

DESCRIPTION

TITLE OF INVENTION: NEGATIVE-TYPE PHOTSENSITIVE RESIN

COMPOSITION, METHOD FOR MANUFACTURING HOLLOW STRUCTURE,
AND METHOD FOR FORMING PATTERN

5

TECHNICAL FIELD

[0001]

The present invention relates to a negative-type photosensitive resin composition, a method for manufacturing a hollow structure, and a method for forming a
10 pattern.

Priority is claimed on Japanese Patent Application No. 2022-170652, filed October 25, 2022, the content of which is incorporated herein by reference.

BACKGROUND ART

[0002]

15 In recent years, the performance of microelectronic devices such as surface acoustic wave (SAW) filters and bulk acoustic wave (BAW) filters has been improved. A package encapsulating such a microelectronic device has a hollow structure for ensuring propagation of the surface acoustic waves and mobility of movable members in the electronic device. In the future, particularly in smartphones and the like that handle
20 a high frequency, there has been an increasing demand for miniaturization of packages having a hollow structure.

[0003]

In the miniaturization of a package having a hollow structure, the size of a cover that covers a microelectronic device is a problem. In order to solve the problem of the
25 miniaturization of a package, a cover method referred to as a thin film package (TFP) has

been suggested (for example, see Patent Document 1 or Non Patent Document 1).

[0004]

FIG. 3 shows an embodiment of a hollow structure that stores a microelectronic device.

5 A hollow structure 100 includes a support 10, a microelectronic device 20 disposed on the support 10, a first cover layer 30 that is formed on the support 10 and covers the microelectronic device 20, and a second cover layer 40 (top plate portion) that covers the first cover layer 30.

10 A hollow portion 50 (cavity) is provided between the support 10 and the first cover layer 30. A plurality of holes 35 penetrating from the hollow portion 50 to the second cover layer 40 are formed in a region of the first cover layer 30 where a top surface of the hollow portion 50 is formed.

 In the hollow structure 100, a bump 60 is provided on the support 10 along the outer periphery of the hollow portion 50.

15 [0005]

 In the hollow structure 100 shown in FIG. 3, the second cover layer 40 mechanically reinforces the device or improves the airtightness of the hollow portion 50. As a result of examination, a resin composition may be used as a material of the second cover layer 40.

20 Citation List

 Patent Document

[0006]

 Patent Document 1: Published Japanese Translation No. 2016-516325 of the PCT International Publication

25 Non Patent Document

[0007]

Non-Patent Document 1: Technological Innovations in SAW Components for
Frontend Modules with High Function Density; 7th international Symposium on
Acoustic Wave Devices for Future Mobile Communication Systems; abstracts, March 6
5 to 7, 2018, Chiba University

SUMMARY OF INVENTION

Technical Problem

[0008]

With the miniaturization of the package having a hollow structure and an
10 increase in density of a wiring and the like, it is necessary to increase the adhesion
strength between layers constituting the hollow structure and between each layer and the
bump, and the conditions of the manufacturing process for this have been examined.
However, in the hollow structure 100, in a case where a resin composition is used as the
material of the second cover layer 40, for example, a problem in that the resin
15 composition flows through the plurality of holes 35 and falls into the hollow portion 50
occurs depending on baking conditions of the manufacturing process.

The present invention has been made in consideration of the above-described
circumstances, and an object thereof is to provide a negative-type photosensitive resin
composition which can stably form a resin film on a cover layer having holes without
20 flowing through the holes of the cover layer and falling into a hollow portion regardless
of conditions of a manufacturing process, and a method for manufacturing a hollow
structure and a method for forming a pattern using the negative-type photosensitive resin
composition.

Solution to Problem

25 [0009]

In order to solve the above-described problems, the present invention has adopted the following configurations.

That is, according to a first aspect of the present invention, there is provided a negative-type photosensitive resin composition including: a bisphenol novolac-type epoxy resin; and a cationic polymerization initiator, in which the bisphenol novolac-type epoxy resin has a weight-average molecular weight of 4000 or greater.

[0010]

According to a second aspect of the present invention, there is provided a method for manufacturing a hollow structure including a support, a cover layer formed on the support, and a top plate portion covering the cover layer, in which a hollow portion is provided between the support and the cover layer, and a hole penetrating from the hollow portion to the top plate portion is formed in the cover layer, the method including: forming the top plate portion using the negative-type photosensitive resin composition according to the first aspect.

[0011]

According to a third aspect of the present invention, there is provided a method for forming a pattern, including: a step of forming a photosensitive resin film on a support using the negative-type photosensitive resin composition according to the first aspect; a step of exposing the photosensitive resin film to light; and a step of developing the photosensitive resin film exposed to light with a developing solution containing an organic solvent, to form a negative-type pattern.

Advantageous Effects of Invention

[0012]

According to the present invention, it is possible to provide a negative-type photosensitive resin composition which can stably form a resin film on a cover layer

having holes without flowing through the holes of the cover layer and falling into a hollow portion regardless of conditions of a manufacturing process, and a method for manufacturing a hollow structure and a method for forming a pattern using the negative-type photosensitive resin composition.

5 BRIEF DESCRIPTION OF DRAWINGS

[0013]

[FIG. 1] A GPC chart of a bisphenol A novolac-type epoxy resin before purification.

10 [FIG. 2] A GPC chart of a bisphenol A novolac-type epoxy resin after purification.

[FIG. 3] A cross-sectional view showing an embodiment of a hollow structure that stores a microelectronic device.

DESCRIPTION OF EMBODIMENTS

[0014]

15 In the present specification and the scope of the present claims, the term “aliphatic” is a relative concept used in relation to the term “aromatic”, and denotes a group, a compound, or the like that has no aromaticity.

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

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

The term “halogenated alkyl group” denotes a group in which some or all hydrogen atoms of an alkyl group have been substituted with halogen atoms. Examples

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

The term “fluorinated alkyl group” denotes a group in which some or all hydrogen atoms of an alkyl group have been substituted with fluorine atoms.

5 The expression “may have a substituent” includes both a case where a hydrogen atom (-H) is substituted with a monovalent group and a case where a methylene (-CH₂-) group is substituted with a divalent group.

The term “light exposure” is a general concept for irradiation with radiation.

[0015]

10 (Negative-type photosensitive resin composition)

A negative-type photosensitive resin composition of the present embodiment contains a bisphenol novolac-type epoxy resin and a cationic polymerization initiator. As the bisphenol novolac-type epoxy resin, a resin having a weight-average molecular weight of 4000 or greater is employed.

15 In a case where a photosensitive resin film is formed using such a negative-type photosensitive resin composition and the photosensitive resin film is selectively exposed, a cation moiety of a cationic polymerization initiator is decomposed to generate an acid, and the epoxy group in the bisphenol novolac-type epoxy resin is subjected to ring-opening polymerization by the action of the acid so that the solubility of the bisphenol
20 novolac-type epoxy resin in a developing solution (organic developing solution) containing an organic solvent is decreased in an exposed portion of the photosensitive resin film, whereas the solubility of the bisphenol novolac-type epoxy resin in an organic developing solution does not change in an unexposed portion of the photosensitive resin film, and thus a difference in solubility in an organic developing solution is generated
25 between the exposed portion and the unexposed portion of the photosensitive resin film.

Therefore, in a case where the photosensitive resin film is developed with an organic developing solution, an unexposed portion is dissolved and removed, and a negative-type pattern is formed.

[0016]

5 Such a negative-type photosensitive resin composition is particularly suitable as a material used for to form a top plate portion of a hollow structure including a support, a cover layer formed on the support, and a top plate portion covering the cover layer, in which a hollow portion is provided between the support and the cover layer, and a hole penetrating from the hollow portion to the top plate portion is formed in the cover layer.

10 Such a negative-type photosensitive resin composition is, for example, particularly suitable as a material of a second cover layer 40 in a hollow structure 100 shown in FIG. 3.

[0017]

<Bisphenol novolac-type epoxy resin>

15 The negative-type photosensitive resin composition of the present embodiment contains a bisphenol novolac-type epoxy resin (hereinafter, also referred to as “component (P0)”) having a weight-average molecular weight of 4000 or greater.

 Examples of the bisphenol novolac-type epoxy resin include a polyfunctional epoxy resin produced by a reaction of a bisphenol novolac resin and epichlorohydrin, and
20 a polyfunctional epoxy resin obtained by forming bisphenol glycidyl ether into novolac. Among these, a bisphenol A novolac-type epoxy resin can be suitably used from the viewpoints of availability and the like.

 The component (P0) includes not only a polyfunctional epoxy resin in which the reaction has sufficiently proceeded but also bisphenol epoxy monomers such as
25 bisphenol monoglycidyl ether and bisphenol diglycidyl ether in which the reaction with

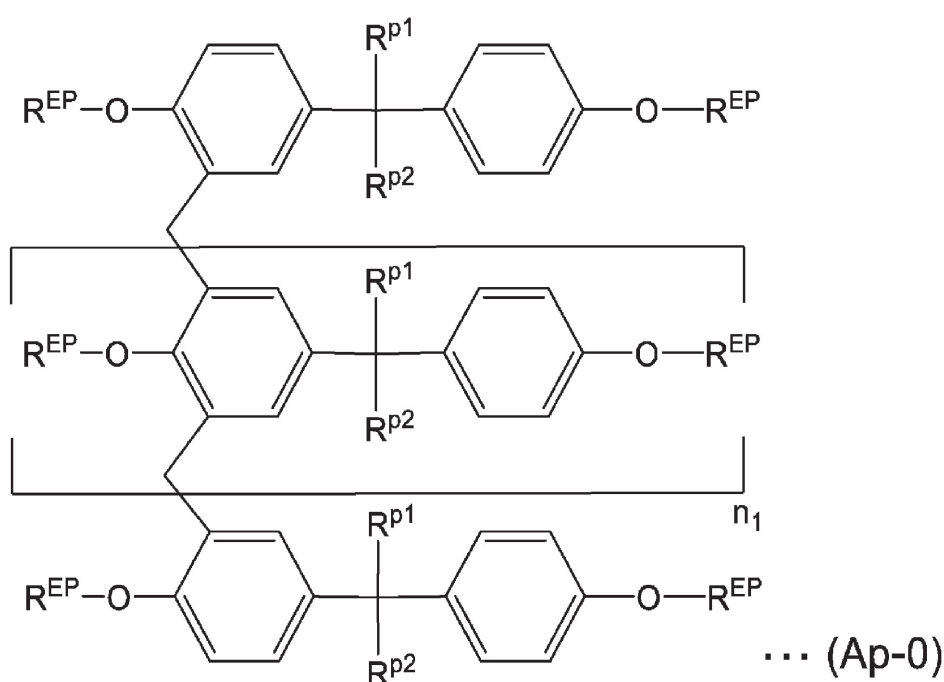
epichlorohydrin has not sufficiently proceeded or formation of novolac has not been sufficiently carried out.

[0018]

Preferred examples of the bisphenol A novolac-type epoxy resin include a resin
5 represented by General Formula (Ap-0).

[0019]

[Chemical Formula 1]



[In Formula (Ap-0), R^{p1} and R^{p2} each independently represent a hydrogen atom
10 or an alkyl group having 1 to 5 carbon atoms. A plurality of R^{p1} 's may be the same as or different from each other. A plurality of R^{p2} 's may be the same as or different from each other. n_1 represents an integer of 1 to 5. R^{EP} represents an epoxy group-containing group. A plurality of R^{EP} 's may be the same as or different from each other.]

[0020]

15 In Formula (Ap-0), the alkyl group having 1 to 5 carbon atoms as R^{p1} and R^{p2} is, for example, a linear, branched, or cyclic alkyl group having 1 to 5 carbon atoms.

Examples of the linear or branched alkyl group include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a tert-butyl group, a pentyl group, an isopentyl group, and a neopentyl group, and examples of the cyclic alkyl group include a cyclobutyl group and a cyclopentyl group.

5 Among these, R^{p1} and R^{p2} represent preferably a hydrogen atom or a linear or branched alkyl group, more preferably a hydrogen atom or a linear alkyl group, and particularly preferably a hydrogen atom or a methyl group.

In Formula (Ap-0), a plurality of R^{p1} 's may be the same as or different from each other. A plurality of R^{p2} 's may be the same as or different from each other.

10 [0021]

In Formula (Ap-0), n_1 represents an integer of 1 to 5, preferably 2 or 3, and more preferably 2.

[0022]

In Formula (Ap-0), R^{EP} represents an epoxy group-containing group.

15 The epoxy group-containing group as R^{EP} is not particularly limited, and examples thereof include a group consisting only of an epoxy group, a group consisting only of an alicyclic epoxy group, and a group containing an epoxy group or an alicyclic epoxy group and a divalent linking group.

20 The alicyclic epoxy group is an alicyclic group having an oxacyclopropane structure as a 3-membered ring ether. Specifically, the alicyclic epoxy group is a group having an alicyclic group and an oxacyclopropane structure.

25 An alicyclic group which is a basic skeleton of the alicyclic epoxy group may be monocyclic or polycyclic. As the monocyclic alicyclic group, a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, and a cyclooctyl group are exemplary examples. In addition, as the polycyclic alicyclic

group, a norbornyl group, an isobornyl group, a tricyclononyl group, a tricyclodecyl group, and a tetracyclododecyl group are exemplary examples. In addition, hydrogen atoms in these alicyclic groups may be substituted with an alkyl group, an alkoxy group, a hydroxyl group, or the like.

5 In a case of the group containing an epoxy group or an alicyclic epoxy group and a divalent linking group, it is preferable that the epoxy group or the alicyclic epoxy group is bonded via the divalent linking group bonded to an oxygen atom (-O-) in the formula.

[0023]

10 Here, the divalent linking group is not particularly limited, and a divalent hydrocarbon group which may have a substituent and a divalent linking group having a heteroatom are suitable exemplary examples.

[0024]

In regard to divalent hydrocarbon group which may have substituent:

15 Such a divalent hydrocarbon group may be an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

The aliphatic hydrocarbon group in the divalent hydrocarbon group may be saturated or unsaturated, and in general, it is preferable that the aliphatic hydrocarbon group is saturated.

20 More specific examples of the aliphatic hydrocarbon group include a linear or branched aliphatic hydrocarbon group and an aliphatic hydrocarbon group having a ring in the structure thereof.

[0025]

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

preferably 1 to 3 carbon atoms. As the linear aliphatic hydrocarbon group, a linear alkylene group is preferable. Specific examples thereof include a methylene group $[-\text{CH}_2-]$, an ethylene group $[-(\text{CH}_2)_2-]$, a trimethylene group $[-(\text{CH}_2)_3-]$, a tetramethylene group $[-(\text{CH}_2)_4-]$, and a pentamethylene group $[-(\text{CH}_2)_5-]$.

- 5 The branched aliphatic hydrocarbon group has preferably 2 to 10 carbon atoms, more preferably 2 to 6 carbon atoms, still more preferably 2 to 4 carbon atoms, and most preferably 2 or 3 carbon atoms. As the branched aliphatic hydrocarbon group, a branched alkylene group is preferable, and specific examples thereof include alkylalkylene groups, for example, alkylmethylene groups such as $-\text{CH}(\text{CH}_3)-$, $-\text{CH}(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_3)-$, and $-\text{C}(\text{CH}_2\text{CH}_3)_2-$; alkylethylene groups such as $-\text{CH}(\text{CH}_3)\text{CH}_2-$, $-\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2\text{CH}_2-$, $-\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2-$, and $-\text{C}(\text{CH}_2\text{CH}_3)_2\text{CH}_2-$; alkyltrimethylene groups such as $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$; and alkyltetramethylene groups such as $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-$. As the alkyl group in the
- 10 alkylalkylene group, a linear alkyl group having 1 to 5 carbon atoms is preferable.
- 15

[0026]

- Examples of the aliphatic hydrocarbon group having a ring in the structure thereof include an alicyclic hydrocarbon group (a group in which two hydrogen atoms have been removed from an aliphatic hydrocarbon ring), a group in which the alicyclic hydrocarbon group is bonded to the terminal of the linear or branched aliphatic hydrocarbon group, and a group in which the alicyclic hydrocarbon group is interposed in the middle of the linear or branched aliphatic hydrocarbon group. Examples of the linear or branched aliphatic hydrocarbon group include the same groups as those described above.
- 20

- 25 The number of carbon atoms in the alicyclic hydrocarbon group is preferably 3

to 20 and more preferably 3 to 12.

The alicyclic hydrocarbon group may be a polycyclic group or a monocyclic group. As the monocyclic alicyclic hydrocarbon group, a group formed by removing two hydrogen atoms from a monocycloalkane is preferable. The monocycloalkane has preferably 3 to 6 carbon atoms, and specific examples thereof include cyclopentane and cyclohexane.

As the polycyclic alicyclic hydrocarbon group, a group formed by removing two hydrogen atoms from a polycycloalkane is preferable. The number of carbon atoms in the polycycloalkane is preferably 7 to 12, and specifically, adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane are exemplary examples.

[0027]

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

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

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

[0028]

The divalent hydrocarbon group may have a substituent.

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

[0029]

The alicyclic hydrocarbon group in the aliphatic hydrocarbon group including a ring in the structure thereof, as the divalent hydrocarbon group, may or may not have a substituent. As the substituent, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, and a carbonyl group are exemplary examples.

As the alkyl group as the substituent, an alkyl group having 1 to 5 carbon atoms

is preferable, and a methyl group, an ethyl group, a propyl group, an n-butyl group, or a tert-butyl group is most preferable.

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

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

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

In the alicyclic hydrocarbon group, some carbon atoms constituting the ring structure thereof may be substituted with a substituent having a heteroatom. As the
 15 substituent having a heteroatom, -O-, -C(=O)-O-, -S-, -S(=O)₂-, or -S(=O)₂-O- is preferable.

[0030]

In the aromatic hydrocarbon group as the divalent hydrocarbon group, a hydrogen atom in the aromatic hydrocarbon group may be substituted with a substituent.
 20 For example, the hydrogen atom bonded to the aromatic ring in the aromatic hydrocarbon group may be substituted with a substituent. As the substituent, an alkyl group, an alkoxy group, a halogen atom, a halogenated alkyl group, and a hydroxyl group are exemplary examples.

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

tert-butyl group is most preferable.

As the alkoxy group, the halogen atom, and the halogenated alkyl group as the above-described substituent, the same as exemplary examples of the substituent which substitutes the hydrogen atom in the alicyclic hydrocarbon group is an exemplary
5 example.

[0031]

In regard to divalent linking group having heteroatom:

The heteroatom in the divalent linking group having a heteroatom is an atom other than a carbon atom and a hydrogen atom, and examples thereof include an oxygen
10 atom, a nitrogen atom, a sulfur atom, and a halogen atom.

[0032]

In the divalent linking group having a heteroatom, preferred examples of the linking group include -O-, -C(=O)-O-, -C(=O)-, -O-C(=O)-O-; -C(=O)-NH-, -NH-, -NH-C(=O)-O-, -NH-C(=NH)- (H may be substituted with a substituent such as an alkyl group
15 or an acyl group); -S-, -S(=O)₂-, -S(=O)₂-O-, and a group represented by General Formula -Y²¹-O-Y²²-, -Y²¹-O-, -Y²¹-C(=O)-O-, -C(=O)-O-Y²¹-, -[Y²¹-C(=O)-O]_m-, Y²²-, or -Y²¹-O-C(=O)-Y²²- [in the formulae, Y²¹ and Y²² each independently represent a divalent hydrocarbon group which may have a substituent, O represents an oxygen atom, and m'' represents an integer of 0 to 3].

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

25 In Formulae -Y²¹-O-Y²²-, -Y²¹-O-, -Y²¹-C(=O)-O-, -C(=O)-O-Y²¹-, -[Y²¹-

$C(=O)-O]_m-Y^{22}-$, and $-Y^{21}-O-C(=O)-Y^{22}-$, Y^{21} and Y^{22} each independently represent a divalent hydrocarbon group which may have a substituent. Examples of the divalent hydrocarbon group include the same groups as those described in the section of “divalent hydrocarbon group which may have a substituent” as the divalent linking group.

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

Y^{22} represents preferably a linear or branched aliphatic hydrocarbon group and more preferably a methylene group, an ethylene group, or an alkylmethylene group.

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

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

[0033]

Among these, a glycidyl group is preferable as the epoxy group-containing group as R^{EP} .

25 [0034]

In the present specification and the scope of the present claims, as the molecular weight of the component (P0), a weight-average molecular weight (Mw) and a number average molecular weight (Mn) in terms of polystyrene, which are measured by gel permeation chromatography (GPC).

5 [0035]

The component (P0) contained in the negative-type photosensitive resin composition of the present embodiment has a weight-average molecular weight (Mw) of 4000 or greater, preferably 4000 or greater and 8000 or less, and more preferably 4000 or greater and 6000 or less.

10 In a case where the weight-average molecular weight of the component (P0) is 4000 or greater, a resin film can be stably formed on the cover layer having holes without the resin composition flowing through the holes of the cover layer and falling into the hollow portion regardless of the conditions of the manufacturing process in a case of manufacturing the hollow structure. In addition, interlayer peeling with the cover layer
15 is unlikely to occur. Meanwhile, in a case where the weight-average molecular weight of the component (P0) is less than or equal to the upper limits of the above-described preferable ranges, the coating properties of the negative-type photosensitive resin composition onto the cover layer can be enhanced, and the hardness of the cured film to be formed can be sufficiently increased.

20 [0036]

As described above, the bisphenol epoxy monomer denotes a monomer including bisphenol monoglycidyl ether and bisphenol diglycidyl ether, and the molecular weight thereof is 500 or less.

[0037]

25 The content proportion of the bisphenol epoxy monomer in the bisphenol

novolac-type epoxy resin (component (P0)) contained in the negative-type photosensitive resin composition of the present embodiment is preferably 2% by mass or less and more preferably 1.5% by mass or less with respect to the total mass of the component (P0), and it is preferable that the content proportion of the bisphenol epoxy monomer in the
5 component (P0) is as small as possible.

In a case where the content proportion of the bisphenol epoxy monomer is less than or equal to the upper limits of the above-described preferable ranges, a resin film can be more stably formed on the cover layer having holes without the resin composition flowing through the holes of the cover layer and falling into the hollow portion regardless
10 of the conditions of the manufacturing process in a case of manufacturing the hollow structure.

[0038]

The polydispersity (M_w/M_n) of the component (P0) is preferably 2.0 or greater and 4.0 or less and more preferably 2.0 or greater and 3.0 or less.
15 [0039]

The epoxy equivalent of the component (P0) is preferably 200 g/eq. or greater and 300 g/eq. or less and more preferably 200 g/eq. or greater and 240 g/eq. or less.
[0040]

The epoxy equivalent of the component (P0) can be measured by potentiometric
20 titration as described in JIS K-7236. Examples of a method for measuring the epoxy equivalent by the potentiometric titration include a hydrochloric acid-dioxane method, a perchloric acid-tetraethylammonium bromide method, a perchloric acid-cetyltrimethylammonium bromide method, a hydrochloric acid-potassium iodide method, and a Dubertaki method using a hydrogen bromide-acetic acid solution.

25 [0041]

The component (P0) may be used alone or in combination of two or more kinds thereof.

In the negative-type photosensitive resin composition of the present embodiment, the content of the component (P0) is preferably 70% by mass or greater, more preferably in a range of 75% to 99% by mass, and still more preferably in a range of 80% to 98% by mass with respect to the total mass (% by mass) of the solid content of the negative-type photosensitive resin composition.

[0042]

<Cationic polymerization initiator>

The cationic polymerization initiator (hereinafter, also referred to as “component (I)”) contained in the negative-type photosensitive resin composition of the present embodiment is a compound that generates a cation by irradiation with active energy rays such as ultraviolet rays, far ultraviolet rays, excimer laser light such as KrF or ArF, X-rays, and electron beams and that can be a polymerization initiator.

Examples of the component (I) include onium borate salts (hereinafter, also referred to as “component (I1)”) and cationic polymerization initiators other than the component (I1) (other cationic polymerization initiators).

[0043]

<<Onium borate salt>>

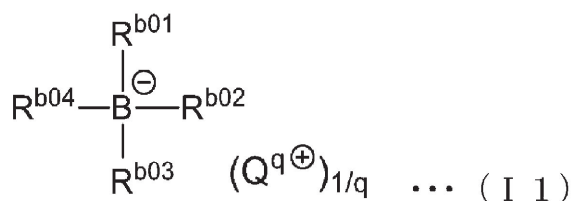
The onium borate salt (component (I1)) generates a relatively strong acid upon light exposure. Therefore, the sensitivity can be sufficiently obtained so that a satisfactory pattern is formed by forming a pattern using the negative-type photosensitive resin composition containing the component (I1). In addition, the risk of toxicity and metal corrosion is decreased by using the component (I1).

Suitable examples of the component (I1) include a compound represented by

General Formula (I1).

[0044]

[Chemical Formula 2]



- 5 [In the formula, R^{b01} to R^{b04} each independently represent an aryl group which may have a substituent or a fluorine atom, q is an integer of 1 or more, and $\text{Q}^{\text{q}+}$ is a q -valent organic cation]

[0045]

.. Anion moiety

- 10 In Formula (I1), the aryl group in R^{b01} to R^{b04} preferably has 5 to 30 carbon atoms, more preferably has 5 to 20 carbon atoms, still more preferably has 6 to 15 carbon atoms, and particularly preferably has 6 to 12 carbon atoms. Specific examples thereof include a naphthyl group, a phenyl group, and an anthracenyl group. Among these, a phenyl group is preferable from the viewpoint of availability.

- 15 The aryl group in R^{b01} to R^{b04} may have a substituent. The substituent is not particularly limited. As the substituent, a halogen atom, a hydroxyl group, an alkyl group (preferably a linear or branched alkyl group having 1 to 5 carbon atoms), or a halogenated alkyl group is preferable, a halogen atom or a halogenated alkyl group having 1 to 5 carbon atoms is more preferable, and a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms is particularly preferable. It is preferable that the aryl group has a fluorine atom because the polarity of the anion moiety is increased.

Among the examples, R^{b01} to R^{b04} in Formula (I1) each represent preferably a

fluorinated phenyl group and particularly preferably a perfluorophenyl group.

[0046]

As the anion moiety of the compound represented by Formula (I1), specifically, tetrakis(pentafluorophenyl)borate ($[\text{B}(\text{C}_6\text{F}_5)_4]^-$); tetrakis[(trifluoromethyl)phenyl]borate
 5 ($[\text{B}(\text{C}_6\text{H}_4\text{CF}_3)_4]^-$); difluorobis(pentafluorophenyl)borate ($[(\text{C}_6\text{F}_5)_2\text{BF}_2]^-$); trifluoro(pentafluorophenyl)borate ($[(\text{C}_6\text{F}_5)\text{BF}_3]^-$); and tetrakis(difluorophenyl)borate ($[\text{B}(\text{C}_6\text{H}_3\text{F}_2)_4]^-$) are preferred exemplary examples.

Among these, tetrakis(pentafluorophenyl)borate ($[\text{B}(\text{C}_6\text{F}_5)_4]^-$) is particularly preferable.

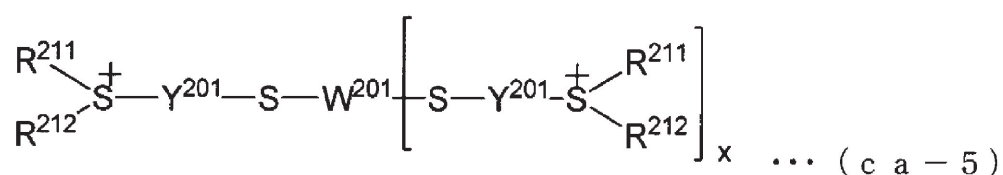
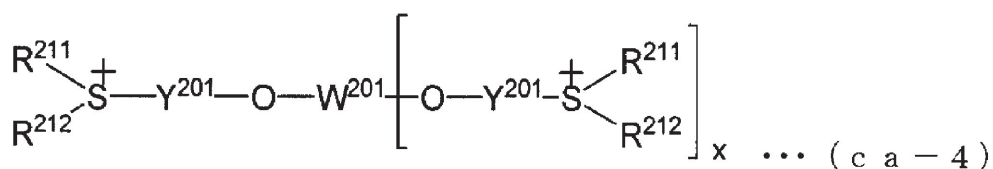
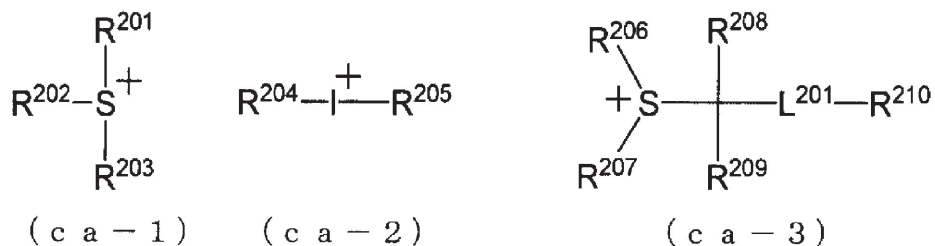
10 [0047]

.. Cation moiety

In Formula (I1), as Q^{q+} , a sulfonium cation and an iodonium cation are suitable exemplary examples, and organic cations each represented by General Formulae (ca-1) to (ca-5) are particularly preferable.

15 [0048]

[Chemical Formula 3]



- [In the formulae, R^{201} to R^{207} , R^{211} , and R^{212} each independently represent an aryl group which may have a substituent, a heteroaryl group, an alkyl group, or an alkenyl group. R^{201} to R^{203} , R^{206} and R^{207} , or R^{211} and R^{212} may be bonded to each other to form a ring together with the sulfur atom in the formula. R^{208} and R^{209} each independently represent a hydrogen atom or an alkyl group having 1 to 5 carbon atoms. R^{210} represents an aryl group which may have a substituent, an alkyl group which may have a substituent, an alkenyl group which may have a substituent, or a $-\text{SO}_2$ -containing cyclic group which may have a substituent. L^{201} represents $-\text{C}(=\text{O})-$ or $-\text{C}(=\text{O})-\text{O}-$. Y^{201} 's each independently represent an arylene group, an alkylene group, or an alkenylene group. x represents 1 or 2. W^{201} represents an $(x + 1)$ -valent linking group.]

[0049]

- As the aryl group represented by R^{201} to R^{207} , R^{211} , and R^{212} , unsubstituted aryl groups having 6 to 20 carbon atoms are exemplary examples. Among these, a phenyl group or a naphthyl group is preferable.

As the heteroaryl group represented by R^{201} to R^{207} , R^{211} , and R^{212} , those in which a part of carbon atoms constituting the aryl group is substituted with a heteroatom are exemplary examples. As the heteroatom, an oxygen atom, a sulfur atom, and a nitrogen atom are exemplary examples. As the heteroaryl group, a group formed by removing one hydrogen atom from 9H-thioxanthene is an exemplary example, and as the substituted heteroaryl group, a group formed by removing one hydrogen atom from 9H-thioxanthen-9-one is an exemplary example.

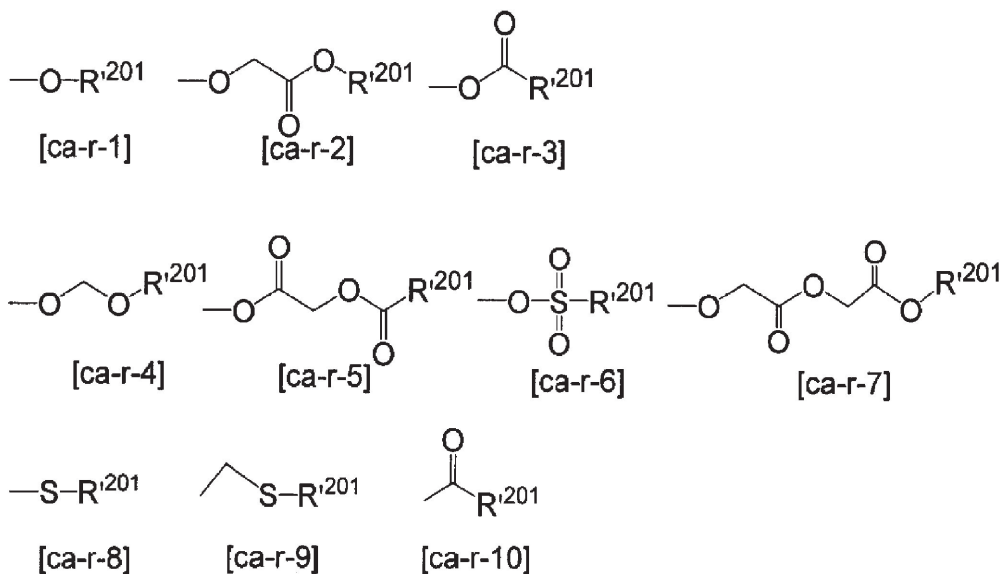
As the alkyl group represented by R^{201} to R^{207} , R^{211} , and R^{212} , a chain-like or cyclic alkyl group having 1 to 30 carbon atoms is preferable.

As the alkenyl group represented by R^{201} to R^{207} , R^{211} , and R^{212} , an alkenyl group having 2 to 10 carbon atoms is preferable.

As the substituent which may be included in R^{201} to R^{207} and R^{210} to R^{212} , an alkyl group, a halogen atom, a halogenated alkyl group, a carbonyl group, a cyano group, an amino group, an oxo group ($=O$), an aryl group, and groups each represented by Formulae (ca-r-1) to (ca-r-10) are exemplary examples.

[0050]

[Chemical Formula 4]



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

5 [0051]

In Formulae (ca-r-1) to (ca-r-10), R'^{201} 's each independently represent a hydrogen atom, a cyclic group which may have a substituent, a chain-like alkyl group which may have a substituent, or a chain-like alkenyl group which may have a substituent.

10 [0052]

Cyclic group which may have substituent:

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

[0053]

The aromatic hydrocarbon group as R'^{201} is a hydrocarbon group having an aromatic ring. The number of carbon atoms in the aromatic hydrocarbon group is preferably 3 to 30, more preferably 5 to 30, still more preferably 5 to 20, particularly
 5 preferably 6 to 15, and most preferably 6 to 10. Here, the number of carbon atoms does not include the number of carbon atoms in a substituent.

Specifically, as the aromatic ring included in the aromatic hydrocarbon group represented by R'^{201} , benzene, fluorene, naphthalene, anthracene, phenanthrene, biphenyl, an aromatic heterocyclic ring in which a part of carbon atoms constituting any
 10 of these aromatic rings are substituted with heteroatom, and a ring in which a part of hydrogen atoms constituting any of these aromatic rings or aromatic heterocyclic rings are substituted with an oxo group are exemplary examples. Examples of the heteroatom in the aromatic heterocyclic rings include an oxygen atom, a sulfur atom, and a nitrogen atom.

15 As the aromatic hydrocarbon group represented by R'^{201} , specifically, a group (an aryl group such as a phenyl group, a naphthyl group, or an anthracenyl group) formed by removing one hydrogen atom from the aromatic ring; a group (for example, an arylalkyl group such as a benzyl group, a phenethyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a 1-naphthylethyl group, and a 2-naphthylethyl group, and the
 20 like) in which one hydrogen atom in the aromatic ring is substituted with an alkylene group; a group formed by removing one hydrogen atom from a ring (such as anthraquinone) in which some hydrogen atoms constituting the aromatic ring is substituted with an oxo group and the like; and a group formed by removing one hydrogen atom from an aromatic heterocyclic ring (such as 9H-thioxanthene or 9H-
 25 thioxanthen-9-one) are exemplary examples. The alkylene group (alkyl chain in the

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

[0054]

Examples of the cyclic aliphatic hydrocarbon group as R'²⁰¹ include an aliphatic hydrocarbon group having a ring in the structure thereof.

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

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

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

[0055]

Among these examples, as the cyclic aliphatic hydrocarbon group as R²⁰¹, a group in which one or more hydrogen atoms have been removed from a monocycloalkane or a polycycloalkane is preferable, a group in which one hydrogen atom has been removed from a polycycloalkane is more preferable, an adamantyl group or a norbornyl group is particularly preferable, and an adamantyl group is most preferable.

[0056]

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

As the linear aliphatic hydrocarbon group, a linear alkylene group is preferable. Specific examples thereof include a methylene group [-CH₂-], an ethylene group [-(CH₂)₂-], a trimethylene group [-(CH₂)₃-], a tetramethylene group [-(CH₂)₄-], and a pentamethylene group [-(CH₂)₅-].

As the branched aliphatic hydrocarbon group, a branched alkylene group is preferable, and specific examples thereof include alkylalkylene groups, for example, alkylmethylene groups such as -CH(CH₃)-, -CH(CH₂CH₃)-, -C(CH₃)₂-, -C(CH₃)(CH₂CH₃)-, -C(CH₃)(CH₂CH₂CH₃)-, and -C(CH₂CH₃)₂-; alkylethylene groups such as -CH(CH₃)CH₂-, -CH(CH₃)CH(CH₃)-, -C(CH₃)₂CH₂-, -CH(CH₂CH₃)CH₂-, and -C(CH₂CH₃)₂-CH₂-; alkyltrimethylene groups such as -CH(CH₃)CH₂CH₂- and -CH₂CH(CH₃)CH₂-; and alkyltetramethylene groups such as -CH(CH₃)CH₂CH₂CH₂- and -CH₂CH(CH₃)CH₂CH₂-. As the alkyl group in the alkylalkylene group, a linear alkyl group having 1 to 5 carbon atoms is preferable.

[0057]

Chain-like alkyl group which may have substituent:

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

The number of carbon atoms in the linear alkyl group is preferably 1 to 20, more preferably 1 to 15, and most preferably 1 to 10. Specifically, a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decanyl group, an undecyl group, a dodecyl group, a tridecyl group, an isotridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, an isohexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl group, an icosyl group, a henicosyl group, and a docosyl group are exemplary examples.

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

[0058]

Chain-like alkenyl group which may have substituent:

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

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

particularly preferable.

[0059]

Examples of the substituent for the cyclic group, the chain-like alkyl group, or the chain-like alkenyl group as R'^{201} include an alkoxy group, a halogen atom, a halogenated alkyl group, a hydroxyl group, a carbonyl group, a nitro group, an amino group, an oxo group, the cyclic group as R'^{201} , an alkylcarbonyl group, and a thienylcarbonyl group.

[0060]

Among these, it is preferable that R'^{201} represents a cyclic group which may have a substituent or a chain-like alkyl group which may have a substituent.

[0061]

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

[0062]

In Formula (ca-3), R^{208} and R^{209} each independently represent a hydrogen atom

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

[0063]

5 In Formula (ca-3), R^{210} represents an aryl group which may have a substituent, an alkyl group which may have a substituent, an alkenyl group which may have a substituent, or a $-SO_2$ -containing cyclic group which may have a substituent.

As the aryl group represented by R^{210} , unsubstituted aryl groups having 6 to 20 carbon atoms are exemplary examples, and a phenyl group or a naphthyl group is

10 preferable.

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

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

[0064]

15 In Formulae (ca-4) and (ca-5), Y^{201} 's each independently represent an arylene group, an alkylene group, or an alkenylene group.

Examples of the arylene group as Y^{201} include a group in which one hydrogen atom has been removed from an aryl group described as the aromatic hydrocarbon group as R^{201} .

20 Examples of the alkylene group and alkenylene group as Y^{201} include a group in which one hydrogen atom has been removed from a group described as the chain-like alkyl group or the chain-like alkenyl group as R^{201} .

[0065]

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

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

linking group.

As the divalent linking group represented by W^{201} , a divalent hydrocarbon group which may have a substituent is preferable. Further, the same divalent hydrocarbon groups which may have a substituent as those for R^{EP} in Formula (Ap-0) described above are preferable. The divalent linking group as W^{201} may be linear, branched chain-like, or cyclic and cyclic is more preferable. Among these, a group in which two carbonyl groups are combined at both ends of an arylene group, or a group consisting only of an arylene group is preferable. Examples of the arylene group include a phenylene group and a naphthylene group. Among these, a phenylene group is particularly preferable.

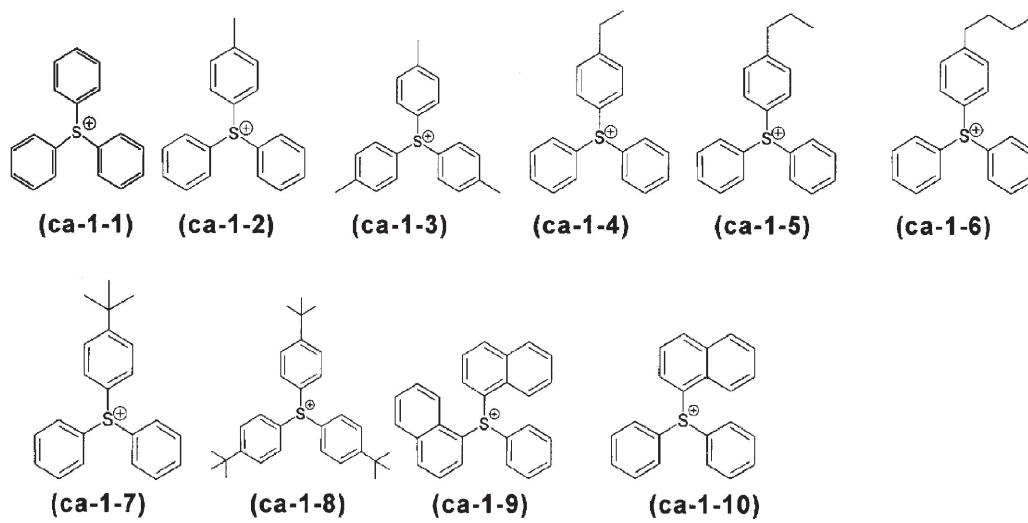
Examples of the trivalent linking group as W^{201} include a group in which one hydrogen atom has been removed from a divalent linking group as W^{201} and a group in which the divalent linking group has been further bonded to the divalent linking group. As the trivalent linking group as W^{201} , a group in which two carbonyl groups are bonded to an arylene group is preferable.

[0066]

Specific examples of suitable cations represented by Formula (ca-1) include cations each represented by Formulae (ca-1-1) to (ca-1-24).

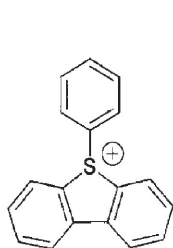
[0067]

[Chemical Formula 5]

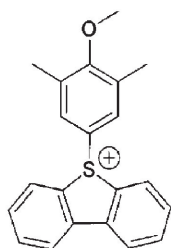


[0068]

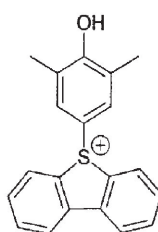
[Chemical Formula 6]



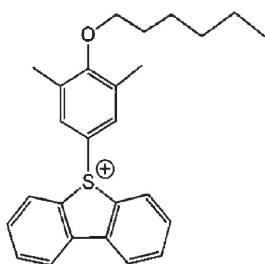
(ca-1-11)



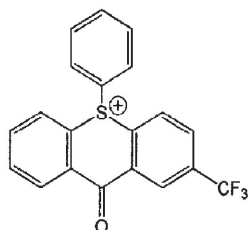
(ca-1-12)



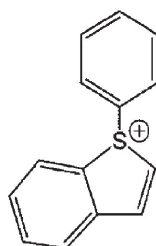
(ca-1-13)



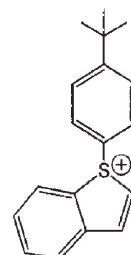
(ca-1-14)



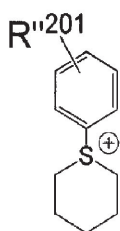
(ca-1-15)



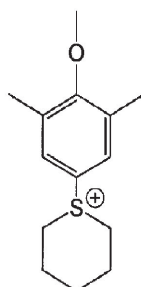
(ca-1-16)



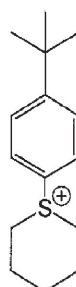
(ca-1-17)



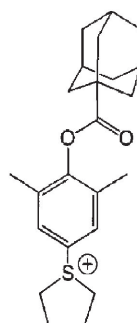
(ca-1-18)



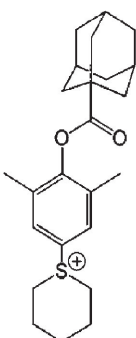
(ca-1-19)



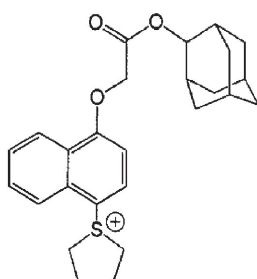
(ca-1-20)



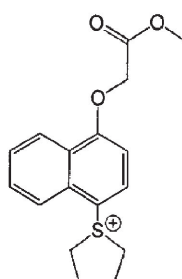
(ca-1-21)



(ca-1-22)



(ca-1-23)



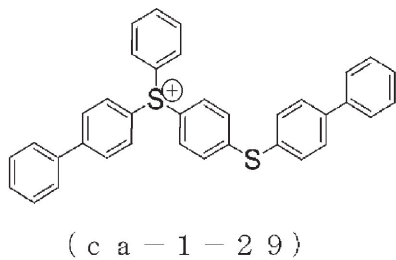
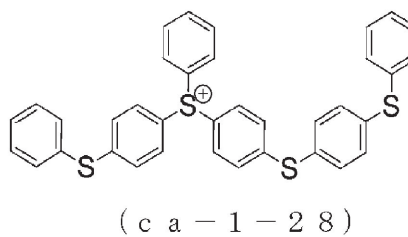
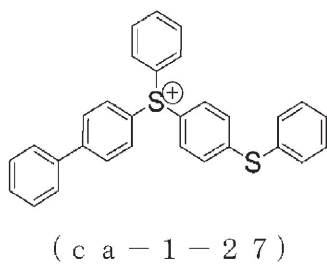
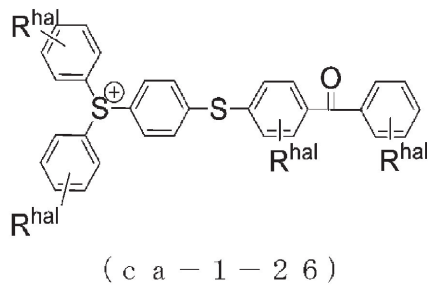
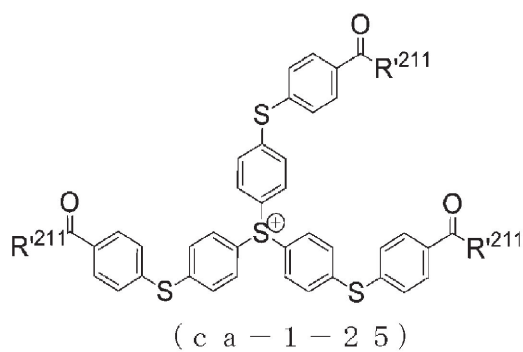
(ca-1-24)

[In the formula, R''^{201} represents a hydrogen atom or a substituent. The substituent has the same definition as the exemplary examples of the substituent which may be included in R^{201} to R^{207} and R^{210} to R^{212} described above.]

Further, as the cation represented by Formula (ca-1), cations each represented by General Formulae (ca-1-25) to (ca-1-35) are also preferable.

[0070]

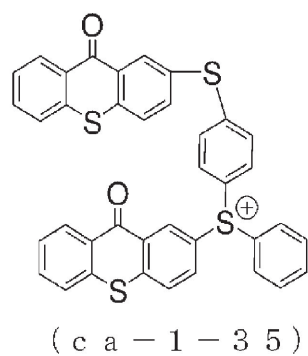
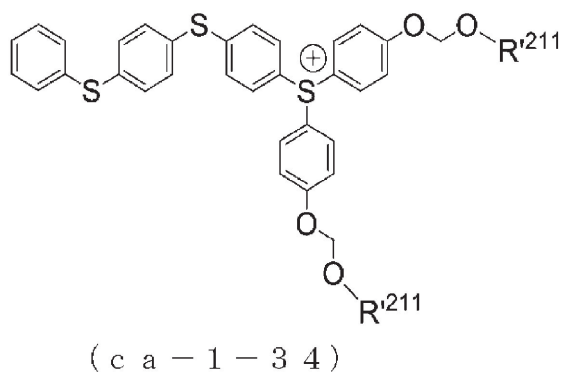
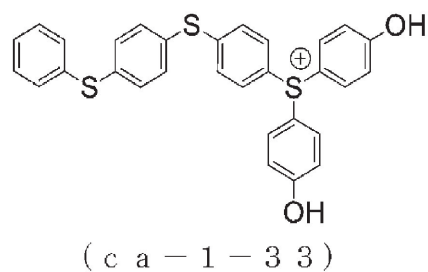
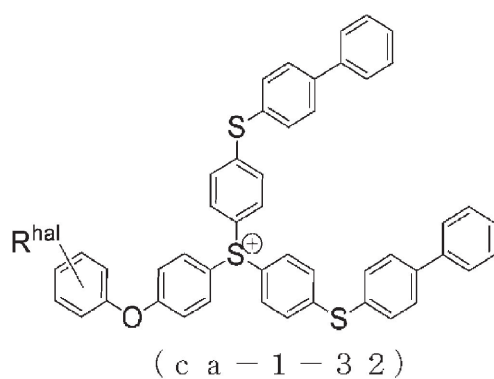
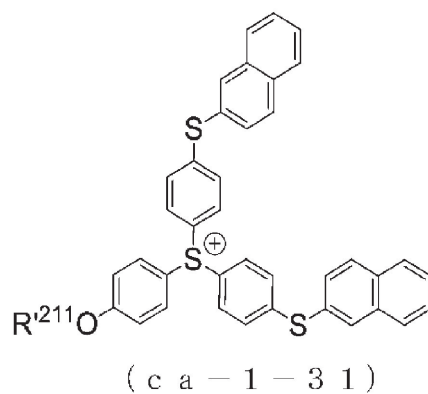
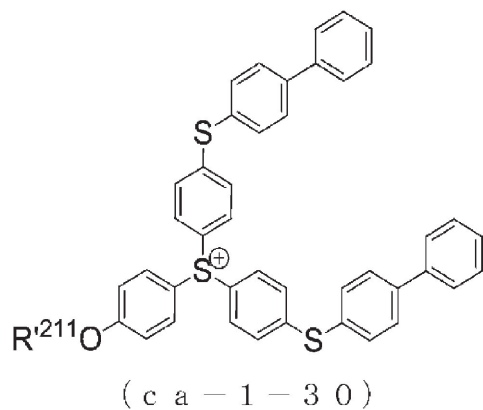
[Chemical Formula 7]



5

[0071]

[Chemical Formula 8]



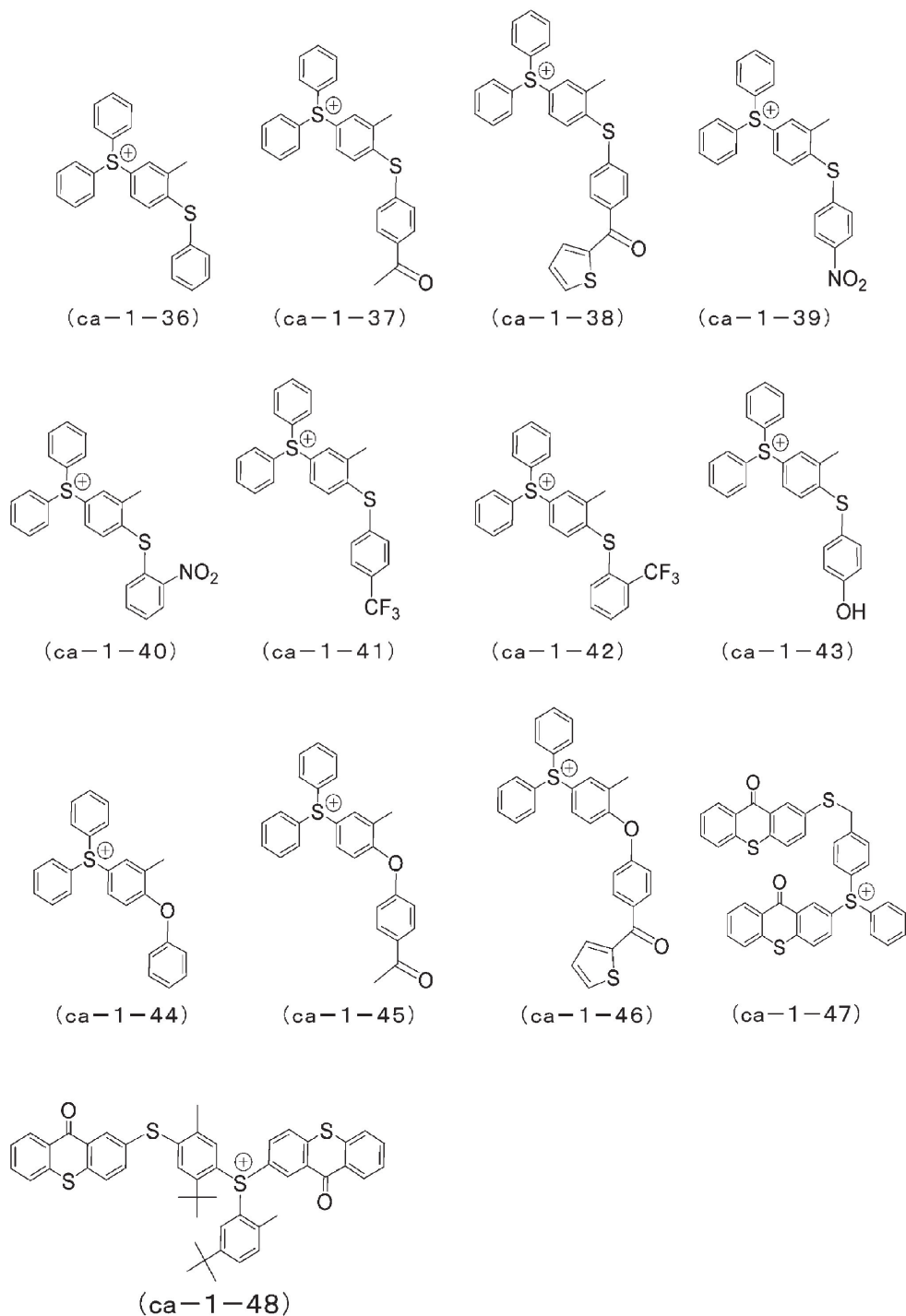
[In the formula, R'^{211} represents an alkyl group. R'^{hal} represents a hydrogen atom or a halogen atom.]

[0072]

- 5 Further, as the cation represented by Formula (ca-1), cations each represented by Chemical Formulae (ca-1-36) to (ca-1-48) are also preferable.

[0073]

[Chemical Formula 9]

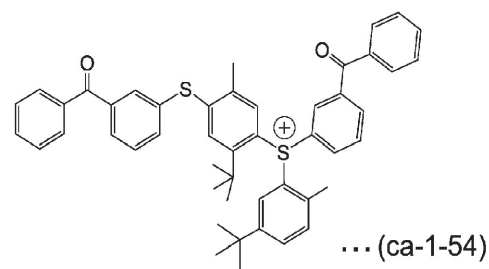
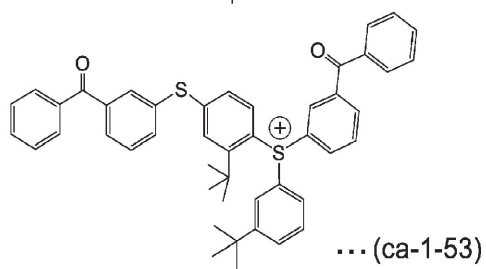
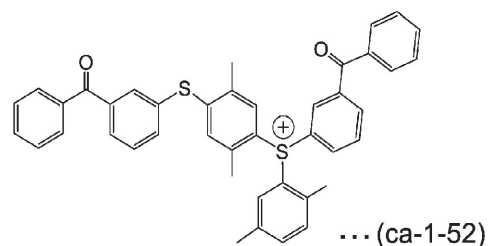
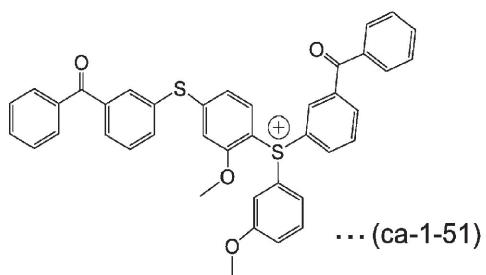
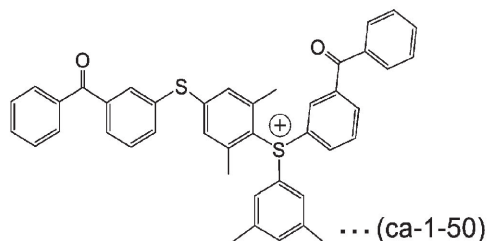
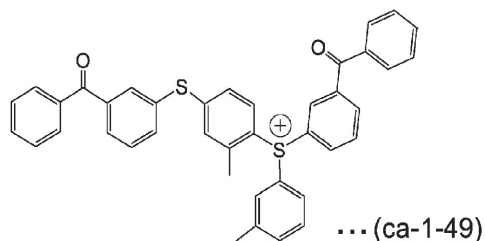


[0074]

In addition, as the cation represented by Formula (ca-1), cations each
 5 represented by Chemical Formulae (ca-1-49) to (ca-1-54) which contain a benzoylphenyl
 group are also preferable.

[0075]

[Chemical Formula 10]



[0076]

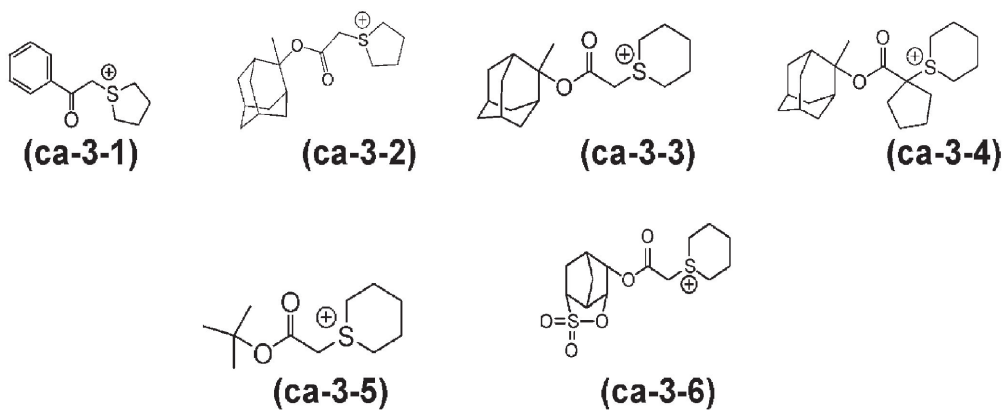
- 5 Specific examples of suitable cations represented by Formula (ca-2) include a diphenyliodonium cation and a bis(4-tert-butylphenyl)iodonium cation.

[0077]

Specific examples of suitable cations represented by Formula (ca-3) include cations each represented by Formulae (ca-3-1) to (ca-3-6).

10 [0078]

[Chemical Formula 11]

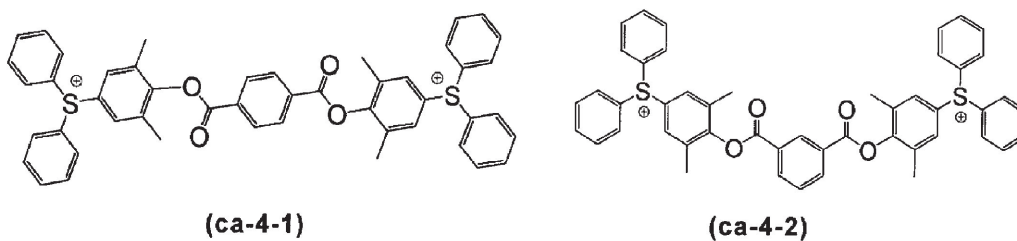


[0079]

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

5 [0080]

[Chemical Formula 12]



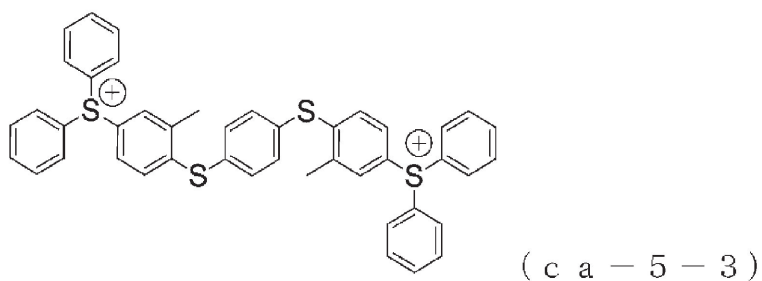
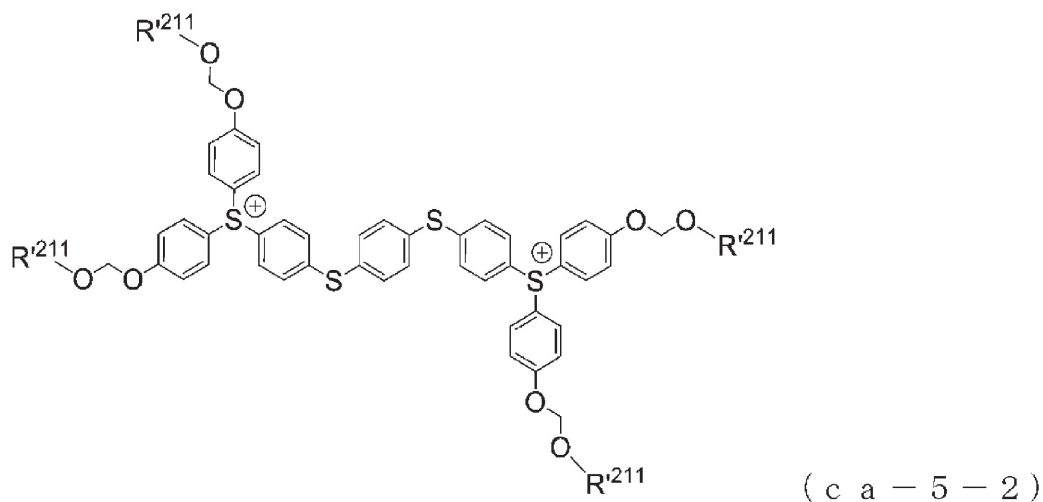
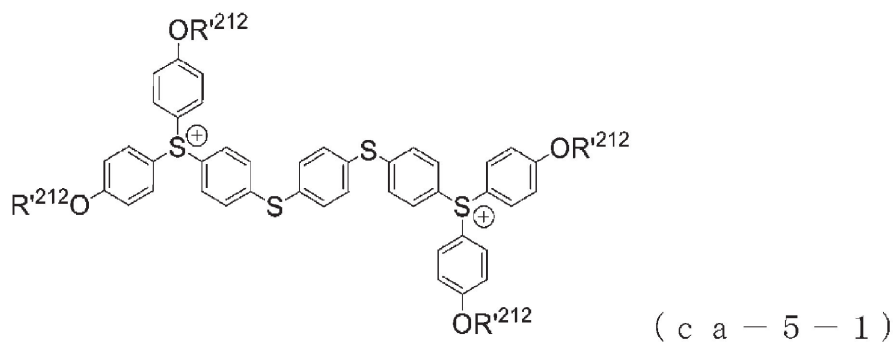
[0081]

Further, as the cation represented by Formula (ca-5), cations each represented by

10 General Formulae (ca-5-1) to (ca-5-3) are also preferable.

[0082]

[Chemical Formula 13]



[In the formula, R'^{212} represents an alkyl group or a hydrogen atom, and R'^{211} represents an alkyl group.]

[0083]

- 5 Among the examples, the cation moiety $[(Q^{q+})_{1/q}]$ is preferably a cation represented by General Formula (ca-1), more preferably a cation represented by any of Formulae (ca-1-1) to (ca-1-54), and still more preferably a cation represented by any of Formulae (ca-1-49) to (ca-1-54).

[0084]

<<Other cationic polymerization initiators>>

Examples of the cationic polymerization initiator other than the above-described component (I1) include a compound represented by General Formula (I2-1) or (I2-2) (hereinafter, referred to as “component (I2)”) and a compound represented by General Formula (I3-1) or (I3-2) (hereinafter, referred to as “component (I3)”).

[0085]

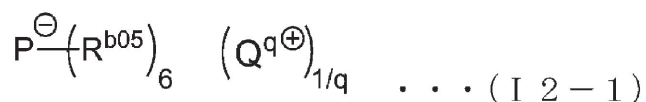
In regard to component (I2):

The component (I2) is a compound represented by General Formula (I2-1) or (I2-2).

Since the component (I2) generates a relatively strong acid upon light exposure, in a case where a pattern is formed using the negative-type photosensitive resin composition containing the component (I), the sensitivity can be sufficiently obtained and a satisfactory pattern can be formed.

[0086]

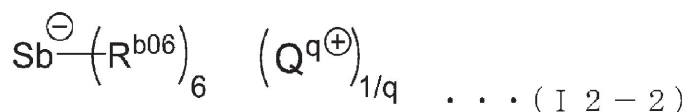
[Chemical Formula 14]



[In the formula, R^{b05} represents a fluorinated alkyl group which may have a substituent or a fluorine atom. A plurality of R^{b05} 's may be the same as or different from each other. q is an integer of 1 or more, and $\text{Q}^{\text{q}\oplus}$ is a q -valent organic cation.]

[0087]

[Chemical Formula 15]



[In the formula, R^{b06} represents a fluorinated alkyl group which may have a substituent or a fluorine atom. A plurality of R^{b06} 's may be the same as or different from each other. q represents an integer of 1 or more, and Q^{q+} is a q -valent organic cation.]

5 [0088]

.. Anion moiety

In Formula (I2-1), R^{b05} represents a fluorinated alkyl group which may have a substituent or a fluorine atom. A plurality of R^{b05} 's may be the same as or different from each other.

10 The fluorinated alkyl group as R^{b05} has preferably 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms, and still more preferably 1 to 5 carbon atoms. Specific examples thereof include an alkyl group having 1 to 5 carbon atoms, in which some or all hydrogen atoms have been substituted with fluorine atoms.

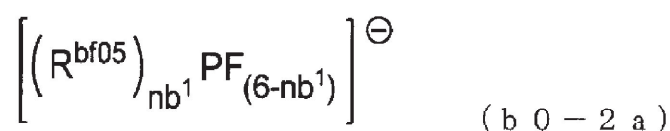
Among the examples, R^{b05} represents preferably a fluorine atom or a fluorinated
15 alkyl group having 1 to 5 carbon atoms, more preferably a fluorine atom or a perfluoroalkyl group having 1 to 5 carbon atoms, and still more preferably a fluorine atom, a trifluoromethyl group, or a pentafluoroethyl group.

[0089]

It is preferable that the anion moiety of the compound represented by Formula
20 (I2-1) is an anion moiety represented by General Formula (b0-2a).

[0090]

[Chemical Formula 16]



[In the formula, R^{b05} represents a fluorinated alkyl group which may have a substituent. nb^1 represents an integer of 1 to 5.]

[0091]

In Formula (b0-2a), examples of the fluorinated alkyl group which may have a substituent as R^{b05} are the same as those for the fluorinated alkyl group which may have a substituent as R^{b05} .

In Formula (b0-2a), nb^1 represents preferably an integer of 1 to 4, more preferably an integer of 2 to 4, and most preferably 3.

[0092]

In Formula (I2-2), R^{b06} represents a fluorinated alkyl group which may have a substituent or a fluorine atom. A plurality of R^{b06} 's may be the same as or different from each other.

The fluorinated alkyl group as R^{b06} has preferably 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms, and still more preferably 1 to 5 carbon atoms. Specific examples thereof include an alkyl group having 1 to 5 carbon atoms, in which some or all hydrogen atoms have been substituted with fluorine atoms.

Among these, R^{b06} represents preferably a fluorine atom or a fluorinated alkyl group having 1 to 5 carbon atoms, more preferably a fluorine atom or a perfluoroalkyl group having 1 to 5 carbon atoms, and still more preferably a fluorine atom.

[0093]

.. Cation moiety

In Formula (I2-1) and Formula (I2-2), q represents an integer of 1 or greater, and Q^{q+} represents a q -valent organic cation.

Examples of Q^{q+} include the cations as those for Q^{q+} in Formula (I1). Among these, a cation represented by General Formula (ca-1) is preferable, and a cation

represented by any of Formulae (ca-1-1) to (ca-1-54) is more preferable.

[0094]

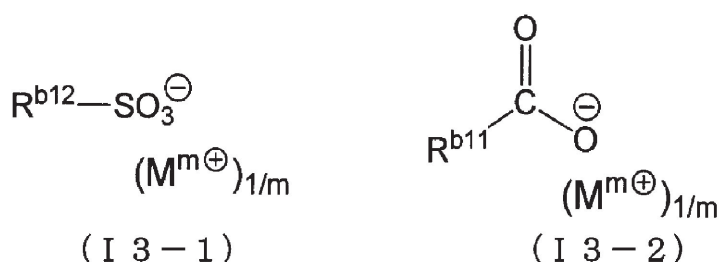
In regard to component (I3):

The component (I3) is a compound represented by General Formula (I3-1) or

5 (I3-2).

[0095]

[Chemical Formula 17]



[In the formulae, $\text{R}^{\text{b}11}$ and $\text{R}^{\text{b}12}$ represent a cyclic group which may have a
 10 substituent other than a halogen atom, a chain-like alkyl group which may have a
 substituent other than a halogen atom, or a chain-like alkenyl group which may have a
 substituent other than a halogen atom. m represents an integer of 1 or greater, and
 $\text{M}^{\text{m}+}$'s each independently represent an m -valent organic cation.]

[0096]

15 { Component (I3-1) }

.. Anion moiety

In Formula (I3-1), $\text{R}^{\text{b}12}$ represents a cyclic group which may have a substituent
 other than a halogen atom, a chain-like alkyl group which may have a substituent other
 than a halogen atom, or a chain-like alkenyl group which may have a substituent other
 20 than a halogen atom, and examples thereof include groups having no substituent or
 having a substituent other than a halogen atom among the cyclic group, the chain-like
 alkyl group, and the chain-like alkenyl group as $\text{R}^{\text{'201}}$ described above.

It is preferable that R^{b12} represents a chain-like alkyl group which may have a substituent other than a halogen atom or an aliphatic cyclic group which may have a substituent other than a halogen atom.

The number of carbon atoms in the chain-like alkyl group is preferably 1 to 10 and more preferably 3 to 10. As the aliphatic cyclic group, a group (which may have a substituent other than a halogen atom) formed by removing one or more hydrogen atoms from adamantane, norbornane, isobornane, tricyclodecane, tetracyclododecane, or the like; or a group formed by removing one or more hydrogen atoms from camphor or the like is more preferable.

The hydrocarbon group as R^{b12} may have a substituent other than a halogen atom, and those same as the substituents other than a halogen atom, which may be included in the hydrocarbon group (such as an aromatic hydrocarbon group, an aliphatic cyclic group, or a chain-like alkyl group) in R^{b11} in Formula (I3-2) are exemplary examples.

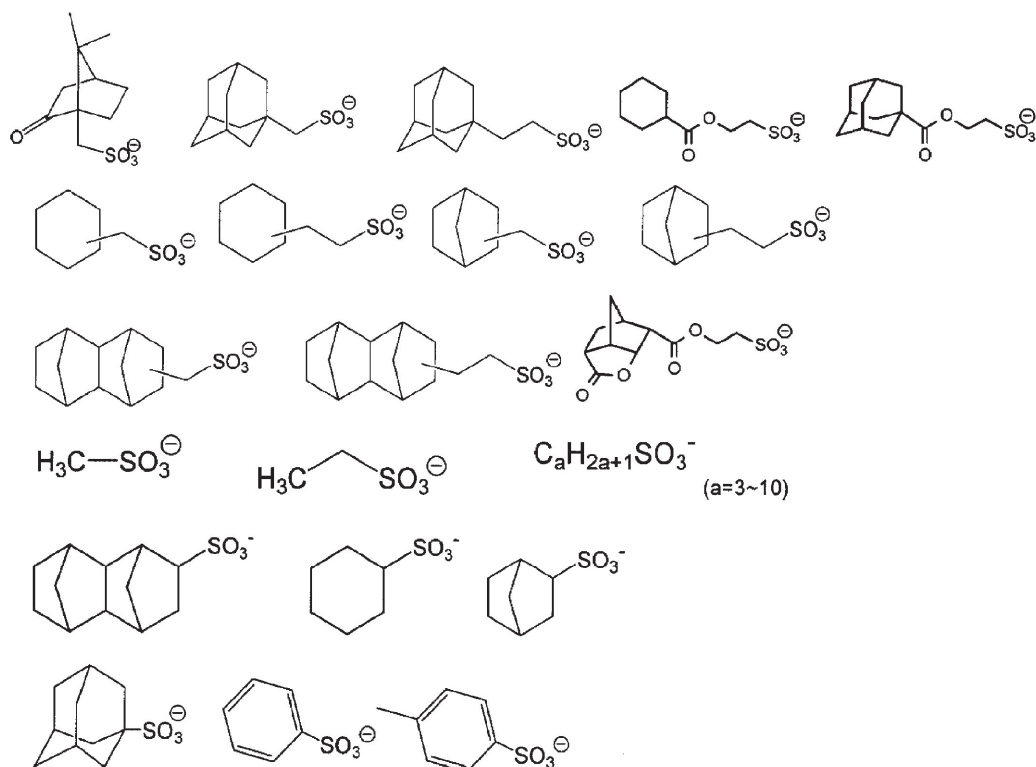
Here, the expression of “may have a substituent other than a halogen atom” excludes not only a case of having a substituent consisting only of a halogen atom, but also a case of having a substituent having even one halogen atom (for example, a case where the substituent is a fluorinated alkyl group).

[0097]

Specific preferred examples of the anion moiety of the component (I3-1) are shown below.

[0098]

[Chemical Formula 18]



[0099]

.. Cation moiety

In Formula (I3-1), M^{m+} represents an m-valent organic cation.

- 5 As the organic cation as M^{m+} , the same cations each represented by General Formulae (ca-1) to (ca-5) described above are suitable exemplary examples, and among these, the cation represented by the General Formula (ca-1) is more preferable. Among these, a sulfonium cation, in which at least one of R^{201} , R^{202} , and R^{203} in General Formula (ca-1) is an organic group (such as an aryl group, a heteroaryl group, an alkyl group, or
- 10 an alkenyl group) which may have a substituent and has 16 or more carbon atoms, is particularly preferable from the viewpoint of improving resolution and roughness characteristics.

As the substituent which may be included in the organic group, an alkyl group, a halogen atom, a halogenated alkyl group, a carbonyl group, a cyano group, an amino

group, an oxo group (=O), an aryl group, and groups each represented by Formulae (ca-r-1) to (ca-r-10) are exemplary examples, as described above.

The number of carbon atoms in the above-described organic group (such as an aryl group, a heteroaryl group, an alkyl group, and an alkenyl group) is preferably 16 to 25, more preferably 16 to 20, and particularly preferably 16 to 18. As the organic cation as M^{m+} , cations represented by Formulae (ca-1-25), (ca-1-26), (ca-1-28) to (ca-1-36), (ca-1-38), (ca-1-46), and (ca-1-47) are suitable exemplary examples, and among these, the cation represented by Formula (ca-1-29) is particularly preferable.

[0100]

10 {Component (I3-2)}
 .. Anion moiety

In Formula (I3-2), R^{b11} represents a cyclic group which may have a substituent other than a halogen atom, a chain-like alkyl group which may have a substituent other than a halogen atom, or a chain-like alkenyl group which may have a substituent other than a halogen atom, and examples thereof include groups having no substituent or having a substituent other than a halogen atom among the cyclic group, the chain-like alkyl group, and the chain-like alkenyl group as R'^{201} described above.

[0101]

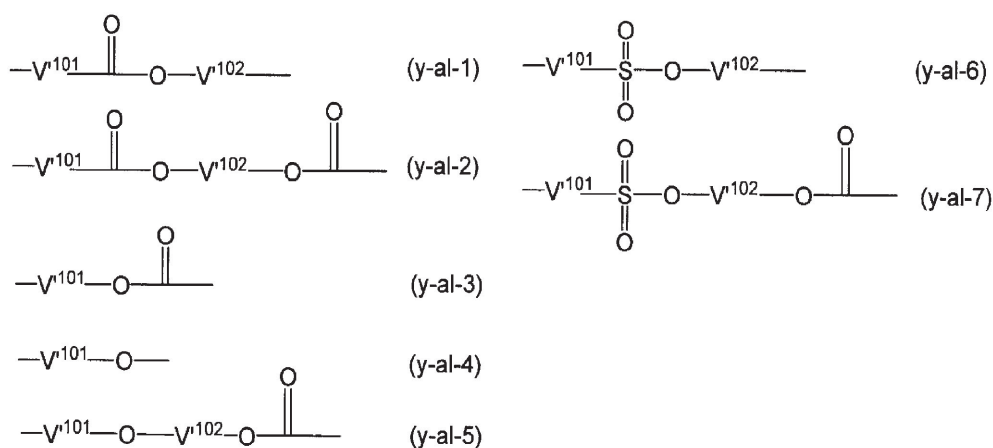
Among these, it is preferable that R^{b11} represents an aromatic hydrocarbon group which may have a substituent other than a halogen atom, an aliphatic cyclic group which may have a substituent other than a halogen atom, or a chain-like alkyl group which may have a substituent other than a halogen atom. Examples of the substituents that these groups may have include a hydroxyl group, an oxo group, an alkyl group, an aryl group, a lactone-containing cyclic group, an ether bond, an ester bond, and a combination thereof.

In a case where an ether bond or an ester bond is included as the substituent, the substituent may be bonded through an alkylene group, and linking groups represented by General Formulae (y-al-1) to (y-al-7) are preferable as the substituent in this case.

- In General Formulae (y-al-1) to (y-al-7), V'^{101} in General Formulae (y-al-1) to (y-al-7) is bonded to R^{b11} of Formula (I3-2).

[0102]

[Chemical Formula 19]



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

[0103]

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

[0104]

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

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

In addition, a part of methylene groups in the alkylene group as V'^{101} or V'^{102} may be substituted with a divalent aliphatic cyclic group having 5 to 10 carbon atoms. As the aliphatic cyclic group, a divalent group in which one hydrogen atom has been removed from the cyclic aliphatic hydrocarbon group (a monocyclic alicyclic hydrocarbon group or a polycyclic alicyclic hydrocarbon group) as R'^{201} is preferable, and a cyclohexylene group, a 1,5-adamantylene group, or a 2,6-adamantylene group is more preferable.

[0105]

A phenyl group or a naphthyl group is more preferable as the aromatic hydrocarbon group.

As the aliphatic cyclic group, a group formed by removing one or more hydrogen atoms from a polycycloalkane such as adamantane, norbornane, isobornane, tricyclodecane, and tetracyclododecane is more preferable.

It is preferable that the chain-like alkyl group has 1 to 10 carbon atoms, and specific examples thereof include a linear alkyl group such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an

octyl group, a nonyl group, or a decyl group; and a branched alkyl group such as a 1-methylethyl group, a 1-methylpropyl group, a 2-methylpropyl group, a 1-methylbutyl group, a 2-methylbutyl group, a 3-methylbutyl group, a 1-ethylbutyl group, a 2-ethylbutyl group, a 1-methylpentyl group, a 2-methylpentyl group, a 3-methylpentyl group, or a 4-methylpentyl group.

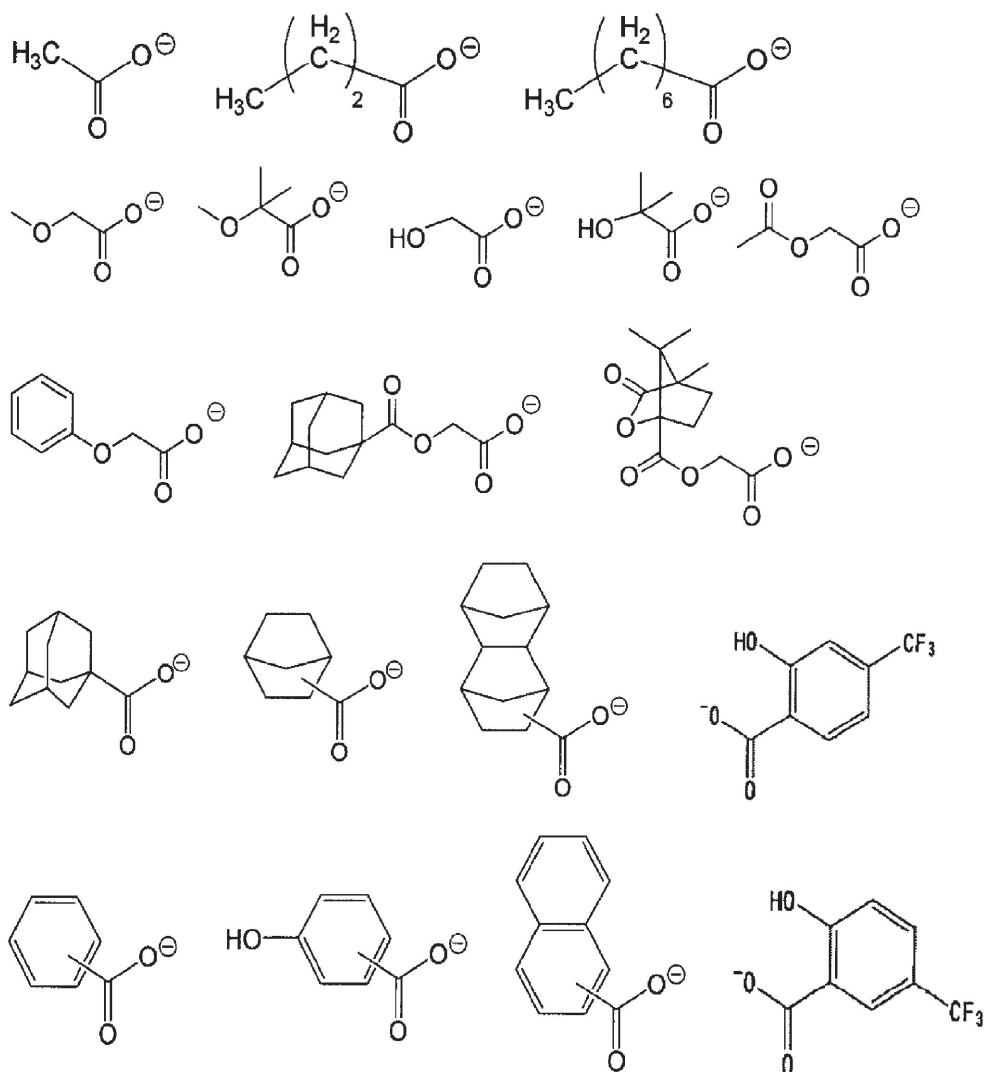
[0106]

It is preferable that R^{b11} represents a cyclic group which may have a substituent other than a halogen atom.

Specific preferred examples of the anion moiety of the component (I3-2) are shown below.

[0107]

[Chemical Formula 20]



[0108]

.. Cation moiety

In Formula (I3-2), M^{m+} represents an m-valent organic cation and has the same
 5 definition as that for M^{m+} in Formula (I3-1).

[0109]

From the viewpoint of high elasticity of a resin film and ease of forming a fine
 structure without residues, it is preferable that the component (I) is a cationic
 polymerization initiator which generates an acid having a pKa (acid dissociation
 10 constant) of -5 or less upon light exposure. It is possible to obtain high sensitivity to

light exposure by using a cationic polymerization initiator which generates an acid having a pKa of more preferably -6 or less and still more preferably -8 or less. The lower limit of the pKa of the acid generated from the component (I) is preferably -15 or greater. The sensitivity is likely to be increased by using a cationic polymerization
5 initiator which generates an acid having a pKa in the above-described suitable ranges.

Here, the term “pKa (acid dissociation constant)” is an index that has been typically used to show the acid strength of a target substance. Further, the pKa in the present specification is a value under a temperature condition of 25°C. Further, the pKa value can be acquired by performing measurement using a known method. In addition,
10 calculated values using known software such as “ACD/Labs” (trade name, manufactured by Advanced Chemistry Development, Inc.) can also be used.

[0110]

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

15 In the negative-type photosensitive resin composition used in the present embodiment, the component (I) is preferably at least one selected from the group consisting of the component (I1), the component (I2), and the component (I3) and more preferably the component (I1).

[0111]

20 In the negative-type photosensitive resin composition used in the present embodiment, the content of the component (I) is preferably in a range of 0.05 to 5 parts by mass, more preferably in a range of 0.1 to 3 parts by mass, still more preferably in a range of 0.15 to 3 parts by mass, and particularly preferably in a range of 0.2 to 1 part by mass in a case where the total mass of the component (P0) is set to 100 parts by mass.

25 In a case where the content of the component (I) is greater than or equal to the

lower limits of the above-described preferable ranges, the sensitivity can be sufficiently obtained, and lithography characteristics of the pattern are further improved. In addition, the hardness of the resin cured film is further increased. Meanwhile, in a case where the content thereof is less than or equal to the upper limits of the above-described preferable ranges, the sensitivity is moderately controlled, and a pattern having a satisfactory shape is likely to be obtained.

[0112]

<Other components>

The negative-type photosensitive resin composition according to the present embodiment may contain other components as necessary, in addition to the component (P0) and the component (I) described above.

As desired, additives having miscibility, for example, an epoxy group-containing compound other than the component (P0), a silane coupling agent, a sensitizer component, a metal oxide (MO), a solvent, an additional resin for improving the film performance, a dissolution inhibitor, a basic compound, a plasticizer, a stabilizer, a colorant, and a halation prevention agent can be appropriately added to the negative-type photosensitive resin composition of the embodiment.

[0113]

The negative-type photosensitive resin composition of the present embodiment may contain an epoxy group-containing compound other than the component (P0).

Examples of the epoxy group-containing compound other than the component (P0) include a bisphenol-type epoxy resin (a bisphenol A-type epoxy resin or a bisphenol F-type epoxy resin), an acrylic resin, and an aliphatic epoxy resin.

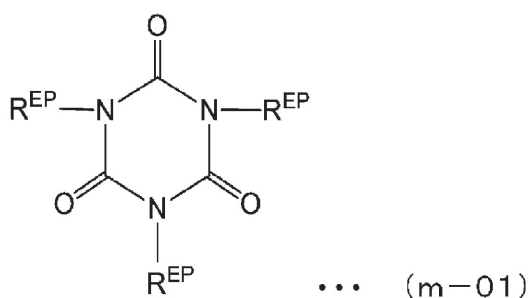
[0114]

In addition, suitable examples of the epoxy group-containing compound other

than the component (P0) include a compound represented by General Formula (m-01) (hereinafter, this compound will also be referred to as “component (m01)”).

[0115]

[Chemical Formula 21]



[In the formula, R^{EP} represents an epoxy group-containing group. A plurality of R^{EP}'s may be the same as or different from each other.]

[0116]

In Formula (m-01), R^{EP} represents an epoxy group-containing group and has the same definition as that for R^{EP} in Formula (Ap-0).

[0117]

Examples of a commercially available product which can be used as the component (m01) include TEPIC series such as TEPIC, TEPIC-VL, TEPIC-PAS, TEPIC-G, TEPIC-S, TEPIC-SP, TEPIC-SS, TEPIC-HP, TEPIC-L, TEPIC-FL, and TEPIC-UC (manufactured by Nissan Chemical Industries, Ltd.); and MA-DGIC, DA-MGIC, and TOIC (manufactured by SHIKOKU KASEI HOLDINGS CORPORATION).

[0118]

The component (m01) may be used alone or in combination of two or more kinds thereof.

The content of the component (m01) in the negative-type photosensitive resin composition used in the present embodiment is preferably in a range of 1 to 15 parts by

mass and more preferably in a range of 3 to 10 parts by mass in a case where the total mass of the component (P0) is set to 100 parts by mass.

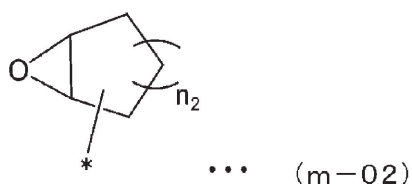
Alternatively, the content of the component (m01) in the negative-type photosensitive resin composition used in the present embodiment is preferably in a range of 1 to 25 parts by mass and more preferably in a range of 3 to 20 parts by mass in a case where the total mass of the component (P0) is set to 100 parts by mass.

[0119]

In addition, suitable examples of the epoxy group-containing compound other than the component (P0) include a compound represented by General Formula (m-02) (hereinafter, this compound will also be referred to as “component (m02)”).

[0120]

[Chemical Formula 22]



[In the formula, n_2 represents an integer of 1 to 4. * represents a bonding site.]

[0121]

In Formula (m-02), n_2 represents an integer of 1 to 4, preferably an integer of 1 to 3, and more preferably 2.

[0122]

Examples of the component (m02) include a compound in which a plurality of partial structures represented by General Formula (m-02) are bonded via a divalent linking group or a single bond. Among these, a compound in which a plurality of the partial structures represented by General Formula (m-02) are bonded via a divalent linking group is preferable.

Here, the divalent linking group is not particularly limited, and suitable examples thereof include a divalent hydrocarbon group which may have a substituent and a divalent linking group having a heteroatom.

Here, the divalent hydrocarbon group which may have a substituent and the
 5 divalent linking group having a heteroatom are each the same as the divalent hydrocarbon group which may have a substituent and the divalent linking group having a heteroatom, described in the section of R^{EP} (epoxy group-containing group) in Formula (Ap-0). Among these, the divalent linking group having a heteroatom is preferable, and a group represented by $-Y^{21}-C(=O)-O-$ or a group represented by $-C(=O)-O-Y^{21}-$ is more
 10 preferable. As Y^{21} , a linear aliphatic hydrocarbon group is preferable, a linear alkylene group is more preferable, a linear alkylene group having 1 to 5 carbon atoms is still more preferable, and a methylene group or an ethylene group is particularly preferable.

[0123]

Examples of a commercially available product that can be used as the
 15 component (m02) include ADEKA RESIN EP-4080S, ADEKA RESIN EP-4085S, and ADEKA RESIN EP-4088S (all trade names, manufactured by ADEKA Corporation); CELLOXIDE 2021P, CELLOXIDE 2081, CELLOXIDE 2083, CELLOXIDE 2085, CELLOXIDE 8000, CELLOXIDE 8010, EHPE-3150, EPOLEAD PB 3600, and EPOLEAD PB 4700 (all trade names, manufactured by Daicel Corporation); DENACOL
 20 EX-211L, DENACOL EX-212L, DENACOL EX-214L, DENACOL EX-216L, DENACOL EX-321L, and DENACOL EX-850L (all trade names, manufactured by Nagase ChemteX Corporation); and EPOCHALIC THI-DE, EPOCHALIC DE-102, and EPOCHALIC DE-103 (all trade names, manufactured by ENEOS Corporation).

[0124]

25 The component (m02) may be used alone or in combination of two or more

kinds thereof.

The content of the component (m02) in the negative-type photosensitive resin composition used in the present embodiment is preferably in a range of 1 to 20 parts by mass and more preferably in a range of 5 to 15 parts by mass in a case where the total
5 mass of the component (P0) is set to 100 parts by mass.

[0125]

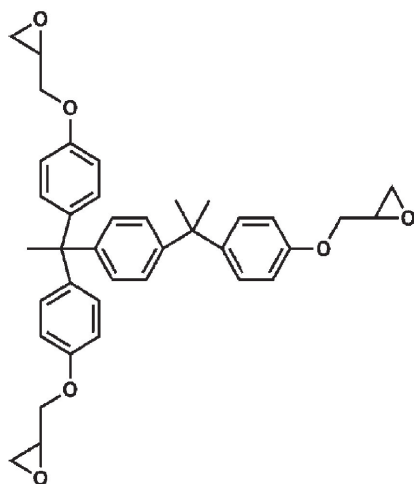
In addition, as the epoxy group-containing compound other than the component (P0), for example, a compound represented by Chemical Formula (m-03-1) or a compound represented by Chemical Formula (m-03-2) (hereinafter, these compounds
10 will also be collectively referred to as “component (m03)”) may be used.

Examples of a commercially available product that can be used as the compound represented by Chemical Formula (m-03-1) include TECHMORE VG-3101L (manufactured by Printec, Inc.).

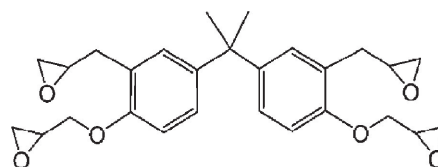
Examples of a commercially available product that can be used as the compound
15 represented by Chemical Formula (m-03-2) include SHOFREE (registered trademark) BATG (manufactured by Showa Denko K.K.).

[0126]

[Chemical Formula 23]



(m-03-1)



(m-03-2)

[0127]

The content of the component (m03) in the negative-type photosensitive resin composition used in the present embodiment is preferably in a range of 1 to 15 parts by mass and more preferably in a range of 5 to 15 parts by mass in a case where the total mass of the component (P0) is set to 100 parts by mass.

[0128]

The negative-type photosensitive resin composition according to the present embodiment may further contain an adhesion assistant in order to improve adhesiveness to the substrate. A silane coupling agent is preferable as the adhesion assistant. That is, the negative-type photosensitive resin composition according to the present embodiment may further contain a silane coupling agent.

Examples of the silane coupling agent include silane coupling agents having reactive substituents such as a carboxy group, a methacryloyl group, an isocyanate group, and an epoxy group. Specific examples thereof include trimethoxysilylbenzoic acid, γ -methacryloxypropyltrimethoxysilane, vinyltriacetoxysilane, vinyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, and β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

The silane coupling agent may be used alone or in combination of two or more

kinds thereof.

In a case where the negative-type photosensitive resin composition contains the silane coupling agent, the content of the silane coupling agent is preferably in a range of 0.1 to 10 parts by mass, more preferably in a range of 0.5 to 5 parts by mass, and still
5 more preferably 1 to 3 parts by mass with respect to 100 parts by mass of the component (P0).

In a case where the content of the silane coupling agent is in the above-described preferable ranges, the hardness of the cured film is further enhanced. In addition, the adhesiveness between the cured film and the substrate is further strengthened.

10 [0129]

The negative-type photosensitive resin composition according to the present embodiment may further contain a sensitizer component.

The sensitizer component is not particularly limited as long as the sensitizer component can absorb energy upon light exposure and transmit the energy to other
15 substances.

As the sensitizer component, specifically, benzophenone-based photosensitizers such as benzophenone and p,p'-tetramethyldiaminobenzophenone; carbazole-based photosensitizers; acetophenone-based photosensitizers; naphthalene-based photosensitizers such as 1,5-dihydroxynaphthalene; phenol-based photosensitizers;
20 anthracene-based photosensitizers such as 9,10-dibutoxyanthracene, 9,10-diethoxyanthracene, 9-ethoxyanthracene; and known photosensitizers such as biacetyl, eosin, rose bengal, pyrene, phenothiazine, and anthrone can be used.

The sensitizer component may be used alone or in combination of two or more kinds thereof.

25 In a case where the negative-type photosensitive resin composition contains the

sensitizer component, the content of the sensitizer component is preferably in a range of 0.1 to 10 parts by mass, more preferably in a range of 0.3 to 5 parts by mass, and still more preferably in a range of 0.5 to 3 parts by mass with respect to 100 parts by mass of the component (P0).

5 In a case where the content of the sensitizer component is in the above-described preferable ranges, the sensitivity and the resolution are further enhanced.

[0130]

 Since the cured film having enhanced hardness is easily obtained, the negative-type photosensitive resin composition according to the present embodiment may further
10 contain a metal oxide (MO) (hereinafter, also referred to as “component (MO)”).
Further, in a case where the photosensitive composition contains the component (MO) in combination with other components, a high-resolution pattern having a satisfactory shape can be formed.

 Examples of the component (MO) include oxides of metals such as silicon
15 (metallic silicon), titanium, zirconium, and hafnium. Among these, an oxide of silicon is preferable, and silica is particularly preferable.

 Further, the shape of the component (MO) is preferably particulate.

 As such a particulate component (MO), a component consisting of a group of particles having a volume average particle diameter of 5 to 40 nm is preferable, a
20 component consisting of a group of particles having a volume average particle diameter of 5 to 30 nm is more preferable, and a component consisting of a group of particles having a volume average particle diameter of 10 to 20 nm is still more preferable.

 In a case where the volume average particle diameter of the component (MO) is greater than or equal to the lower limits of the above-described preferable ranges, the
25 hardness of the cured film is likely to be increased. Meanwhile, in a case where the

volume average particle diameter of the component (M) is lower than or equal to the upper limits of the above-described preferable ranges, residues are unlikely to be generated in the formation of a pattern, and a higher-resolution pattern is likely to be formed. In addition, the transparency of the resin film is enhanced.

5 The particle diameter of the component (MO) may be appropriately selected according to the exposure light source. In general, it is considered that particles having a particle diameter of 1/10 or less of the wavelength of light are almost not affected by light scattering. Therefore, for example, in a case where a fine structure is formed by photolithography with i-line (365 nm), it is preferable to use a group of particles having a
10 primary particle diameter (volume average value) of 10 to 20 nm (particularly preferably a group of silica particles) as the component (MO).

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

In a case where the negative-type photosensitive resin composition contains the
15 component (MO), the content of the component (MO) is preferably in a range of 5 to 50 parts by mass and more preferably in a range of 10 to 40 parts by mass with respect to 100 parts by mass of the component (P0).

In a case where the content of the component (MO) is greater than or equal to the lower limits of the above-described preferable ranges, the hardness of the cured film
20 is further enhanced. Meanwhile, in a case where the content of the component (M) is less than or equal to the upper limits of the above-described preferable ranges, the transparency of the resin film is further enhanced.

[0131]

The negative-type photosensitive resin composition according to the present
25 embodiment may further contain a solvent (hereinafter, also referred to as “component

(S)'').

Examples of the component (S) include lactones such as γ -butyrolactone; ketones such as acetone, methyl ethyl ketone (MEK), cyclohexanone, methyl-n-pentyl ketone, methyl isopentyl ketone, and 2-heptanone; polyhydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol, and dipropylene glycol; compounds having an ester bond, such as 2-methoxybutyl acetate, 3-methoxybutyl acetate, 4-methoxybutyl acetate, ethylene glycol monoacetate, diethylene glycol monoacetate, propylene glycol monoacetate, and dipropylene glycol monoacetate; polyhydric alcohol derivatives of compounds having an ether bond such as monoalkyl ether or monophenyl ether, such as monomethyl ether, monoethyl ether, monopropyl ether, or monobutyl ether of polyhydric alcohols or compounds having an ester bond [among these, propylene glycol monomethyl ether acetate (PGMEA) and propylene glycol monomethyl ether (PGME) are preferable]; cyclic ethers such as dioxane; esters such as methyl lactate, ethyl lactate (EL), methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate, and ethyl ethoxypropionate; aromatic organic solvents such as anisole, ethylbenzylether, cresylmethylether, diphenylether, dibenzylether, phenetole, butylphenylether, ethylbenzene, diethylbenzene, pentylbenzene, isopropylbenzene, toluene, xylene, cymene, and mesitylene; and dimethylsulfoxide (DMSO).

The component (S) may be used alone or in the form of a mixed solvent obtained by mixing two or more kinds thereof.

[0132]

In a case where the negative-type photosensitive resin composition contains the component (S), the amount of the component (S) to be used is not particularly limited, and is appropriately set according to the thickness of the coating film at a concentration at which the negative-type photosensitive resin composition can be applied onto a

substrate or the like without dripping.

For example, the component (S) can be used such that the solid content concentration is set to 70% by mass or greater, and the component (S) can be used such that the solid content concentration is 60% by mass or greater.

5 Further, an aspect in which the photocurable composition does not substantially contain the component (S) (that is, an aspect in which the solid content concentration is 100% by mass) can also be employed.

[0133]

(Laminated film)

10 A laminated film according to the present embodiment is obtained by laminating a photosensitive resin composition layer formed of the negative-type photosensitive resin composition according to the embodiment described above and a support film.

 Further, in the laminated film, a cover film may be disposed on a side opposite to a side where the support film is present in the photosensitive resin composition layer
15 formed of the negative-type photosensitive resin composition.

[0134]

 For example, the laminated film according to the present embodiment can be produced by coating the support film with the negative-type photosensitive resin composition according to the embodiment described above, drying the negative-type
20 photosensitive resin composition to form the photosensitive resin composition layer, and laminating the cover film on the photosensitive resin composition layer.

 The base film may be coated with the negative-type photosensitive resin composition by an appropriate method using a blade coater, a lip coater, a comma coater, a film coater, or the like.

25 The thickness of the photosensitive resin composition layer is preferably 100 μm

or less and more preferably 5 to 50 μm .

[0135]

A known film can be used as the support film, and for example, a thermoplastic resin film or the like is used. As the thermoplastic resin, polyesters such as
5 polyethylene terephthalate are exemplary examples. The thickness of the base film is preferably in a range of 2 to 150 μm .

As the cover film, known films such as a polyethylene film and a polypropylene film can be used. As the cover film, a film having an adhesive force to the
10 photosensitive resin composition layer, which is less than that of the support film, is preferable. The thickness of the cover film is preferably in a range of 2 to 150 μm , more preferably in a range of 2 to 100 μm , and still more preferably in a range of 5 to 50 μm .

The support film and the cover film may be formed of the same film material, or may be formed of different film materials.

15 [0136]

(Method for manufacturing hollow structure)

A method for manufacturing a hollow structure according to the present
embodiment is a method for manufacturing a hollow structure including a support, a
cover layer formed on the support, and a top plate portion covering the cover layer, in
20 which a hollow portion is provided between the support and the cover layer, and a hole
penetrating from the hollow portion to the top plate portion is formed in the cover layer.

In the present embodiment, the top plate portion is formed of the negative-type photosensitive resin composition of the embodiment described above.

[0137]

25 For example, the method for manufacturing a hollow structure according to the

present embodiment can be used for manufacturing the hollow structure 100 shown in FIG. 3.

As an example of a method for manufacturing the hollow structure 100, first, the microelectronic device 20 is disposed on the support 10. Examples of the support 10 include a substrate containing a material selected from glass and silicon (Si). Examples of the microelectronic device 20 include a SAW filter and a BAW filter. A conductive wire (not shown) is connected to the microelectronic device 20.

[0138]

Next, the entire microelectronic device 20 disposed on the support 10 is covered with a sacrificial layer. The space occupied by the sacrificial layer corresponds to the hollow portion 50 (cavity). The sacrificial layer is formed of an organic material.

[0139]

Next, the sacrificial layer is covered with the first cover layer 30. At the same time, the first cover layer 30 is provided to cover a part of the support 10 in the outer periphery of the sacrificial layer. The first cover layer 30 is formed of a so-called TFP film, and contains, for example, a material selected from SiO₂ (silicon dioxide), Si₃N₄ (silicon nitride), and Al₂O₃ (aluminum oxide). Sputtering, thermal vapor deposition, chemical vapor deposition, physical vapor deposition, pulse laser deposition, molecular beam epitaxy, or the like can be used for forming the first cover layer 30.

[0140]

Next, the hole pattern is processed in the first cover layer 30 such that a plurality of holes 35 penetrating to the sacrificial layer are formed.

Thereafter, the sacrificial layer is removed through the plurality of holes 35. In order to remove the sacrificial layer, a method such as wet etching or dry etching in an oxidizing atmosphere or ashing can be used. The hollow portion 50 (cavity) is formed

by removing the sacrificial layer. In the hollow portion 50 (cavity), the microelectronic device 20 is disposed without coming into contact with the first cover layer 30.

[0141]

Next, the first cover layer 30 is covered with the second cover layer 40 (top plate portion). The negative-type photosensitive resin composition of the embodiment described above is used as a material for forming the second cover layer 40 (top plate portion). In addition, the bump 60 is disposed to be in contact with the conductive wire and the support 10 exposed to the outer periphery of the first cover layer 30.

In order to form the second cover layer 40, a photosensitive resin film is formed on the first cover layer 30 using the negative-type photosensitive resin composition of the embodiment described above (step (i)).

In the operation of the step (i), first, the first cover layer 30 is coated with the negative-type photosensitive resin composition of the embodiment described above by a known method such as a spin coating method, a roll coating method, a screen printing method, or a doctor blade coating method, subjected to a bake (post applied bake (PAB)) treatment, for example, under a temperature condition of 60°C to 100°C for 2 to 60 minutes, and further subjected to a bake treatment under a temperature condition of 100°C to 200°C for 1 to 30 minutes to form a photosensitive resin film.

[0142]

Next, the photosensitive resin film is exposed and developed to form a bump via. After forming the via, the film is cured under a temperature condition of 100°C to 200°C for 1 hour to 4 hours to form a cured film.

Next, a metal can be sputtered on the formed via bottom portion to form a bump by plating.

In this manner, the hollow structure 100 can be manufactured.

[0143]

In the method for manufacturing a hollow structure of the present embodiment described above, the negative-type photosensitive resin composition containing a bisphenol novolac-type epoxy resin having a weight-average molecular weight of 4000 or greater and a cationic polymerization initiator is used to form the second cover layer 40. Therefore, the negative-type photosensitive resin composition which is a photosensitive resin film can stably form a resin film (second cover layer 40) on the first cover layer 30 having the holes 35 without flowing through the plurality of holes 35 formed in the first cover layer 30 and falling into the hollow portion 50 regardless of the conditions of a manufacturing process, for example, even in a case where the temperature of the curing treatment is set to be high.

[0144]

According to the present embodiment, since the temperature of the curing treatment can be set to be higher than that in the related art, the adhesion strength between the first cover layer 30 and the second cover layer 40 or between each layer and the bump 60 can be increased.

[0145]

(Method for forming pattern)

A method for forming a pattern according to the present embodiment includes a step of forming a photosensitive resin film on a support (hereinafter, referred to as “film formation step”) using the negative-type photosensitive resin composition according to the embodiment described above; a step of exposing the photosensitive resin film to light (hereinafter, referred to as “exposure step”); and a step of developing the photosensitive resin film exposed to light with a developing solution containing an organic solvent, to form a negative-type pattern (hereinafter, referred to as “development step”).

For example, the method for forming a pattern according to the present embodiment can be performed in the following manner.

[0146]

[Film formation step]

5 First, the support is coated with the negative-type photosensitive resin composition of the embodiment described above by a known method such as a spin coating method, a roll coating method, a screen printing method, or a doctor blade coating method and subjected to a bake (post applied bake (PAB)) treatment, for example, under a temperature condition of 60°C to 180°C for 2 to 60 minutes to form a
10 photosensitive resin film.

Further, the film formation step can also be performed by disposing the photosensitive resin composition layer of the above-described laminated film on the support.

[0147]

15 The support is not particularly limited and a known support of the related art can be used, and examples thereof include a substrate for an electronic component and a substrate on which a predetermined wiring pattern has been formed. More specifically, substrates of metals such as silicon, silicon nitride, titanium, tantalum, lithium tantalate (LiTaO₃), niobium, lithium niobate (LiNbO₃), palladium, titanium tungsten, copper,
20 chromium, iron, and aluminum, and glass substrates are exemplary examples. As the materials of the wiring pattern, copper, aluminum, nickel, or gold can be used.

[0148]

For example, the method for forming a pattern according to the present embodiment is a method useful for lithium tantalate (LiTaO₃) substrates and lithium
25 niobate (LiNbO₃) substrates for SAW devices mounted in communication terminals.

[0149]

The film thickness of the photosensitive resin film to be formed of the negative-type photosensitive resin composition is not particularly limited, but is preferably about 10 to 100 μm . Even in a case where a thick film is formed using the negative-type
5 photosensitive resin composition according to the embodiment described above, satisfactory characteristics are obtained.

[0150]

[Exposure step]

Next, the formed photosensitive resin film is exposed through a mask having a
10 predetermined pattern (mask pattern) formed thereon using a known exposure device or selectively exposed through drawing or the like by performing direct irradiation with electron beams without using a mask pattern therebetween. In addition, a bake (post exposure bake (PEB)) treatment is performed as necessary, for example, under a temperature condition of 80°C to 150°C for 40 to 1200 seconds, preferably 40 to 1000
15 seconds, and more preferably 60 to 900 seconds.

[0151]

The wavelength used for the light exposure is not particularly limited, and radiation such as ultraviolet rays having a wavelength of 300 to 500 nm, i-rays (wavelength of 365 nm), or visible rays is used for selective irradiation (exposure). A
20 low-pressure mercury lamp, a high-pressure mercury lamp, an ultra-high pressure mercury lamp, a metal halide lamp, an argon gas laser, or the like can be used as a source of the radiation described above.

The radiation here denotes ultraviolet rays, visible rays, far ultraviolet rays, X-rays, electron beams, or the like. The irradiation amount of radiation varies depending
25 on the type and blending amount of each component in the composition, the film

thickness of the coating film, and the like, and is in a range of 100 to 2000 mJ/cm², for example, in a case of using an ultra-high pressure mercury lamp.

[0152]

The method of exposing the photosensitive resin film may be performed by
5 general exposure (dry exposure) conducted in air or an inert gas such as nitrogen or by liquid immersion exposure (liquid immersion lithography).

[0153]

The photosensitive resin film after the exposure step has high transparency and, for example, the haze value of the photosensitive resin film in a case of irradiation with i-
10 line (wavelength of 365 nm) is preferably 3% or less and more preferably in a range of 1.0% to 2.5%.

As described above, the photosensitive resin film formed of the negative-type photosensitive resin composition according to the embodiment described above has high transparency. Therefore, in a case of light exposure for pattern formation, the light
15 transmittance increases, and thus a negative-type pattern with satisfactory lithography characteristics is likely to be obtained.

The haze value of the photosensitive resin film after the exposure step is measured by a method in conformity with JIS K 7136 (2000).

[0154]

20 [Development step]

Next, the exposed photosensitive resin film is developed with a developing solution containing an organic solvent (organic developing solution). After the development, it is preferable to perform a rinse treatment. A bake treatment (post bake) may be performed as necessary.

25 [0155]

The organic solvent contained in the organic developing solution may be obtained by dissolving a component (P0) (component (P0) before light exposure) and can be appropriately selected from known organic solvents. Specific examples thereof include a polar solvent such as a ketone-based solvent, an ester-based solvent, an alcohol-based solvent, a nitrile-based solvent, an amide-based solvent, and an ether-based solvent, and a hydrocarbon-based solvent.

[0156]

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

[0157]

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

propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, 2-ethoxybutyl acetate, 4-ethoxybutyl acetate, 4-propoxybutyl acetate, 2-methoxypentyl acetate, 3-methoxypentyl acetate, 4-methoxypentyl acetate, 2-methyl-3-methoxypentyl acetate, 3-methyl-3-methoxypentyl acetate, 3-methyl-4-methoxypentyl acetate, 4-methyl-4-methoxypentyl acetate, propylene glycol diacetate, methyl formate, ethyl formate, butyl formate, propyl formate, ethyl lactate, butyl lactate, propyl lactate, ethyl carbonate, propyl carbonate, butyl carbonate, methyl pyruvate, ethyl pyruvate, propyl pyruvate, butyl pyruvate, methyl acetoacetate, ethyl acetoacetate, methyl propionate, ethyl propionate, propyl propionate, isopropyl propionate, methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, methyl-3-methoxypropionate, ethyl-3-methoxypropionate, ethyl-3-ethoxypropionate, and propyl-3-methoxypropionate. Among these, butyl acetate or PGMEA is preferable as the ester-based solvent.

[0158]

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

[0159]

Known additives can be blended into the organic developing solution as necessary. Examples of the additive include a surfactant. The surfactant is not particularly limited, and for example, an ionic or non-ionic fluorine-based and/or silicon-based surfactant can be used.

As the surfactant, a non-ionic surfactant is preferable, and a non-ionic fluorine-based surfactant or a non-ionic silicon-based surfactant is more preferable.

In a case where a surfactant is blended into the solution, the amount of the surfactant to be blended is typically in a range of 0.001% to 5% by mass, preferably in a range of 0.005% to 2% by mass, and more preferably in a range of 0.01% to 0.5% by

mass with respect to the total amount of the organic developing solution.

[0160]

The developing treatment can be performed by a known developing method, and examples thereof include a method of immersing a support in a developing solution for a certain time (a dip method), a method of raising a developing solution on the surface of a support using the surface tension and maintaining the state for a certain time (a puddle method), a method of spraying a developing solution to the surface of a support (spray method), and a method of continuously ejecting a developing solution onto a support rotating at a certain rate while scanning a developing solution ejection nozzle at a certain rate (dynamic dispense method).

[0161]

The rinse treatment carried out using a rinse solution (washing treatment) can be performed according to a known rinse method. Examples of the method of performing the rinse treatment include a method of continuously ejecting a rinse solution onto a support rotating at a certain rate (rotary coating method), a method of immersing a support in a rinse solution for a certain time (dip method), and a method of spraying a rinse solution to the surface of a support (spray method).

It is preferable that the rinse treatment is performed with a rinse solution containing an organic solvent.

[0162]

A negative-type pattern can be formed by performing the above-described film formation step, exposure step, and development step.

[0163]

(Cured film)

The cured film according to the present embodiment is obtained by curing the

negative-type photosensitive resin composition according to the embodiment described above.

[0164]

(Cured film production method)

5 The method for manufacturing a cured film according to the present embodiment includes a step (i) of forming a photosensitive resin film on a support using the negative-type photosensitive resin composition according to the embodiment described above, and a step (ii) of curing the photosensitive resin film to obtain a cured film.

10 The operation of the step (i) can be performed in the same manner as in the section of [film formation step] described above. The bake treatment can be performed, for example, under a temperature condition of 60°C to 150°C for 40 to 600 seconds.

 The curing treatment in the step (ii) can be performed, for example, under the conditions of a temperature of 100°C to 250°C for 0.5 to 2 hours.

15 The cured film production method according to the embodiment may include other steps in addition to the step (i) and the step (ii). For example, [Exposure step] described above may be provided between the step (i) and the step (ii), and a cured film can be obtained by selectively exposing the photosensitive resin film formed in the step (i) and curing the photosensitive resin film (pre-cured film) on which a bake (PEB)
20 treatment has been performed as necessary.

 According to the above-described cured film production method according to the embodiment, a cured film which faithfully reproduces the mask pattern can be easily produced.

Examples

25 [0165]

Hereinafter, the present invention will be described based on the examples, but the present invention is not limited to the following examples.

[0166]

<Preparation of negative-type photosensitive resin composition>

5 (Examples 1 to 8 and Comparative Example 1)

Each component listed in Table 1 was dissolved in ethyl lactate and mixed, and the mixture was filtered through a PTFE filter (pore size: 1 μ m, manufactured by PALL Corporation) to prepare a negative-type photosensitive resin composition (solution having a solid content of 65% by mass) of each example.

10 [0167]

[Table 1]

Negative-type photosensitive resin composition	Component (P)	Component (M)	Component (I)	Other components
Comparative Example 1	(P)-1 [100]	(M)-1 [3]	(I)-1 [0.4]	(Add)-1 [1.5]
Example 1	(P)-2 [100]	(M)-1 [3]	(I)-1 [0.4]	(Add)-1 [1.5]
Example 2	(P)-2 [100]	(M)-1 [10]	(I)-1 [0.4]	(Add)-1 [1.5]
Example 3	(P)-2 [100]	(M)-2 [10]	(I)-1 [0.4]	(Add)-1 [1.5]
Example 4	(P)-2 [100]	(M)-3 [10]	(I)-1 [0.4]	(Add)-1 [1.5]
Example 5	(P)-2 [100]	(M)-4 [10]	(I)-1 [0.4]	(Add)-1 [1.5]
Example 6	(P)-2 [100]	(M)-2 [5]	(I)-1 [0.4]	(Add)-1 [1.5]
Example 7	(P)-2 [100]	(M)-2 [15]	(I)-1 [0.4]	(Add)-1 [1.5]
Example 8	(P)-2 [100]	(M)-1 [25] (M)-2 [15]	(I)-1 [1]	(Add)-1 [1.5]

[0168]

In Table 1, each abbreviation has the following meaning. The numerical

values in the brackets denote the blending amounts of the components (parts by mass; in terms of solid content).

Component (P): bisphenol novolac-type epoxy resin

P-(1):

5 bisphenol A novolac-type epoxy resin represented by Chemical Formula (Ap-1) (trade name “jER-157S70”, manufactured by Mitsubishi Chemical Corporation), weight-average molecular weight: 2900, polydispersity: 4.23, epoxy equivalent: 220 g/eq, content proportion of bisphenol epoxy monomer in bisphenol A novolac-type epoxy resin: 17% by mass

10 [0169]

P-(2):

 bisphenol A novolac-type epoxy resin represented by Chemical Formula (Ap-2), purified product obtained by purifying bisphenol A novolac-type epoxy resin (trade name “jER-157S70”, manufactured by Mitsubishi Chemical Corporation) by purification
15 method shown below, weight-average molecular weight: 4500, polydispersity: 2.17, epoxy equivalent: 226 g/eq; content proportion of bisphenol epoxy monomer in bisphenol A novolac-type epoxy resin: 1.5% by mass

[0170]

[First step of purification method]

20 300 g (300 parts by mass) of ethanol was added to 100 g (100 parts by mass) of the bisphenol A novolac-type epoxy resin (trade name “jER-157S70”, manufactured by Mitsubishi Chemical Corporation). Next, the mixture was heated to 70°C to melt the bisphenol A novolac-type epoxy resin (trade name “jER-157S70”, manufactured by Mitsubishi Chemical Corporation) in ethanol, thereby obtaining a mixed solution.

25 The obtained mixed solution was refluxed at 77°C for 1 hour.

[0171]

[Second step of purification method]

The mixed solution after the reflux was allowed to stand to be cooled to 25°C.

As a result, the melted resin was solidified in the mixed solution.

5 [0172]

[Third step of purification method]

The solidified product and the remaining mixed solution (ethanol and the like) were separated from each other to recover the solidified product.

[0173]

10 Next, an operation of performing the first step, the second step, and the third step in this order was further performed three times on the recovered solidified product. That is, the purification operation of performing the first step, the second step, and the third step in this order was performed four times in total on the bisphenol A novolac-type epoxy resin (trade name “jER-157S70”, manufactured by Mitsubishi Chemical Corporation).

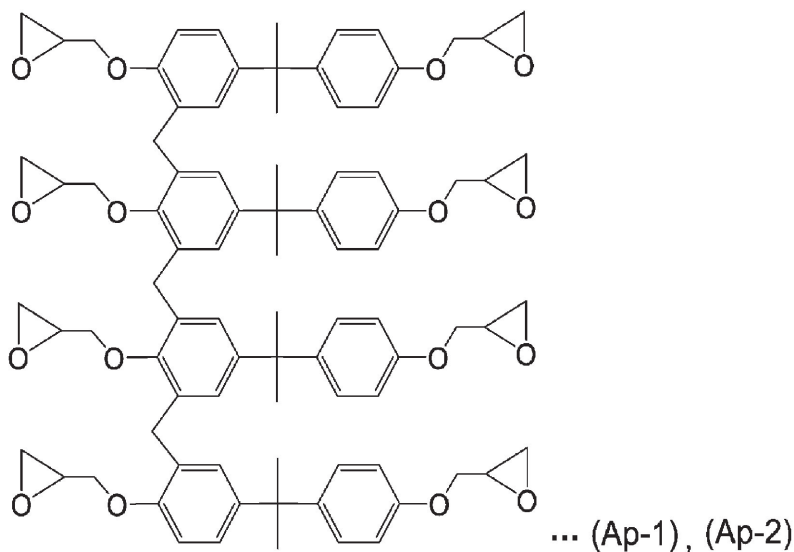
15

[0174]

Next, the solidified product recovered after the purification operation performed four times at 100°C overnight was dried using a vacuum oven to obtain a purified product of the bisphenol A novolac-type epoxy resin.

20 [0175]

[Chemical Formula 24]



[0176]

[Measurement of weight-average molecular weight]

The weight-average molecular weight of each of the bisphenol A novolac-type epoxy resin (trade name “jER-157S70”, manufactured by Mitsubishi Chemical Corporation) before the purification and the purified product after the purification was set under the following conditions and measured by gel permeation chromatography (GPC method).

- Device: HLC-8320 (manufactured by Tosoh Corporation)
- Column: TSK Gel Super HM-N (3 columns connected)
- Eluent: tetrahydrofuran
- Flow rate: 0.6 mL/min
- Column temperature: 40°C
- Detector: RI
- Polystyrene standard

[0177]

FIGS. 1 and 2 show GPC charts obtained from the signals of the RI detector.

FIG. 1 is a GPC chart for a bisphenol A novolac-type epoxy resin before the

purification. FIG. 2 is a GPC chart for the bisphenol A novolac-type epoxy resin after the purification. The vertical axis indicates the detection intensity (mV), and the horizontal axis indicates the retention time (min).

Measurement of bisphenol epoxy monomer content:

5 The content proportion of the bisphenol epoxy monomer in the bisphenol A novolac-type epoxy resin was determined as follows.

That is, the content proportion of the bisphenol epoxy monomer was calculated as a ratio of a peak area in a retention time of 14.4 min to 15.3 min to a peak area in a retention time of 9.5 min to 15.3 min in the GPC chart.

10 [0178]

[Measurement of epoxy equivalent]

Preparation of sodium carbonate/acetic acid solution

A sodium carbonate/acetic acid solution was prepared by the following procedure.

15 First, about 10 g of sodium carbonate was placed in a crucible and heated in an electric furnace at 500°C for 1 hour.

Next, the heated sodium carbonate was placed in a desiccator and allowed to stand for 1 hour until the temperature reached room temperature.

Next, about 2.5 to 3.0 g of sodium carbonate after the standing at room
20 temperature was precisely weighed and put into a 500 mL volumetric flask. Next, acetic acid was added until the volume reached 500 mL, and sodium carbonate was dissolved.

[0179]

Calculation of factor F of hydrogen bromide/acetic acid solution:

25 5 mL of the prepared sodium carbonate/acetic acid solution was placed in a

disposable cup using a hole pipette.

Next, about 30 mL of toluene was added to the disposable cup. Next, acetic acid was added to an extent that the electrode was immersed.

Next, a small amount of a crystal violet/acetic acid solution was added as an indicator. The obtained solution was titrated with a hydrogen bromide/acetic acid solution.

Next, the factor F of the hydrogen bromide/acetic acid solution was calculated from the following equation. S represents the mass (g) of sodium carbonate. P represents the purity (%) of sodium carbonate. A represents the amount (mL) of the hydrogen bromide/acetic acid solution added dropwise.

$$F = \{S \times (5/500) \times (P/100)\} / (0.0053 \times A)$$

[0180]

Measurement of concentration oxirane oxygen:

Wg of an epoxy resin as a measurement target was placed in a disposable cup.

Next, about 30 mL of toluene was added to the disposable cup. Next, acetic acid was added to an extent that the electrode was immersed. Next, a small amount of a crystal violet/acetic acid solution was added as an indicator. The obtained solution was titrated with a hydrogen bromide/acetic acid solution. The end point was set to a point where the solution changed from blue to green and the potential difference was large.

Next, a concentration X (%) of oxirane oxygen was calculated from the following equation. T represents the amount (mL) of the hydrogen bromide/acetic acid solution added dropwise.

$$X = (0.16 \times T \times F) / W$$

[0181]

Calculation of epoxy equivalent:

An epoxy equivalent Y was calculated from the following equation.

$$Y = (16 \times 100)/X$$

[0182]

Component (M): epoxy group-containing compound other than component (P)

5 (M)-1: epoxy group-containing monomer represented by Chemical Formula (m-1)

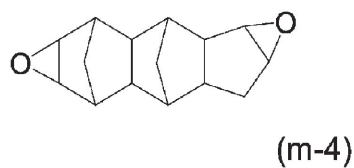
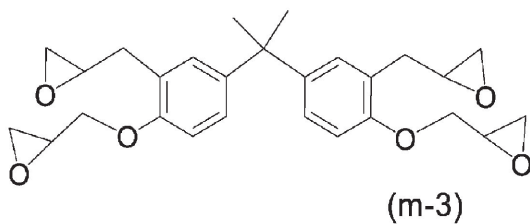
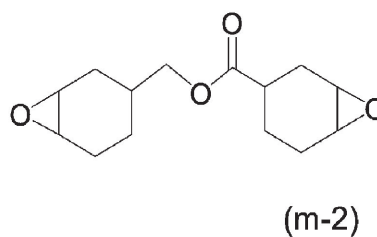
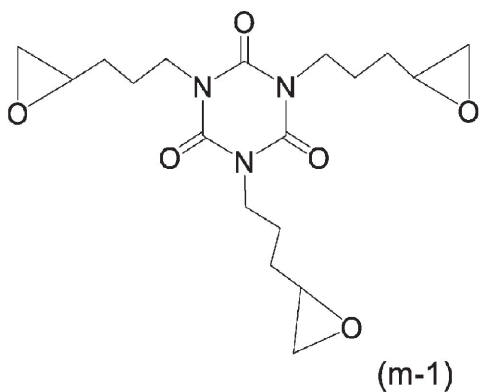
(M)-2: epoxy group-containing monomer represented by Chemical Formula (m-2)

10 (M)-3: epoxy group-containing monomer represented by Chemical Formula (m-3)

(M)-4: epoxy group-containing monomer represented by Chemical Formula (m-4)

[0183]

[Chemical Formula 25]



15

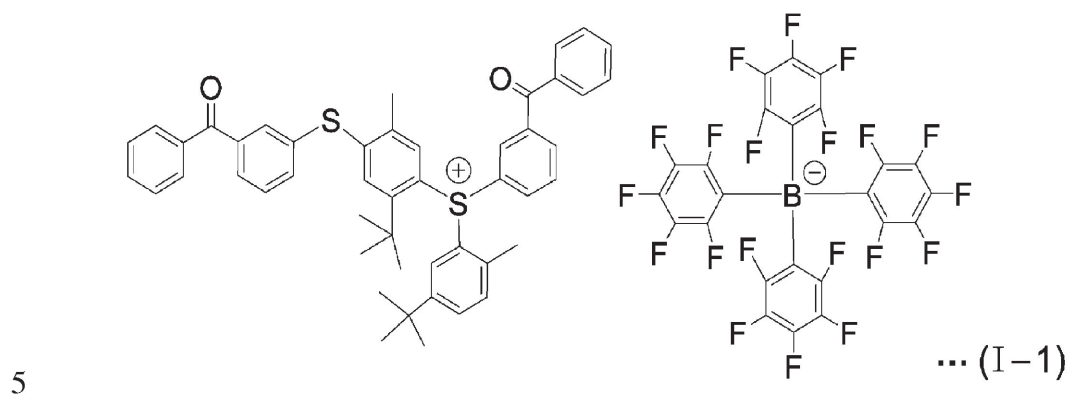
[0184]

Component (I): cationic polymerization initiator

(I)-1: cationic polymerization initiator represented by Chemical Formula (I-1)

[0185]

[Chemical Formula 26]



[0186]

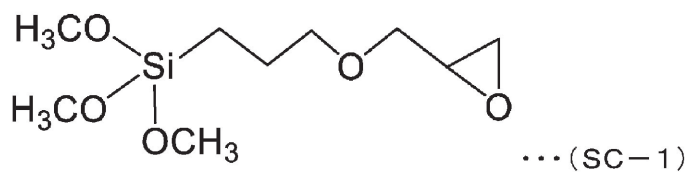
Silane coupling agent as other components

(Add)-1: compound represented by Chemical Formula (SC-1)

[0187]

10

[Chemical Formula 27]



[0188]

<Evaluation>

15 In a case of manufacturing the hollow structure, the following evaluation was performed as a model test in which the negative-type photosensitive resin composition flows through the hole of the cover layer and falls into the hollow portion.

[0189]

The property of the negative-type photosensitive resin composition of each

example to fall into the hole portion was evaluated by the model test described below.

Method of model test:

A substrate including a SiO₂ layer on which a hole pattern having 60 holes with a height of 50 μm and a diameter of 5 μm was formed was prepared. The substrate was coated with the negative-type photosensitive resin composition of each example using a spin coater, and heated with a hot plate under the soft bake conditions in the table to form a photosensitive resin film (film thickness: 20 μm).

After the heating, the number of holes into which the resin composition had fallen was confirmed by observation with an optical microscope. This evaluation was performed three times for each resin composition, and the average number thereof is listed in the columns of “(number of holes into which resin composition had fallen)/60 holes” in the table.

[0190]

The soft bake conditions in the table are as follows.

“65°C, 20 min” denotes that the heating treatment was performed at a temperature of 65°C for 20 minutes.

“65°C, 20 min → 120°C, 4 min” denotes that the heating treatment was performed at a temperature of 65°C for 20 minutes, and the heating treatment was continuously performed at a temperature of 120°C for 4 minutes.

“65°C, 20 min → 150°C, 4 min” denotes that the heating treatment is performed at a temperature of 65°C for 20 minutes, and the heating treatment was continuously performed at a temperature of 150°C for 4 minutes.

“65°C, 20 min → 180°C, 4 min” denotes that the heating treatment was performed at a temperature of 65°C for 20 minutes, and the heating treatment was continuously performed at a temperature of 180°C for 4 minutes.

[0191]

[Table 2]

	Property of resin composition to fall into hole portion (number of holes into which resin composition had fallen)/60 holes			
Soft bake conditions	65°C, 20 min	65°C, 20 min ↓ 120°C, 4 min	65°C, 20 min ↓ 150°C, 4 min	65°C, 20 min ↓ 180°C, 4 min
Comparative Example 1	0/60	0/60	18/60	30/60
Example 1	0/60	0/60	0/60	0/60
Example 2	0/60	0/60	0/60	6/60
Example 3	0/60	0/60	0/60	0/60
Example 4	0/60	0/60	0/60	0/60
Example 5	0/60	0/60	0/60	0/60
Example 6	0/60	0/60	0/60	0/60
Example 7	0/60	0/60	0/60	0/60
Example 8	0/60	0/60	0/60	0/60

[0192]

As shown in the results listed in Table 2, it was confirmed that in a case where the negative-type photosensitive resin compositions of Examples 1 to 8 to which the present invention was applied were used, even in a case where the temperature during the soft bake was increased, the resin film could be stably formed on the cover layer having the holes without the composition flowing into the holes of the cover layer and falling into the hollow portion.

Meanwhile, it was confirmed that in a case where the negative-type photosensitive resin composition of Comparative Example 1 was used, the composition did not fall into the hollow portion at a temperature of 120°C during the soft bake, but the falling of the composition into the hollow portion was confirmed at 150°C and 180°C in a case where the temperature during the soft bake was further increased.

[0193]

While preferred embodiments of the present invention have been described and illustrated above, it should be understood that these are exemplary of the present invention and are not to be considered as limiting. Additions, omissions, substitutions, and other modifications can be made without departing from the scope of the present invention. The present invention is not limited by the description above, but is limited only by the scope of the appended claims.

REFERENCE SIGNS LIST

[0194]

	10 Support
10	20 Microelectronic device
	30 First cover layer
	35 Hole
	40 Second cover layer
	50 Hollow portion
15	60 Bump
	100 Hollow structure

CLAIMS

[Claim 1] A negative-type photosensitive resin composition comprising:

a bisphenol novolac-type epoxy resin; and

a cationic polymerization initiator,

5 wherein the bisphenol novolac-type epoxy resin has a weight-average molecular weight of 4000 or greater.

[Claim 2] The negative-type photosensitive resin composition according to Claim 1,

wherein a content proportion of a bisphenol epoxy monomer in the bisphenol novolac-type epoxy resin is 2% by mass or less with respect to a total mass of the

10 bisphenol novolac-type epoxy resin.

[Claim 3] The negative-type photosensitive resin composition according to Claim 1 or 2,

wherein the bisphenol novolac-type epoxy resin is a bisphenol A novolac-type epoxy resin.

15 [Claim 4] The negative-type photosensitive resin composition according to Claim 1 or 2,

wherein the negative-type photosensitive resin composition is used to form a top plate portion of a hollow structure including a support, a cover layer formed on the support, and a top plate portion covering the cover layer,

20 in which a hollow portion is provided between the support and the cover layer, and

a hole penetrating from the hollow portion to the top plate portion is formed in the cover layer.

[Claim 5] A method for manufacturing a hollow structure including a support, a cover

25 layer formed on the support, and a top plate portion covering the cover layer, in which a

hollow portion is provided between the support and the cover layer, and a hole penetrating from the hollow portion to the top plate portion is formed in the cover layer, the method comprising:

- forming the top plate portion using the negative-type photosensitive resin composition according to Claim 1 or 2.

[Claim 6] A method for forming a pattern, comprising:

- a step of forming a photosensitive resin film on a support using the negative-type photosensitive resin composition according to Claim 1 or 2;
- a step of exposing the photosensitive resin film to light; and
- a step of developing the photosensitive resin film exposed to light with a developing solution containing an organic solvent, to form a negative-type pattern.