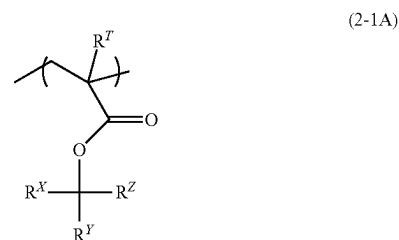
a structural unit which comprises an acid-labile group and which is represented by at least one formula selected from the group consisting of formula (2-1A), formula (2-1B), formula (2-2A), and formula (2-2B):



wherein, in the formula (1), one of R¹ and R² represents a substituted or unsubstituted hydrocarbon group which is a substituted or unsubstituted monovalent chain hydrocarbon group having 1 to 20 carbon atoms, a substituted or unsubstituted monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, a substituted or unsubstituted monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, or combinations thereof; the other one of R¹ and R² represents a substituted or unsubstituted hydrocarbon group which is a substituted or unsubstituted monovalent chain hydrocarbon group having 1 to 20 carbon atoms, a substituted or unsubstituted monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, or combinations thereof; provided that in a case where R¹ or R² comprises a methylene group, the methylene group optionally replaced with an ester group, an ether group, or both; X represents a divalent organic group having 1 to 20 carbon atoms; and Y represents a divalent hydrocarbon group having 1 to 20 carbon atoms, wherein the divalent organic group represented

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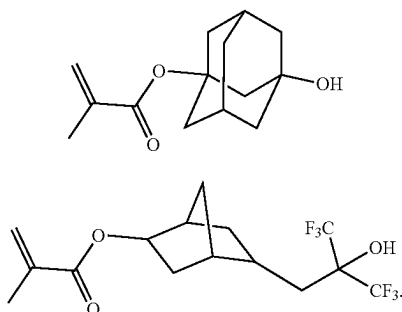
by X, the monovalent organic group represented by R², or both has a fluorine atom,



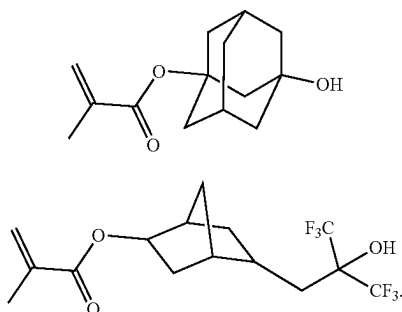
wherein R^T represents a hydrogen atom, a fluorine atom, a methyl group, or a trifluoromethyl group; R^X represents a monovalent hydrocarbon group having 1 to 20 carbon atoms; R^Y and R^Z each independently represent a monovalent hydrocarbon group having 1 to 20 carbon atoms, or R^Y and R^Z taken together represent an alicyclic structure having 3 to 20 ring atoms, together with the carbon atom to which R^Y and R^Z bond; R^U represents a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms; and R^V and R^W each independently represent a monovalent hydrocarbon group having 1 to 20 carbon atoms, or R^V and R^W taken together represent an aliphatic heterocyclic structure having 4 to 20 ring atoms, together with the carbon atom to which R^V bonds and the oxygen atom adjacent to the carbon atom.

10. The radiation-sensitive resin composition according to claim 1, wherein the second polymer further comprises a structural unit which comprises a group represented by formula (m-12) and/or a group represented by formula (m-14):

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11. The polymer according to claim 9, further comprising a structural unit which comprises a group represented by formula (m-12) and/or a group represented by formula (m-14):



12. The radiation-sensitive resin composition according to claim 1, wherein an amount of the structural unit which comprises an acid-labile group in the second polymer is 10 to 50 mol % relative to total structural units in the second polymer.

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13. The polymer according to claim 9, wherein an amount of the structural unit which comprises an acid-labile group in the polymer is 10 to 50 mol % relative to total structural units in the polymer.

14. The polymer according to claim 9, wherein in the formula (1), R^1 represents a group in which at least one methylene group in a substituted or unsubstituted hydrocarbon group having at least 2 carbon atoms is replaced with an ester group, an ether group, or both.

15. The polymer according to claim 9, wherein in the formula (1), R^2 represents a group in which at least one methylene group in a substituted or unsubstituted hydrocarbon group having at least 2 carbon atoms is replaced with an ester group.

16. The radiation-sensitive resin composition according to claim 1, wherein the monovalent organic group having 1 to 20 carbon atoms represented by R^2 is $-(CH_2)_3CF_2(CF_3)$.

17. The polymer according to claim 9, wherein the monovalent organic group having 1 to 20 carbon atoms represented by R^2 is $(CH_2)_3CF_2(CF_3)$.

18. The radiation-sensitive resin composition according to claim 1, wherein R^1 represents a group in which at least one methylene group in a substituted or unsubstituted hydrocarbon group having at least 2 carbon atoms is replaced with an ester group.

19. The polymer according to claim 9, wherein R^1 represents a group in which at least one methylene group in a substituted or unsubstituted hydrocarbon group having at least 2 carbon atoms is replaced with an ester group.

20. The radiation-sensitive resin composition according to claim 1, wherein R^2 represents an unsubstituted hydrocarbon group which is an unsubstituted monovalent chain hydrocarbon group having 1 to 20 carbon atoms, an unsubstituted monovalent alicyclic hydrocarbon group having 3 to 20 carbon atoms, an unsubstituted monovalent aromatic hydrocarbon group having 6 to 20 carbon atoms, or combinations thereof.

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