

CHEMICALLY-AMPLIFIED POSITIVE PHOTSENSITIVE RESIN  
COMPOSITION, MANUFACTURING METHOD OF SUBSTRATE WITH  
CASTING MOLD, AND MANUFACTURING METHOD OF ELECTROPLATED  
MOLDED ARTICLE

5

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The invention relates to a chemically-amplified positive photosensitive resin  
10 composition, a manufacturing method of a substrate with a casting mold, and a  
manufacturing method of an electroplated molded article, and more particularly, to a  
chemically-amplified positive photosensitive resin composition that can alleviate the  
issue of poor sensitivity and rectangularity, a manufacturing method of a substrate with  
a casting mold formed by the chemically-amplified positive photosensitive resin  
15 composition, and a manufacturing method of an electroplated molded article formed by  
the substrate with the casting mold.

Description of Related Art

[0002] Currently, photoelectric processing has become the mainstream of precision  
microfabrication techniques. "Photoelectric processing" is the general term for  
20 techniques of manufacturing various precision parts such as a semiconductor packaged  
body by coating a photoresist composition on a processed article surface to form a  
photoresist layer, patterning the photoresist layer using a lithography technique, and then  
performing chemical etching, electrolytic etching, or electroforming based on

electroplating using the patterned photoresist layer (photoresist pattern) as a mask.

[0003] Moreover, in recent years, as electronic equipment became smaller, high-density assembly techniques of the semiconductor packaged body have advanced rapidly, and as a result, increased assembly density of multi-pin film assembly, miniaturization of packaged body size, flip-chip 2D assembly techniques, and 3D assembly techniques are desired. Among these high-density assembly techniques, the connection terminal, for instance, is disposed on a substrate at high-precision density to connect a protruding electrode (assembly terminal) such as a bump protruding toward the packaged body, a wire extended from the peripheral terminal on a wafer, and a metal column of an assembly terminal.

[0004] The photoelectric processing uses a photoresist composition, and such a photoresist composition includes a chemically-amplified photoresist composition containing an acid generator (refer to patent literature 1 and 2...etc.) The chemically-amplified photoresist composition generates acid via an acid generator and radiation (exposure), and acid diffusion is promoted via a heat treatment to trigger an acid catalyst reaction with, for instance, the matrix resin in the composition to change the alkali solubility thereof.

[0005] Such a chemically-amplified positive photoresist composition is used in, for instance, the forming of an electroplated molded article such as a bump or metal column in a plating step. Specifically, the chemically-amplified photoresist composition is used, a photoresist layer having the desired film thickness is formed on a support body such as a metal substrate, and exposure and development are performed with a predetermined mask pattern in between to form a photoresist pattern used as a template,

wherein the portion for forming a bump or metal column is selectively removed (stripped). Next, after a conductor such as copper is embedded in the removed portion (non-photoresist portion) via plating, the surrounding photoresist pattern is removed to form a bump or metal column.

5   **[0006]** However, the chemically-amplified positive photosensitive resin composition has the drawbacks of poor sensitivity and poor photoresist pattern rectangularity, and therefore cannot be accepted by the industry. Therefore, how to provide a chemically-amplified positive photoresist composition that can form a photoresist pattern having good sensitivity and rectangularity is an important issue for those skilled  
10 in the art.

[Patent literature]

**[0007]** [Patent literature 1] JP H09-176112

[Patent literature 2] JP H11-052562

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## SUMMARY OF THE INVENTION

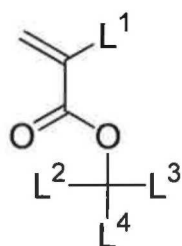
**[0008]** Accordingly, the invention provides a chemically-amplified positive photosensitive resin composition, and the use of the chemically-amplified positive photosensitive resin composition can alleviate the issue of poor sensitivity and rectangularity.

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**[0009]** The invention provides a chemically-amplified positive photosensitive resin composition including: a resin (A) obtained by the copolymerization of a monomer mixture and containing an acid dissociative protecting group, a novolac resin (B), a photoacid generator (C), and a solvent (D). The novolac resin (B) includes a

high-ortho novolac resin (B-1), and the high-ortho novolac resin (B-1) has 18% to 25% of a methylene group bonded in an ortho-ortho arrangement.

[0010] In an embodiment of the invention, the monomer mixture includes a monomer (a1) having a structure represented by formula (A-1) below:

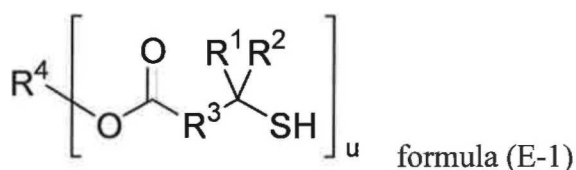


formula (A-1)

in formula (A-1),  $\text{L}^1$  represents a hydrogen atom, a  $\text{C}_1$  to  $\text{C}_6$  straight or branched alkyl group, a fluorine atom, or a  $\text{C}_1$  to  $\text{C}_6$  straight or branched fluorinated alkyl group;  $\text{L}^2$ ,  $\text{L}^3$ , and  $\text{L}^4$  respectively independently represent a  $\text{C}_1$  to  $\text{C}_6$  straight or branched alkyl group or a  $\text{C}_1$  to  $\text{C}_6$  straight or branched fluoroalkyl group, or  $\text{L}^3$  and  $\text{L}^4$  are bonded to each other to form a  $\text{C}_5$  to  $\text{C}_{20}$  hydrocarbon ring.

[0011] In an embodiment of the invention, the monomer mixture includes a monomer (a2), and the monomer (a2) contains a cyclic ether group.

[0012] In an embodiment of the invention, the chemically-amplified positive photosensitive resin composition further includes a thiol compound (E) having the structure represented by formula (E-1) below:



formula (E-1)

in formula (E-1),  $\text{R}^1$  and  $\text{R}^2$  each independently represent a hydrogen atom or a  $\text{C}_1$  to  $\text{C}_4$  alkyl group,  $\text{R}^3$  represents a single bond or a  $\text{C}_1$  to  $\text{C}_{10}$  alkylene group, and  $\text{R}^4$  represents a u-valence organic group; and u represents an integer of 2 to 6.



[0013] In an embodiment of the invention, the chemically-amplified positive photosensitive resin composition further includes an anthracene compound (F).

[0014] In an embodiment of the invention, based on a total amount of 100 parts by weight of the resin (A), the amount of the novolac resin (B) is 20 parts by weight to 150 parts by weight, the amount of the photoacid generator (C) is 0.5 parts by weight to 5 parts by weight, and the amount of the solvent (D) is 30 parts by weight to 360 parts by weight.

[0015] In an embodiment of the invention, based on a total amount of 100 parts by weight of the resin (A), the amount of the high-ortho novolac resin (B-1) is 20 parts by weight to 120 parts by weight.

[0016] In an embodiment of the invention, based on a total amount of 100 parts by weight of the monomer mixture, the amount of the monomer (a1) is 10 parts by weight to 60 parts by weight.

[0017] In an embodiment of the invention, based on a total amount of 100 parts by weight of the monomer mixture, the amount of the monomer (a2) is 5 parts by weight to 30 parts by weight.

[0018] In an embodiment of the invention, based on a total amount of 100 parts by weight of the resin (A), the amount of the thiol compound (E) is 0.3 parts by weight to 3 parts by weight.

[0019] In an embodiment of the invention, based on a total amount of 100 parts by weight of the resin (A), the amount of the anthracene compound (F) is 0.2 parts by weight to 1.5 parts by weight.

[0020] The invention also provides a manufacturing method of a substrate with a

casting mold, including: a lamination step, laminating a photosensitive resin layer formed by the chemically-amplified positive photosensitive resin composition above on the metal surface of a substrate, an exposure step, irradiating actinic ray or radiation on the photosensitive resin layer, and a developing step, developing the photosensitive resin layer after exposure to form a casting mold forming an electroplated molded article.

[0021] The invention further provides a manufacturing method of an electroplated molded article including: a step of electroplating the substrate with a casting mold formed by the manufacturing method of the substrate with a casting mold to form an electroplated molded article in the casting mold.

[0022] Based on the above, the chemically-amplified positive photosensitive resin composition of the invention contains 18% to 25% of a methylene group bonded to the high-ortho novolac resin (B-1) bonded in an ortho-ortho arrangement, and therefore the issue of poor sensitivity and rectangularity can be alleviated.

[0023] In order to make the aforementioned features and advantages of the disclosure more comprehensible, embodiments accompanied with figures are described in detail below.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0024] The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

[0025] FIG. 1 is a schematic of the measurement of the rectangularity of a photoresist pattern.

## DESCRIPTION OF THE EMBODIMENTS

### 5 [0026] <Chemically-amplified positive photosensitive resin composition>

The invention provides a chemically-amplified positive photosensitive resin composition including: a resin (A) obtained by the copolymerization of a monomer mixture and containing an acid dissociative protecting group, a novolac resin (B), a photoacid generator (C), and a solvent (D). The novolac resin (B) includes a  
10 high-ortho novolac resin (B-1), and the high-ortho novolac resin (B-1) has 18% to 25% of a methylene group bonded in an ortho-ortho arrangement. Moreover, the chemically-amplified positive photosensitive resin composition of the invention can further contain a thiol compound (E), an anthracene compound (F), and an additive (G).

[0027] In the following, the individual components used in the chemically-amplified  
15 positive photosensitive resin composition of the invention are described in detail.

[0028] It should be mentioned that, in the following, (meth)acrylic acid represents acrylic acid and/or methacrylic acid, and (meth)acrylate represents acrylate and/or methacrylate. Similarly, a (meth)acryloyl group represents an acryloyl group and/or methacryloyl group.

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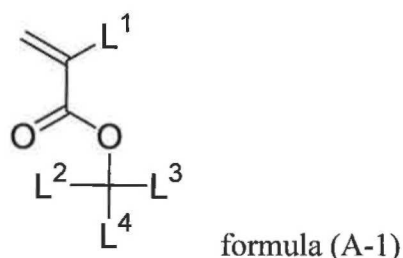
#### Resin (A)

[0029] The resin (A) is obtained by copolymerizing a monomer mixture and contains an acid-dissociated protecting group. Specifically, the monomer mixture can include a

monomer (a1) having a structure represented by formula (A-1), a monomer (a2) containing a cyclic ether group, a monomer (a3) having a structure represented by formula (A-2) or formula (A-3), and other monomers (a4).

## 5 Monomer (a1) having structure represented by formula (A-1)

[0030] The monomer (a1) having the structure represented by formula (A-1) is as shown below:



in formula (A-1),  $L^1$  represents a hydrogen atom, a  $C_1$  to  $C_6$  straight or branched alkyl group, a fluorine atom, or a  $C_1$  to  $C_6$  straight or branched fluorinated alkyl group;  $L^2$ ,  $L^3$ , and  $L^4$  respectively independently represent a  $C_1$  to  $C_6$  straight or branched alkyl group or a  $C_1$  to  $C_6$  straight or branched fluoroalkyl group, or  $L^3$  and  $L^4$  are bonded to each other to form a  $C_5$  to  $C_{20}$  hydrocarbon ring.

[0031] Moreover, the straight or branched alkyl group can include, for instance, 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, or a neopentyl group. Moreover, the fluorinated alkyl group refers to the alkyl group for which some or all of the hydrogen atoms are substituted by fluorine atoms.

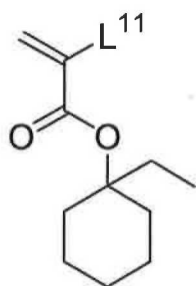
[0032] When  $L^3$  and  $L^4$  are not bonded to each other to form a hydrocarbon ring,  $L^2$ ,  $L^3$ , and  $L^4$  are preferably  $C_2$  to  $C_4$  straight or branched alkyl groups.

[0033] The  $L^3$  and  $L^4$  can form a  $C_5$  to  $C_{20}$  aliphatic cyclic group together with a

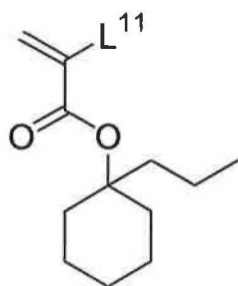
carbon atom bonded to the two. Specific examples of the aliphatic cyclic group can include groups for which 1 or more hydrogen atoms are removed from polycycloalkane such as monocycloalkane, bicycloalkane, tricycloalkane, or tetracycloalkane. Specifically, a group for which 1 or more hydrogen atoms are removed by  
 5 monocycloalkane such as cyclopentane, cyclohexane, cycloheptane, or cyclooctane or polycycloalkane such as adamantane, norbornane, isobornylene, tricyclodecane, or tetracyclododecane can be used. In particular, a group (can further have a substituent) for which 1 or more hydrogen atoms are removed by cyclohexane or adamantane is preferred.

10 **[0034]** Moreover, when the aliphatic cyclic group formed by the  $L^3$  and  $L^4$  has a substituent on the ring skeleton thereof, examples of the substituent can include a polar group such as a hydroxyl group, carboxyl group, cyano group, or oxygen atom (=O), or a  $C_1$  to  $C_4$  straight or branched alkyl group. The polar group is preferably an oxygen atom (=O).

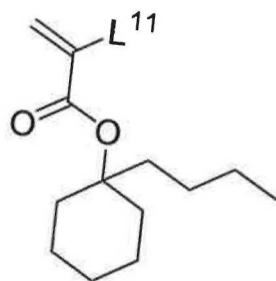
15 **[0035]** Specific examples of the monomer (a1) having the structure represented by formula (A-1) can include compounds represented by formula (A-1-1) to formula (A-1-33) below:



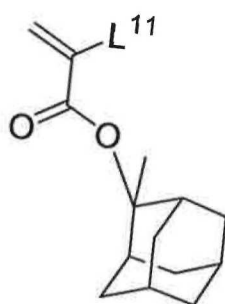
formula (A-1-1)



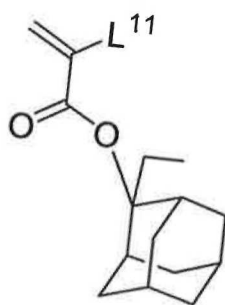
formula (A-1-2)



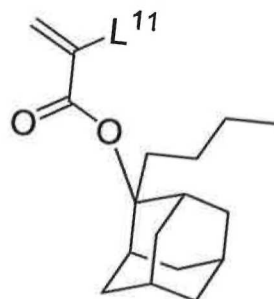
formula (A-1-3)



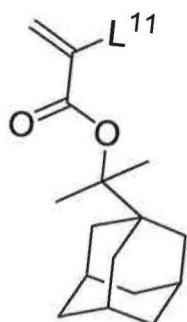
formula (A-1-4)



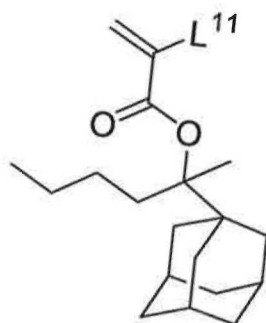
formula (A-1-5)



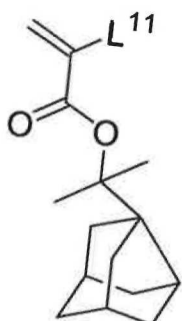
formula (A-1-6)



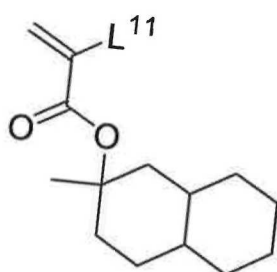
formula (A-1-7)



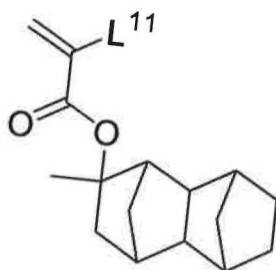
formula (A-1-8)



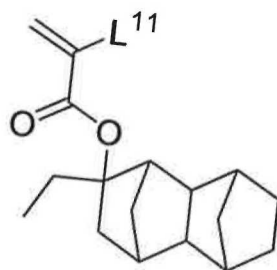
formula (A-1-9)



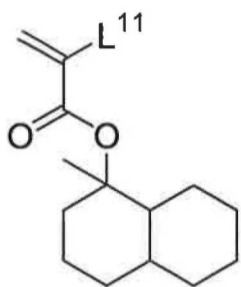
formula (A-1-10)



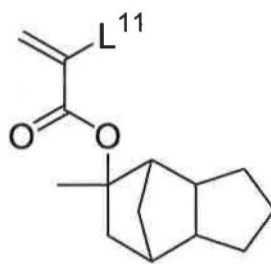
formula (A-1-11)



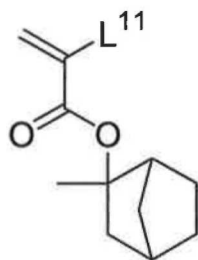
formula (A-1-12)



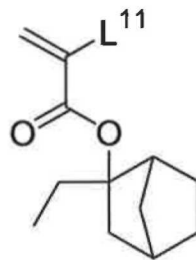
formula (A-1-13)



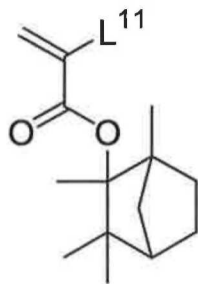
formula (A-1-14)



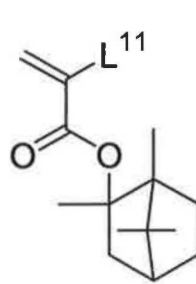
formula (A-1-15)



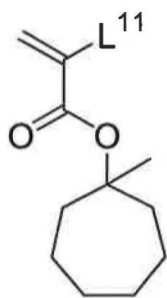
formula (A-1-16)



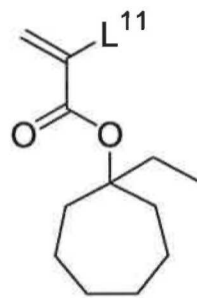
formula (A-1-17)



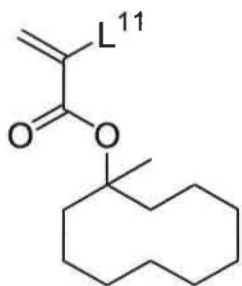
formula (A-1-18)



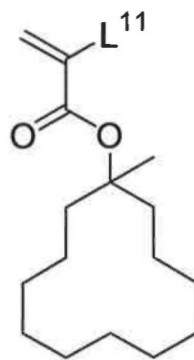
formula (A-1-19)



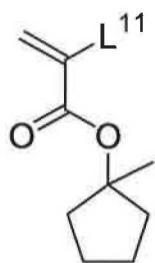
formula (A-1-20)



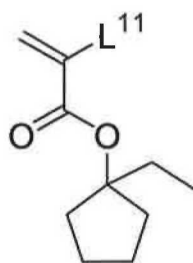
formula (A-1-21)



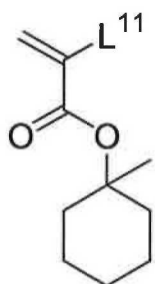
formula (A-1-22)



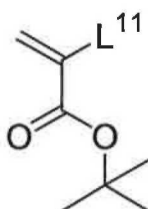
formula (A-1-23)



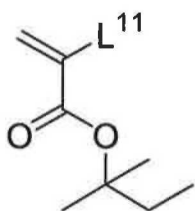
formula (A-1-24)



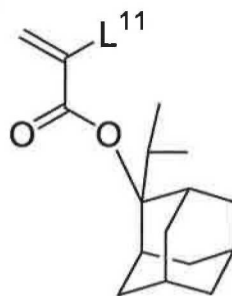
formula (A-1-25)



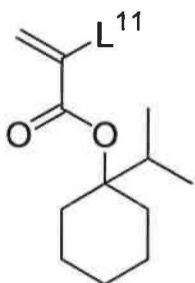
formula (A-1-26)



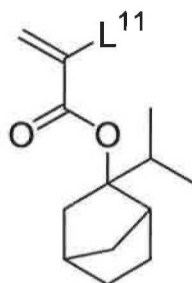
formula (A-1-27)



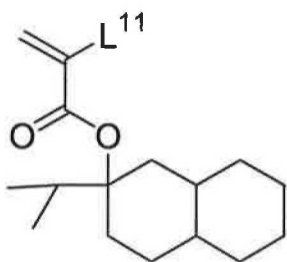
formula (A-1-28)



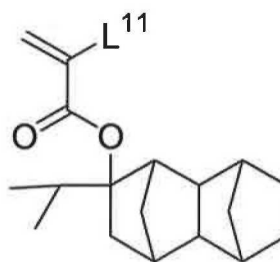
formula (A-1-29)



formula (A-1-30)

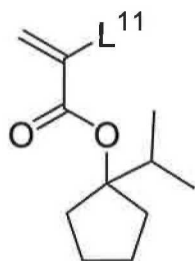


formula (A-1-13)



formula (A-1-32)





formula (A-1-33)

In formula (A-1-1) to formula (A-1-33),  $L^{11}$  represents a hydrogen atom or a methyl group.

[0036] Based on a total amount of 100 parts by weight of the monomer mixture, the amount of the monomer (a1) is 10 parts by weight to 60 parts by weight, preferably 12 parts by weight to 55 parts by weight, and more preferably 15 parts by weight to 50 parts by weight.

[0037] If the monomer mixture includes the monomer (a1) having the structure represented by formula (A-1), then the rectangularity of the chemically-amplified positive photosensitive resin composition can be further improved.

#### Monomer (a2) containing cyclic ether group

[0038] The monomer (a2) containing a cyclic ether group can include a three-membered ring such as glycidyl methacrylate, 2-methyl glycidyl (meth)acrylate, 3,4-epoxybutyl (meth)acrylate, 6,7-epoxyheptyl (meth)acrylate, 3,4-epoxycyclohexyl (meth)acrylate, or 3,4-epoxycyclohexyl methyl (meth)acrylate; a four-membered ring such as 3-(meth)acryloyloxymethyl oxetane, 3-(meth)acryloyloxymethyl-3-ethyl oxetane, 3-(meth)acryloyloxymethyl-2-methyl oxetane, 3-(meth)acryloyloxymethyl-2-trifluoromethyl oxetane, 3-(meth)acryloyloxymethyl-2-pentafluoroethyl oxetane, 3-(meth)

acryloyloxymethyl-2-phenyl oxetane, 3-(meth)acryloyloxymethyl-2,2-difluoro oxetane,  
 3-(meth)acryloyloxymethyl-2,2,4-trifluoro oxetane, 3-(meth)acryloyloxymethyl-2,2,4,4-  
 tetrafluoro oxetane, 3-(meth)acryloyloxyethyl oxetane, 3-(meth)acryloyloxyethyl-3-ethyl  
 oxetane, 2-ethyl-3-(meth)acryloyloxyethyl oxetane, 3-(meth)acryloyloxyethyl-2-tri-  
 5 fluoromethyl oxetane, 3-(meth)acryloyloxyethyl-2-pentafluoroethyl oxetane,  
 3-(meth)acryloyloxyethyl-2-phenyl oxetane, 2,2-difluoro-3-(meth)acryloyloxyethyl  
 oxetane, 3-(meth)acryloyloxyethyl-2,2,4-trifluoro oxetane, 3-(meth)acryloyloxyethyl-  
 2,2,4,4-tetrafluoro oxetane, 2-(meth)acryloyloxymethyl oxetane, 2-methyl-2-  
 (meth)acryloyloxymethyl oxetane, 3-methyl-2-(meth)acryloyloxymethyl oxetane,  
 10 4-methyl-2-(meth)acryloyloxymethyl oxetane, 2-(meth)acryloyloxymethyl-2-tri-  
 fluoromethyl oxetane, 2-(meth)acryloyloxymethyl-3-trifluoromethyl oxetane,  
 2-(meth)acryloyloxymethyl-4-trifluoromethyl oxetane, 2-(meth)acryloyloxymethyl-  
 2-pentafluoroethyl oxetane, 2-(meth)acryloyloxymethyl-3-pentafluoroethyl oxetane,  
 2-(meth)acryloyloxymethyl-4-pentafluoroethyl oxetane, 2-(meth)acryloyloxymethyl-2-  
 15 phenyl oxetane, 2-(meth)acryloyloxymethyl-3-phenyl oxetane, 2-(meth)acryloyl-  
 oxymethyl-4-phenyl oxetane, 2,3-difluoro-2-(meth)acryloyloxymethyl oxetane,  
 2,4-difluoro-2-(meth)acryloyloxymethyl oxetane, 3,3-difluoro-2-(meth)acryloyl-  
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 2-(meth)acryloyloxymethyl oxetane, 2-(meth)acryloyloxymethyl-3,3,4-trifluoro oxetane,  
 20 2-(meth)acryloyloxymethyl-3,4,4-trifluoro oxetane, 2-(meth)acryloyloxymethyl-3,3,4,4-  
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oxetane, 2-(meth)acryloyloxyethyl-4-trifluoromethyl oxetane, 2-(meth)acryloyl-  
 oxyethyl-2-pentafluoroethyl oxetane, 2-(meth)acryloyloxyethyl-3-pentafluoroethyl  
 oxetane, 2-(meth)acryloyloxyethyl-4-pentafluoroethyl oxetane, 2-(meth)acryloyl-  
 oxyethyl-2-phenyl oxetane, 2-(meth)acryloyloxyethyl-3-phenyl oxetane, 2-(meth)  
 5 acryloyloxyethyl-4-phenyl oxetane, 2,3-difluoro-2-(meth)acryloyloxyethyl oxetane,  
 2,4-difluoro-2-(meth)acryloyloxyethyl oxetane, 3,3-difluoro-2-(meth)acryloyloxyethyl  
 oxetane, 3,4-difluoro-2-(meth)acryloyloxyethyl oxetane, 4,4-difluoro-2-(meth)acryloyl-  
 oxyethyl oxetane, 2-(meth)acryloyloxyethyl-3,3,4-trifluoro oxetane, 2-(meth)acryloyl-  
 oxyethyl-3,4,4-trifluoro oxetane, 2-(meth)acryloyloxyethyl-3,3,4,4-tetrafluoro oxetane; a  
 10 five-membered ring such as tetrahydrofurfuryl (meth)acrylate, caprolactone-modified  
 tetrahydrofurfuryl (meth)acrylate, (2-methyl-2-isobutyl-1,3-dioxolan-4-yl)methyl  
 (meth)acrylate, (2-ethyl-2-methyl-1,3-dioxolan-4-yl)methyl (meth)acrylate,  
 (1,4-dioxaspiro[4,5]dec-2-yl)methyl (meth)acrylate, (2,2-dimethyl-1,3-dioxolan-4-yl)  
 methyl (meth)acrylate; a six-membered ring compound such as 3-vinylcyclohexyl  
 15 (meth)acrylate, 3,3,5-trimethylcyclohexyl (meth)acrylate, 1-methylcyclohexyl  
 (meth)acrylate, 4-tert-butylcyclohexyl (meth)acrylate, 3-vinyl-2-butylcyclohexyl  
 (meth)acrylate, cyclohexyl (meth)acrylate, (meth)acryloyl morpholine, tetrahydropyran  
 (meth)acrylate, 2-methyltetrahydropyran (meth)acrylate. In particular, a cyclic ether  
 acrylate monomer having four rings or more is preferred, and a cyclic ether acrylate  
 20 monomer having five rings or more is more preferred.

**[0039]** The monomer (a2) containing a cyclic ether group can be used alone or in multiple combinations.

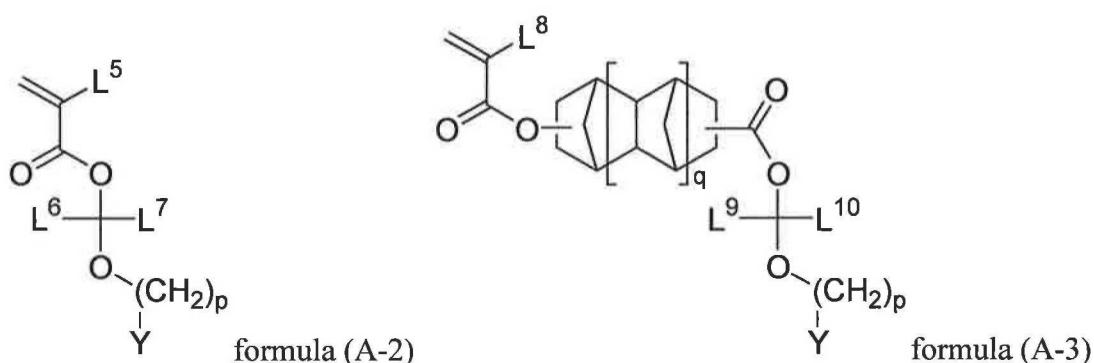
**[0040]** Based on a total amount of 100 parts by weight of the monomer mixture, the

amount of the monomer (a2) is 5 parts by weight to 30 parts by weight; preferably 8 parts by weight to 28 parts by weight; and more preferably 10 parts by weight to 25 parts by weight.

[0041] If the monomer mixture includes the monomer (a2) containing a cyclic ether group, then the sensitivity of the chemically-amplified positive photosensitive resin composition can be further improved.

**Monomer (a3) having structure represented by formula (A-2) or formula (A-3)**

[0042] The monomer (a3) having the structure represented by formula (A-2) or formula (A-3) is as shown below:



In formula (A-2) and formula (A-3),  $L^5$  to  $L^{10}$  respectively independently represent a hydrogen atom, a  $C_1$  to  $C_6$  straight or branched alkyl group, a fluorine atom, or a  $C_1$  to  $C_6$  straight or branched fluorinated alkyl group; Y represents an alicyclic group or an alkyl group that can have a substituent, p represents an integer of 0 to 4, and q represents 0 or 1.

[0043] Moreover, in formula (A-2) and formula (A-3), the  $L^5$  to  $L^{10}$  straight or branched alkyl group and straight or branched fluorinated alkyl group are defined the same as the  $L^1$  straight or branched alkyl group and straight or branched fluorinated

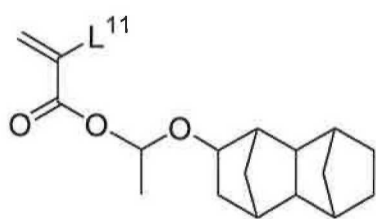
alkyl group in formula (A-1) and are not repeated herein.

[0044] When Y is an alicyclic group or alkyl group, groups for which 1 or more hydrogen atoms are removed from polycycloalkane such as monocycloalkane, bicycloalkane, tricycloalkane, or tetracycloalkane can be used. Specifically, a group  
5 for which 1 or more hydrogen atoms are removed by monocycloalkane such as cyclopentane, cyclohexane, cycloheptane, or cyclooctane or polycycloalkane such as adamantane, norbornane, isobornylene, tricyclodecane, or tetracyclododecane can be used. In particular, a group (can further have a substituent) for which 1 or more hydrogen atoms are removed by adamantane is preferred.

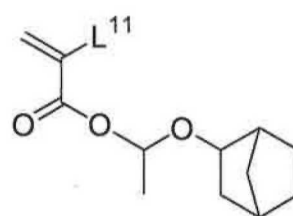
10 [0045] Moreover, when the alicyclic group represented by Y has a substituent on the ring skeleton thereof, examples of the substituent can include a polar group such as a hydroxyl group, carboxyl group, cyano group, or oxygen atom (=O), or a C<sub>1</sub> to C<sub>4</sub> straight or branched alkyl group. The polar group is preferably an oxygen atom (=O).

[0046] Moreover, when Y is an alkyl group, a C<sub>1</sub> to C<sub>20</sub>, preferably C<sub>6</sub> to C<sub>15</sub>, straight  
15 or branched alkyl group is preferred. Such an alkyl group is preferably an alkoxyalkyl group, and such an alkoxyalkyl group can include, for instance, 1-methoxyethyl, 1-ethoxyethyl, 1-n-propoxyethyl, 1-isopropoxyethyl, 1-n-butoxyethyl, 1-isobutoxyethyl, 1-tert-butoxyethyl, 1-methoxypropyl, 1-ethoxypropyl, 1-methoxy-1-methyl-ethyl, or 1-ethoxy-1-methylethyl.

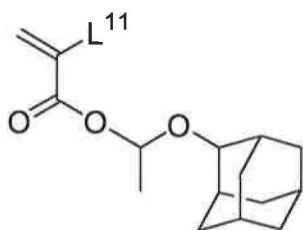
20 [0047] Specific examples of the monomer (a3) having the structure represented by formula (A-2) or formula (A-3) can include compounds represented by formula (A-2-1) to formula (A-2-24) and formula (A-3-1) to formula (A-3-15):



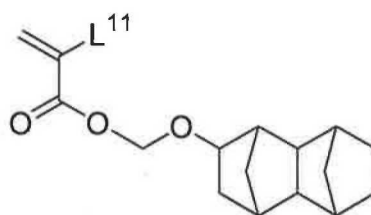
formula (A-2-1)



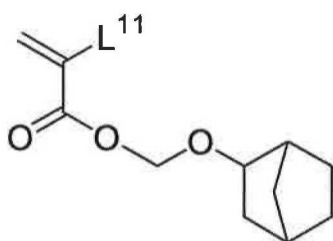
formula (A-2-2)



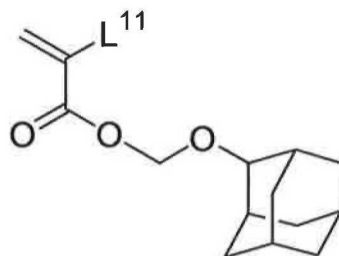
formula (A-2-3)



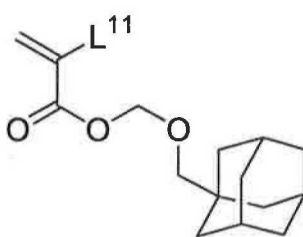
formula (A-2-4)



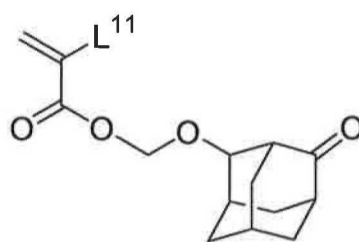
formula (A-2-5)



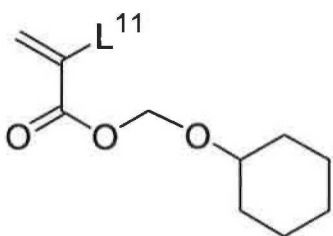
formula (A-2-6)



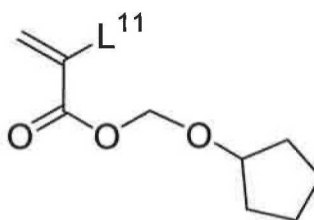
formula (A-2-7)



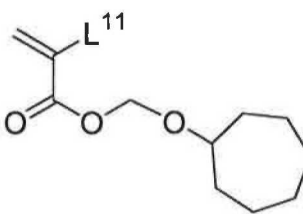
formula (A-2-8)



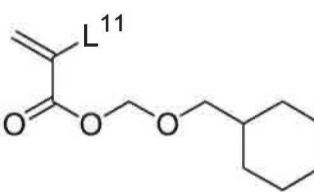
formula (A-2-9)



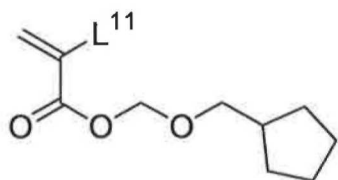
formula (A-2-10)



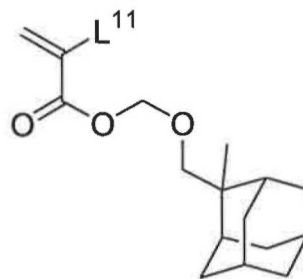
formula (A-2-11)



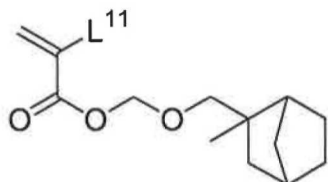
formula (A-2-12)



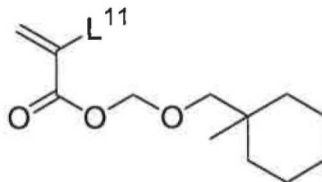
formula (A-2-13)



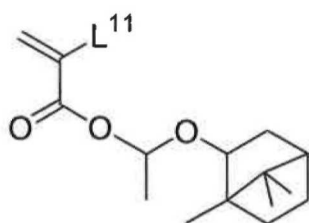
formula (A-2-14)



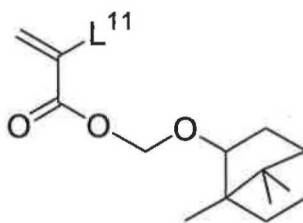
formula (A-2-15)



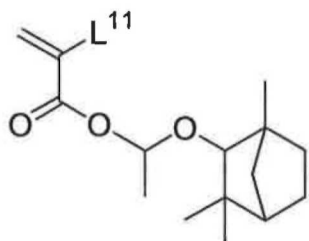
formula (A-2-16)



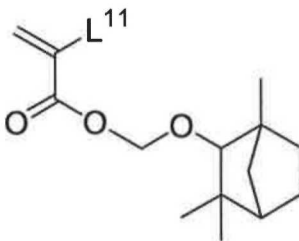
formula (A-2-17)



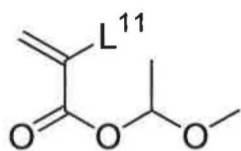
formula (A-2-18)



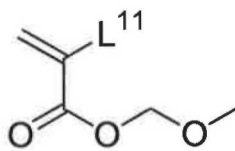
formula (A-2-19)



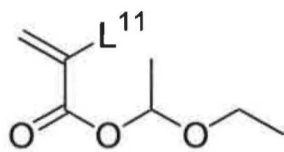
formula (A-2-20)



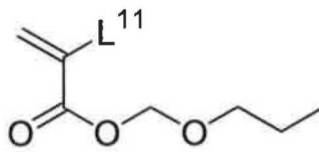
formula (A-2-21)



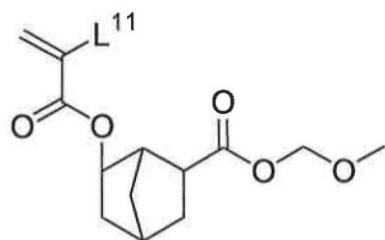
formula (A-2-22)



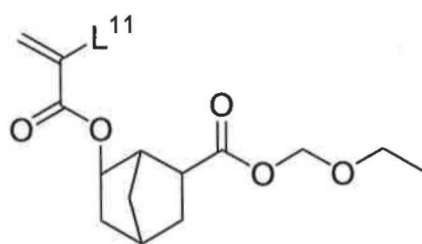
formula (A-2-23)



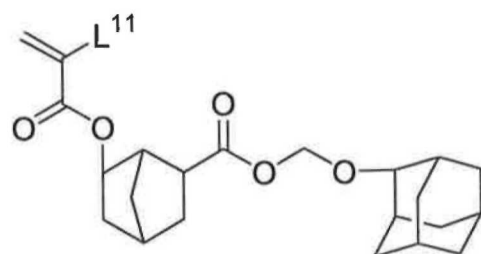
formula (A-2-24)



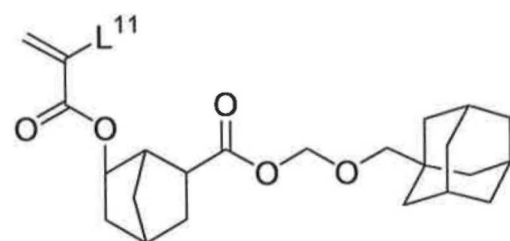
formula (A-3-1)



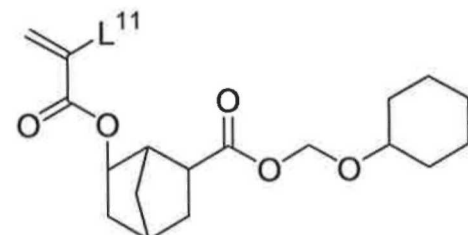
formula (A-3-2)



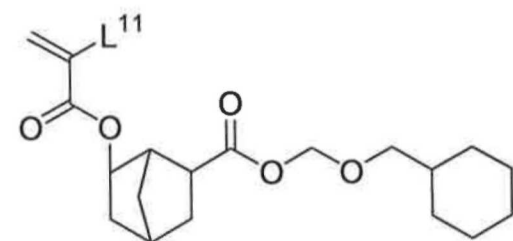
formula (A-3-3)



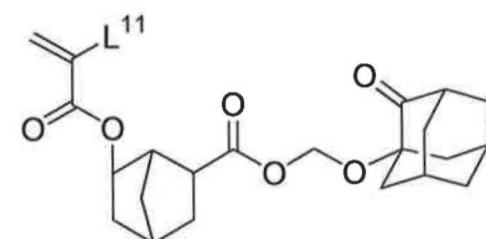
formula (A-3-4)



formula (A-3-5)

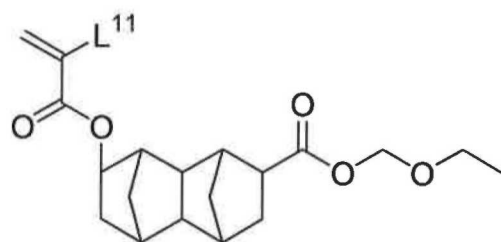


formula (A-3-6)

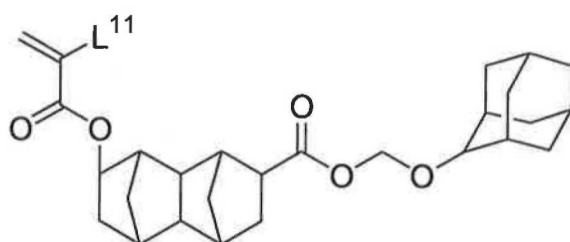


formula (A-3-7)

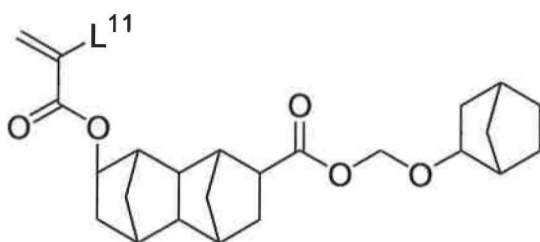




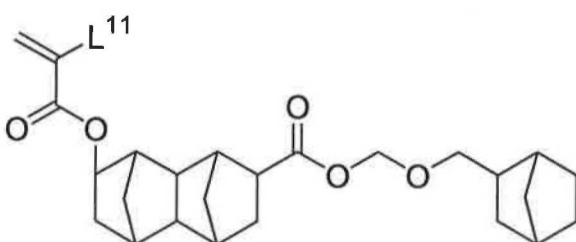
formula (A-3-8)



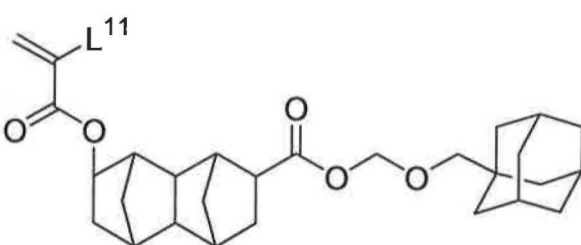
formula (A-3-9)



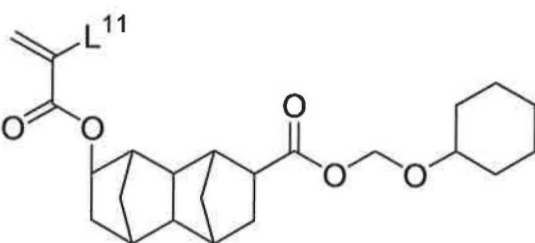
formula (A-3-10)



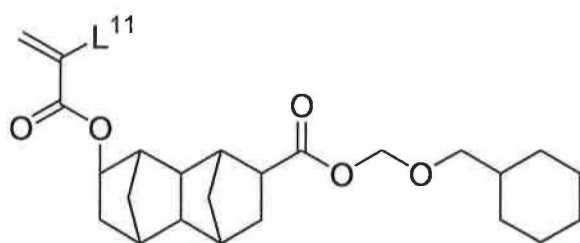
formula (A-3-11)



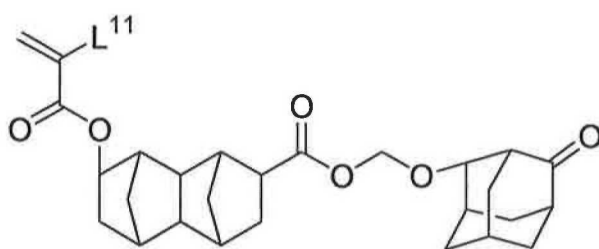
formula (A-3-12)



formula (A-3-13)



formula (A-3-14)



formula (A-3-15)

In formula (A-2-1) to formula (A-2-24) and formula (A-3-1) to formula (A-3-15),  $L^{11}$  represents a hydrogen atom or a methyl group.

5

#### Other monomers (a4)

[0048] The monomer mixture can further include other monomers (a4) other than the monomer (a1) to the monomer (a3) without affecting the efficacy of the invention.

The other monomers (a4) are, for instance, known free-radical polymerizable compounds or anionic polymerizable compounds.

10

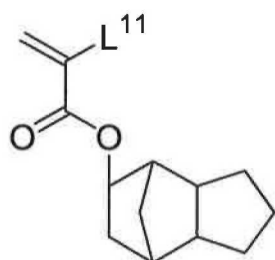
[0049] Such a polymerizable compound can include, for instance, monocarboxylic acid such as acrylic acid, methacrylic acid, or crotonic acid; dicarboxylic acid such as maleic acid, fumaric acid, or itaconic acid; methacrylic acid derivative having a carboxyl group and an ester bond such as 2-methacryloyloxyethylsuccinic acid, 2-methacryloyloxyethylmaleic acid, 2-methacryloyloxyethyl phthalic acid, or 2-methacryloyloxyethylhexahydrophthalic acid; alkyl (meth)acrylate such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, or cyclohexyl (meth)acrylate; hydroxyalkyl (meth)acrylate such as 2-hydroxyethyl (meth)acrylate or 2-hydroxypropyl

15

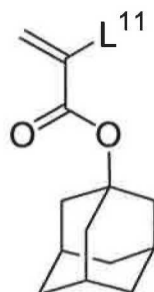
(meth)acrylate; aryl (meth)acrylate such as phenyl (meth)acrylate or benzyl (meth)acrylate; dicarboxylic acid diester such as diethyl maleate or dibutyl fumarate; an aromatic compound containing a vinyl group such as styrene,  $\alpha$ -methylstyrene, chlorostyrene, chloromethylstyrene, vinyl toluene, hydroxystyrene,  $\alpha$ -methylhydroxystyrene, or  $\alpha$ -ethylhydroxystyrene; an aliphatic compound containing a vinyl group such as vinyl acetate; conjugated diene such as butadiene or isoprene; a polymerizable compound containing a nitrile group such as acrylonitrile or methacrylonitrile; a polymerizable compound containing chlorine such as vinyl chloride or vinylidene chloride; a polymerizable compound containing an amide bond such as acrylamide or methacrylamide.

[0050] Moreover, the polymerizable compound can include, for instance, (meth)acrylate having a non-acid-dissociable aliphatic polycyclic group or an aromatic compound containing a vinyl group. The non-acid-dissociable aliphatic polycyclic group is preferably, for instance, tricyclodecanyl, adamantyl, tetracyclic dodecyl, isobornyl, or norbornyl in terms of, for instance, industrial availability. Such an aliphatic polycyclic group can also have a C<sub>1</sub> to C<sub>5</sub> straight or branched alkyl group as a substituent.

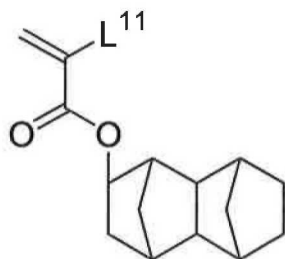
[0051] The non-acid-dissociable aliphatic polycyclic group (meth)acrylate can specifically include compounds represented by formula (A-4-1) to formula (A-4-5) below:



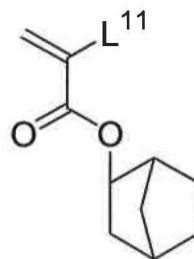
formula (A-4-1)



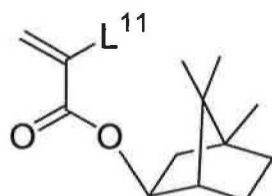
formula (A-4-2)



formula (A-4-3)



formula (A-4-4)



formula (A-4-5)

In formula (A-4-1)) to formula (A-4-5),  $L^{11}$  represents a hydrogen atom or a

5 methyl group.

[0052] Based on a total amount of 100 parts by weight of the monomer mixture, the amount of the other monomers (a4) is 20 parts by weight to 85 parts by weight; preferably 25 parts by weight to 80 parts by weight; and more preferably 30 parts by weight to 75 parts by weight.

10

### Manufacturing method of resin (A)

[0053] The solvent used to prepare the resin (A) includes, but is not limited to, (1) an alcohol compound such as methanol, ethanol, benzyl alcohol, 2-phenylethanol, or 3-phenyl-1-propanol; (2) an ether compound such as tetrahydrofuran; (3) a glycol ether

compound such as ethylene glycol monopropyl ether, ethylene glycol monomethyl ether, or ethylene glycol monoethyl ether; (4) ethylene glycol alkyl ether acetate such as ethylene glycol butyl ether acetate, ethylene glycol ether acetate, or ethylene glycol methyl ether acetate; (5) a diethylene glycol compound such as diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, or diethylene glycol methyl ethyl ether; (6) a dipropylene glycol compound such as dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol dimethyl ether, dipropylene glycol diethyl ether, or dipropylene glycol methyl ethyl ether; (7) a propylene glycol monoalkyl ether compound such as propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monopropyl ether, or propylene glycol monobutyl ether; (8) a propylene glycol alkyl ether acetate compound such as propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, or propylene glycol monobutyl ether acetate; (9) a propylene glycol alkyl ether propionate compound such as propylene glycol methyl ether propionate, propylene glycol ethyl ether propionate, propylene glycol propyl ether propionate, or propylene glycol butyl ether propionate; (10) an aromatic hydrocarbon compound such as toluene or xylene; (11) a ketone compound such as methyl ethyl ketone, cyclohexanone, or diacetone alcohol; (12) an ester compound such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate, ethyl 2-hydroxypropionate, 2-hydroxy-2-methylpropionate, 2-hydroxy-2-methylpropionate, methyl hydroxyacetate, ethyl hydroxyacetate, butyl hydroxyacetate, methyl lactate, propyl lactate, butyl lactate, methyl 3-hydroxypropionate, ethyl 3-hydroxypropionate,

propyl 3-hydroxypropionate, butyl 3-hydroxypropionate, 2-hydroxy-3-methylbutanoate, methyl methoxyacetate, ethyl methoxyacetate, butyl methoxyacetate, methyl ethoxyacetate, ethyl ethoxyacetate, propyl ethoxyacetate, butyl ethoxyacetate, methyl propoxyacetate, ethyl propoxyacetate, propyl propoxyacetate, butyl propoxyacetate, 5 methyl butoxyacetate, ethyl butoxyacetate, propyl butoxyacetate, butyl butoxyacetate, 3-methoxybutyl acetate, methyl 2-methoxypropionate, ethyl 2-methoxypropionate, propyl 2-methoxypropionate, butyl 2-methoxy propionate, methyl 2-ethoxypropionate, ethyl 2-ethoxypropionate, propyl 2-ethoxypropionate, butyl 2-ethoxypropionate, methyl 2-butoxypropionate, ethyl 2-butoxypropionate, propyl 2-butoxypropionate, butyl 10 2-butoxypropionate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, propyl 3-methoxypropionate, butyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, propyl 3-ethoxypropionate, butyl 3-ethoxypropionate, methyl 3-propoxypropionate, ethyl 3-propoxypropionate, propyl 3-propoxypropionate, butyl 3-propoxypropionate, methyl 3-butoxypropionate, ethyl 3-butoxypropionate, propyl 15 3-butoxypropionate, or butyl 3-butoxypropionate, and the solvent can be used alone or in combination.

**[0054]** The polymerization initiator used to prepare the resin (A) contains, but is not limited to, an azo compound or peroxide, and can be used alone or as a mixture.

**[0055]** The azo compound is, but not limited to, for instance, 2,2'-azobis- 20 isobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis-2-methyl butyronitrile, 4,4'-azobis(4-cyanovaleric acid), dimethyl 2,2'-azobis(2-methyl propionate), or 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile).

[0056] The peroxide is, but not limited to, for instance: dibenzoyl peroxide, lauroyl peroxide, tert-butylperoxy-tert-valerate, 1,1-bis(tert-butylperoxy)cyclohexane, or hydrogen peroxide.

[0057] The reaction temperature for preparing the resin (A) is 40 °C to 120 °C, and

5 the polymerization time is 3 hours to 12 hours.

[0058] The weight-average molecular weight of the resin (A) is 5,000 to 50,000; preferably 6,000 to 45,000; and more preferably 7,000 to 40,000.

### **Novolac resin (B)**

10 [0059] The novolac resin (B) contains a high-ortho novolac resin (B-1) and the high-ortho novolac resin (B-1) has 18% to 25% of a methylene group bonded in an ortho-ortho arrangement. The novolac resin (B) can also optionally contain other novolac resins (B-2).

### **15 High-ortho novolac resin (B-1)**

[0060] The high-ortho novolac resin (B-1) is generally obtained by dehydrating an aromatic hydroxyl compound and aldehyde under reduced pressure in the presence of a divalent metal salt catalyst in an acidic environment (pH of 1 to 5), and then performing condensation. Next, an acid catalyst can be optionally added to perform a dehydration  
20 condensation reaction and remove unreacted monomers, wherein the dehydration condensation reaction is as provided in JP S55-090523, JP S59-080418, and JP S62-230815 and is not repeated herein.

[0061] Specific examples of the aromatic hydroxyl compound are, for instance:

phenol; cresol such as m-cresol, p-cresol, or o-cresol; xlenol such as 2,3-xlenol, 2,5-xlenol, 3,5-xlenol, or 3,4-xlenol; alkyl phenol such as m-ethylphenol, p-ethylphenol, o-ethylphenol, 2,3,5-trimethylphenol, 2,3,5-triethylphenol, 4-tert-butylphenol, 3-tert-butylphenol, 2-tert-butylphenol, 2-tert-butyl-4-methylphenol, 2-tert-butyl-5-methylphenol, or 6-tert-butyl-3-methylphenol; alkoxy phenol such as p-methoxyphenol, m-methoxyphenol, p-ethoxyphenol, m-ethoxyphenol, p-propoxyphenol, or m-propoxyphenol; isopropenyl phenol such as o-isopropenylphenol, p-isopropenylphenol, 2-methyl-4-isopropenylphenol, or 2-ethyl-4-isopropenylphenol; aryl phenol such as phenyl phenol; polyhydroxyphenol such as 4,4'-dihydroxybiphenyl, bisphenol A, resorcinol, hydroquinone, or pyrogallol. The aromatic hydroxyl compound can be used alone or in multiple combinations. In particular, the aromatic hydroxyl compound is preferably, for instance, o-cresol, m-cresol, p-cresol, 2,5-xlenol, 3,5-xlenol, or 2,3,5-trimethylphenol.

[0062] Specific examples of the aldehyde condensed with the aromatic hydroxyl compound include, for instance: formaldehyde, paraformaldehyde, trioxane, acetaldehyde, propionaldehyde, butyraldehyde, trimethylacetaldehyde, acrolein, crotonaldehyde, cyclo hexanealdehyde, furfural, furylacrolein, benzaldehyde, terephthalaldehyde, phenylacetaldehyde,  $\alpha$ -phenylpropanal,  $\beta$ -phenylpropanal, o-hydroxybenzaldehyde, m-hydroxybenzaldehyde, p-hydroxybenzaldehyde, o-methylbenzaldehyde, m-methylbenzaldehyde, p-methylbenzaldehyde, o-chlorobenzaldehyde, m-chloro- benzaldehyde, p-chlorobenzaldehyde, or cinnamaldehyde. The aldehyde can be used alone or in multiple combinations. The aldehyde is preferably formaldehyde.



[0063] When preparing the high-ortho novolac resin (B-1) of the invention, the molar ratio of the aromatic hydroxyl compound and the aldehyde is generally 1:0.5 to 0.85, preferably 1:0.55 to 0.82, and more preferably 1:0.6 to 0.8.

[0064] Specific examples of the divalent metal salt catalyst include, for instance: zinc acetate, manganese acetate, barium acetate, manganese nitrate, zinc borate, zinc chloride, or zinc oxide. The divalent metal catalyst can be used alone or in multiple combinations. Based on 100 parts by weight of the aromatic hydroxyl compound, the amount of the divalent metal catalyst is generally 0.01 parts by weight to 1.0 part by weight, preferably 0.03 parts by weight to 0.8 parts by weight, and more preferably 0.05 parts by weight to 0.5 parts by weight.

[0065] Specific examples of the acid catalyst include, for instance: dimethyl sulfate, diethyl sulfate, or dipropyl sulfate. The acid catalyst can be used alone or in multiple combinations. Based on 100 parts by weight of the aromatic hydroxyl compound, the amount of the acid catalyst is generally 0.005 parts by weight to 1.0 part by weight, preferably 0.008 parts by weight to 0.8 parts by weight, and more preferably 0.01 parts by weight to 0.5 parts by weight.

[0066] The high-ortho novolac resin (B-1) of the invention generally has 18% to 25% of a methylene group bonded in an ortho-ortho arrangement, preferably has 19% to 25% of a methylene group bonded in an ortho-ortho arrangement, and more preferably has 20% to 25% of a methylene group bonded in an ortho-ortho arrangement.

[0067] The weight-average molecular weight of the high-ortho novolac resin (B-1) is 4,000 to 36,000; preferably 5,000 to 30,000; and more preferably 6,000 to 24,000.

[0068] Based on a total amount of 100 parts by weight of the resin (A), the amount of

the high-ortho novolac resin (B-1) is 20 parts by weight to 120 parts by weight, preferably 25 parts by weight to 110 parts by weight, and more preferably 30 parts by weight to 100 parts by weight.

[0069] When the chemically-amplified positive photosensitive resin composition does  
5 not contain the high-ortho novolac resin (B-1), the rectangularity of the chemically-amplified positive photosensitive resin composition is poor.

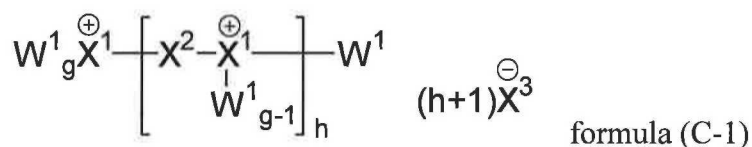
### **Other novolac resins (B-2)**

[0070] The other novolac resins (B-2) are generally obtained by a condensation  
10 reaction of the aromatic hydroxyl compound and aldehyde under normal pressure in the presence of a known organic acid and/or inorganic acid catalyst such as hydrochloric acid, sulfuric acid, formic acid, acetic acid, oxalic acid, or p-toluenesulfonic acid, and then performing dehydration and removing unreacted monomers. For the other novolac resins (B-2), a methylene group is randomly bonded in an ortho-para, para-para,  
15 or ortho-ortho arrangement.

### **Photoacid generator (C)**

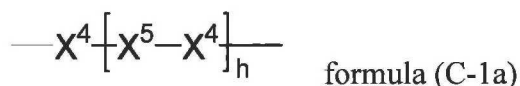
[0071] The photoacid generator (C) is a compound generating acid via actinic ray or radiation and is not particularly limited as long as it is a compound that can directly or  
20 indirectly generate acid via light. The photoacid generator (C) is preferably an acid generator of the first to fifth forms described below. In the following, the first to fifth forms of the photoacid generator (C) suitable for the photosensitive resin composition are described.

[0072] The first form of the photoacid generator (C) can include a compound represented by formula (C-1) below:



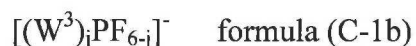
In formula (C-1),  $X^1$  represents a g-valence sulfur atom or iodine atom, and g is 1 or 2. h represents the number of repeating units of the structure in the parenthesis.  $W^1$  is an organic group bonded to  $X^1$ , and represents a  $C_6$  to  $C_{30}$  aryl group, a  $C_4$  to  $C_{30}$  heterocyclic group, a  $C_1$  to  $C_{30}$  alkyl group, a  $C_2$  to  $C_{30}$  alkenyl group, or a  $C_2$  to  $C_{30}$  alkynyl group, and  $W^1$  can be substituted by at least 1 selected from the group consisting of an alkyl group, a hydroxyl group, an alkoxy group, an alkylcarbonyl group, an arylcarbonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an aryl thiocarbonyl group, an acyloxy group, an arylthio group, an alkylthio group, an aryl group, a hetero ring group, an aryloxy group, an alkanesulfinyl group, an aryl sulfonamide group, an alkyl sulfonyl group, an aryl sulfonyl group, an alkoxy group, an amine group, a cyano group, a nitro group, and a halogen. The number of  $W^1$  is  $g+h(g-1)+1$ , and  $W^1$  can respectively be the same or different. Moreover, 2 or more  $W^1$  can be directly bonded to one another or form a ring structure containing  $X^1$  by bonding with -O-, -S-, -SO-, -SO<sub>2</sub>-, -NH-, -NW<sup>2</sup>-, -CO-, -COO-, -CONH-,  $C_1$  to  $C_3$  an alkylene group, or a phenylene group.  $W^2$  is a  $C_1$  to  $C_5$  alkyl group or a  $C_6$  to  $C_{10}$  aryl group.

[0073]  $X^2$  is a structure represented by formula (C-1a) below:

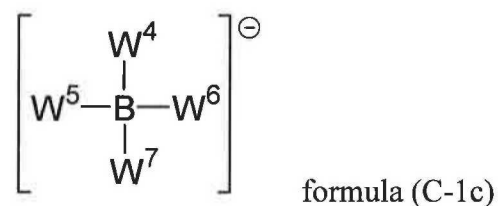


In formula (C-1a),  $X^4$  represents a  $C_1$  to  $C_8$  alkylene group, a  $C_6$  to  $C_{20}$  arylene group, or a  $C_8$  to  $C_{20}$  divalent hybrid, and  $X^4$  can be substituted by at least 1 selected from the group consisting of a  $C_1$  to  $C_8$  alkyl group, a  $C_1$  to  $C_8$  alkoxy group, a  $C_6$  to  $C_{10}$  aryl group, a hydroxyl group, a cyano group, a nitro group, and a halogen.  $X^5$  represents -O-, -S-, -SO-, -SO<sub>2</sub>-, -NH-, -NW<sup>2</sup>-, -CO-, -COO-, -CONH-, a  $C_1$  to  $C_3$  alkylene group, or a phenylene group.  $h$  represents the number of repeating units of the structure in the parenthesis. An  $h+1$  number of  $X^4$  and an  $h$  number of  $X^5$  can respectively be the same or different.  $W^2$  is as defined above.

[0074]  $(X^3)^-$  is the counter ion of onium, and the fluoroalkyl fluorophosphate anion represented by formula (C-1b) or the borate anion represented by formula (C-1c) below can be included:



In formula (C-1b),  $W^3$  represents an alkyl group for which 80% or more of hydrogen atoms are substituted by fluorine atoms.  $j$  represents the number thereof, and is an integer of 1 to 5. A  $j$  number of  $W^3$  can respectively be the same or different.

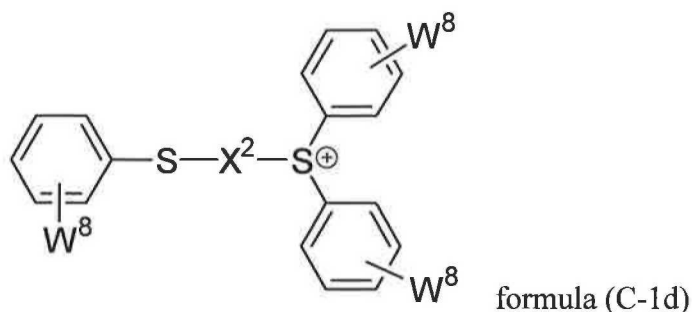


In formula (C-1c),  $W^4$  to  $W^7$  respectively independently represent a fluorine atom or a phenyl group, and some or all of the hydrogen atoms in the phenyl group can be substituted by at least 1 selected from the group consisting of a fluorine atom and a

trifluoromethyl group.

[0075] The onium ion in the compound represented by formula (C-1) can include, for instance, triphenyl sulfonium, tri-p-tolyl sulfonium, 4-(phenylthio)phenyl diphenyl, bis[4-(diphenylchyl)phenyl]sulfide, bis[4-{bis[4-(2-hydroxyethoxy)phenyl]sulfonium} phenyl]sulfide, bis{4-[bis(4-fluorophenyl)sulfonium]phenyl}sulfide, 4-(4-benzyl-2-chlorophenylthio)phenylbis(4-fluorophenyl)sulfonium, 7-isopropyl-9-oxo-10-thia-9,10-dihydroanthracen-2-yl di-p-tolyl sulfonium, 7-isopropyl-9-oxo-10-thia-9,10-dihydroanthracen-2-yl diphenyl sulfonium, 2-[(diphenyl)sulfonium]thioxanthone, 4-[4-(4-tert-butylbenzyl)phenylthio]phenyl di-p-tolylene sulfonium, 4-(4-benzyl-phenylphenylthio)phenyl diphenyl, diphenyl phenylacetyl sulfonium, 4-hydroxy-phenylmethylbenzylidene sulfonium, 2-naphthylmethyl(1-ethoxycarbonyl)ethyl sulfonium, 4-hydroxyphenylmethylphenylethylidene sulfonium, phenyl[4-(4-biphenylthio)phenyl]4-biphenyl sulfonium, phenyl[4-(4-biphenylthio)phenyl]3-biphenyl sulfonium, [4-(4-ethylphenylthio)phenyl]diphenylphosphine sulfonium, octadecyl methyl phenylacetyl sulfonium, diphenyliodonium, di-p-tolyl iodide, bis(4-dodecylphenyl)iodonium, bis(4-methoxyphenyl)iodonium, (4-octyloxyphenyl)phenyl iodonium, bis(4-dodecyloxy)phenyl iodonium, 4-(2-hydroxytetradecanoxy)phenylphenyl, 4-isopropylphenyl (p-tolyl)iodonium, or 4-isobutylphenyl (p-tolyl)iodonium.

[0076] Among the onium ions in the compound represented by formula (C-1), preferred onium ions can include sulfonium ions represented by formula (C-1d) below:



In formula (C-1d),  $W^8$  respectively independently represent a group selected from the group consisting of a hydrogen atom, an alkyl group, a hydroxyl group, an alkoxy group, an alkylcarbonyl group, an alkylcarbonyloxy group, an alkoxy carbonyl group, a halogen atom, an aryl group that can have a substituent, and an arylcarbonyl group.  $X^2$  is defined the same as the  $X^2$  in formula (C-1).

[0077] Specific examples of the sulfonium ion represented by formula (C-1d) can include 4-(phenylthio)phenyl diphenyl sulfonium, 4-(4-benzyl-2-chlorophenylthio)phenylbis(4-fluorophenyl)sulfonium, 4-(4-benzylphenylphenylthio)phenyl diphenyl sulfonium, phenyl[4-(4-biphenylthio)phenyl]4-biphenyl sulfonium, phenyl[4-(4-biphenylthio)phenyl]3-biphenyl sulfonium, [4-(4-ethylphenylthio)phenyl]diphenylphosphine sulfonium, or diphenyl[4-(p-triphenylthio)phenyl]diphenylphosphine sulfonium.

[0078] In the fluoroalkyl fluorophosphate anion represented by formula (C-1b),  $W^3$  represents an alkyl group substituted by a fluorine atom, and is preferably  $C_1$  to  $C_8$ , more preferably  $C_1$  to  $C_4$ . Specific examples of the alkyl group can include, for instance, a straight alkyl group such as methyl group, ethyl group, propyl group, butyl group, pentyl group, or octyl group; a branched alkyl group such as isopropyl group, isobutyl group, sec-butyl group, or tert-butyl group; a cycloalkyl group such as cyclopropyl group, cyclobutyl group, cyclopentyl group, or cyclohexyl group. The

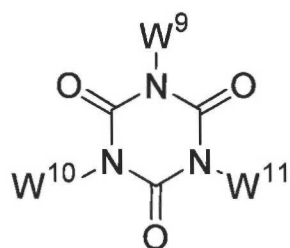
ratio of hydrogen atoms of the alkyl group substituted by fluorine atoms is generally 80% or more, preferably 90% or more, and more preferably 100%. If the substitution rate of the fluorine atom does not reach 80%, then the acid strength of the onium fluoroalkyl fluorophosphate represented by formula (C-1) is reduced.

- 5    **[0079]** More preferably,  $W^3$  is  $C_1$  to  $C_4$ , and the substitution rate of the fluorine atom is 100% of a straight or branched perfluoroalkyl group. Specific examples can include  $CF_3$ ,  $CF_3CF_2$ ,  $(CF_3)_2CF$ ,  $CF_3CF_2CF_2$ ,  $CF_3CF_2CF_2CF_2$ ,  $(CF_3)_2CFCF_2$ ,  $CF_3CF_2(CF_3)CF$ ,  $(CF_3)_3C$ . The number  $j$  of  $W^3$  is an integer of 1 to 5, preferably 2 to 4, and more preferably 2 or 3.
- 10   **[0080]** Preferred specific examples of the fluoroalkyl fluorophosphate anion can include  $[(CF_3CF_2)_2PF_4]^-$ ,  $[(CF_3CF_2)_3PF_3]^-$ ,  $[((CF_3)_2CF)_2PF_4]^-$ ,  $[((CF_3)_2CF)_3PF_3]^-$ ,  $[(CF_3CF_2CF_2)_2PF_4]^-$ ,  $[(CF_3CF_2CF_2)_3PF_3]^-$ ,  $[((CF_3)_2CFCF_2)_2PF_4]^-$ ,  $[((CF_3)_2CFCF_2)_3PF_3]^-$ ,  $[(CF_3CF_2CF_2CF_2)_2PF_4]^-$ , or  $[(CF_3CF_2CF_2)_3PF_3]^-$ . Among these, the following are preferred:  $[(CF_3CF_2)_3PF_3]^-$ ,  $[(CF_3CF_2CF_2)_3PF_3]^-$ ,  $[((CF_3)_2CF)_3PF_3]^-$ ,  $[((CF_3)_2CF)_2PF_4]^-$ ,  
 15    $[((CF_3)_2CFCF_2)_3PF_3]^-$ , or  $[((CF_3)_2CFCF_2)_2PF_4]^-$ .

**[0081]** Preferred specific examples of the borate anion represented by formula (C-1c) can include, for instance,  $[B(C_6F_5)_4]^-$ ,  $[B(C_6H_4CF_3)_4]^-$ ,  $[(C_6F_5)_2BF_2]^-$ ,  $[(C_6F_5)BF_3]^-$ , or  $[B(C_6H_3F_2)_4]^-$ . Among these,  $[B(C_6F_5)_4]^-$  is more preferred.

- [0082]** The second form of the acid generator (A) can include a triazine compound  
 20   containing halogen such as 2,4-bis(trichloromethyl)-6-piperonyl-1,3,5-triazine, 2,4-bis(trichloromethyl)-6-[2-(2-furyl)ethenyl]symmetric triazine, 2,4-bis(trichloromethyl)-6-[2-(5-methyl-2-furyl)ethenyl]symmetric triazine, 2,4-bis(trichloromethyl)-6-[2-(5-ethyl-2-furyl)ethenyl]symmetric triazine, 2,4-bis(trichloromethyl)-6-[2-(5-propyl-

2-furyl)ethenyl]symmetrical triazine, 2,4-bis(trichloromethyl)-6-[2-(3,5-dimethoxyphenyl)ethenyl]symmetric triazine, 2,4-bis(trichloromethyl)-6-[2-(3,5-diethoxyphenyl)ethenyl]symmetric triazine, 2,4-bis(trichloromethyl)-6-[2-(3,5-dipropoxyphenyl)ethenyl]symmetric triazine, 2,4-bis(trichloromethyl)-6-[2-(3-methoxy-5-ethoxyphenyl)ethenyl],  
 5 2,4-bis(trichloromethyl)-6-[2-(3-methoxy-5-propoxyphenyl)ethenyl]symmetric triazine, 2,4-bis(trichloromethyl)-6-[2-(3,4-methylenedioxyphenyl)ethenyl]symmetric triazine, 2,4-bis(trichloromethyl)-6-(3,4-methylenedioxyphenyl)symmetric triazine, 2,4-bis-trichloromethyl-6-(3-bromo-4-methoxy)phenyl symmetric triazine, 2,4-bis-trichloromethyl-6-(2-bromo-4-methoxy)phenyl symmetric triazine, 2,4-bis-trichloromethyl-6-  
 10 (2-bromo-4-methoxy)styrylphenyl symmetric triazine, 2,4-bis-trichloromethyl-6-(3-bromo-4-methoxy)styrylphenyl symmetric triazine, 2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxynaphthyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2-(2-furyl)ethenyl]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2-(5-methyl-2-furyl)ethenyl]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2-(3,5-dimethoxyphenyl)vinyl]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2-(3,4-dimethoxyphenyl)vinyl]-  
 15 4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(3,4-methylenedioxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, tris(1,3-dibromopropyl)-1,3,5-triazine, or tris(2,3-dibromopropyl)-1,3,5-triazine, and a triazine compound containing halogen represented by formula (C-2) below such as tris(2,3-dibromopropyl)triisocyanate.



formula (C-2)

In formula (C-2), W<sup>9</sup> to W<sup>11</sup> respectively independently represent a haloalkyl

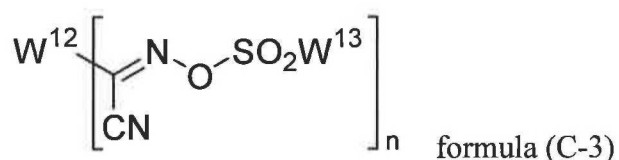


group.

[0083] Moreover, the third form of the photoacid generator (C) can include  $\alpha$ -(p-toluenesulfonyloxyimino)-phenylacetonitrile,  $\alpha$ -(benzenesulfonyloxyimino)-2,4-dichlorophenylacetonitrile,

5  $\alpha$ -(benzenesulfonyloxyimino)-2,6-dichlorophenylacetonitrile,

$\alpha$ -(2-chlorobenzenesulfonyloxyimino)-4-methoxyphenylacetonitrile,  $\alpha$ -(ethylsulfonyloxyimino)-1-chloropentenylacetonitrile, and a compound containing an oxime sulfonate group represented by formula (C-3) below.

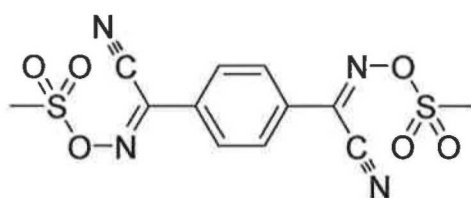


10 In formula (C-3),  $\text{W}^{12}$  represents a monovalent, a divalent, or a trivalent organic group,  $\text{W}^{13}$  represents a substituted or unsubstituted saturated hydrocarbon group, an unsaturated hydrocarbon group, or an aromatic compound group, and  $n$  represents the number of repeating units of the structure in the parenthesis.

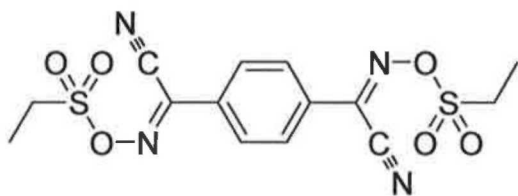
[0084] In formula (C-3), the aromatic compound group represents a group of a  
15 compound that allows an aromatic compound to display special physical properties and chemical properties, and can include, for instance, an aryl group such as phenyl group or naphthyl group or a heteroaryl group such as furanyl group or thienyl group. These can also have 1 or more of a suitable substituent on a ring, such as halogen atom, alkyl group, alkoxy group, or nitro group. Moreover,  $\text{W}^{13}$  is more preferably a  $\text{C}_1$  to  $\text{C}_6$  alkyl  
20 group, and can include a methyl group, an ethyl group, a propyl group, or a butyl group. More preferably,  $\text{W}^{12}$  is an aromatic compound group, and  $\text{W}^{13}$  is a compound of a  $\text{C}_1$  to  $\text{C}_4$  alkyl group.

[0085] For the photoacid generator represented by formula (C-3), when  $n=1$ ,  $W^{12}$  can be any of a phenyl group, methylphenyl group, or methoxyphenyl group,  $W^{13}$  is a compound of a methyl group, and can specifically include, for instance,  $\alpha$ -(methanesulfonyloxyimino)-1-phenylacetonitrile,  $\alpha$ -(methanesulfonyloxyimino)-1-(p-

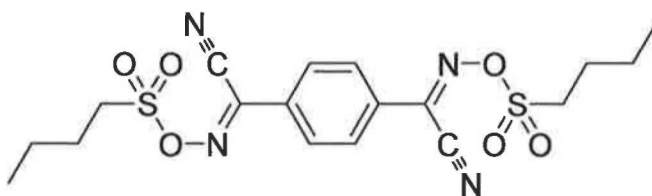
5 methylphenyl)acetonitrile,  $\alpha$ -(methanesulfonyloxyimino)-1-(p-methoxyphenyl)acetonitrile, or [2-(propanesulfoxyimino)-2,3-dihydroxythiophene-3-ylidene](o-tolyl)acetonitrile. When  $n=2$ , the acid generator represented by formula (C-3) specifically can include the acid generators represented by formula (C-3-1) to formula (C-3-8) shown below:



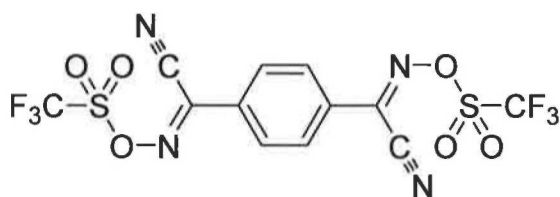
formula (C-3-1)



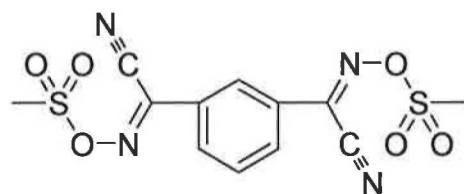
formula (C-3-2)



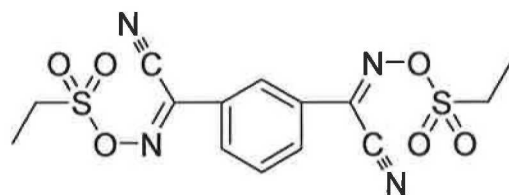
formula (C-3-3)



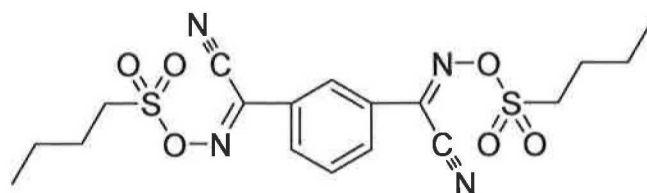
formula (C-3-4)



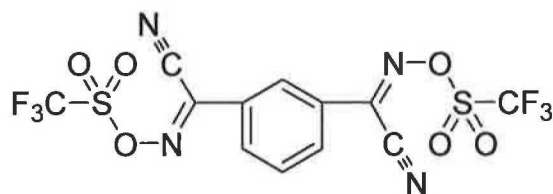
formula (C-3-5)



formula (C-3-6)



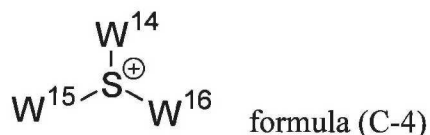
formula (C-3-7)



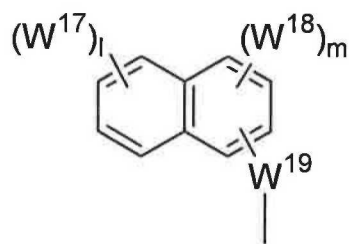
formula (C-3-8)

- 5    **[0086]** Moreover, the fourth form of the photoacid generator (C) can include onium salt for which the cation portion has a naphthalene ring. “Having a naphthalene ring” refers to a structure derived from naphthalene, i.e., a structure of at least 2 rings, and the aromatic properties between the rings can be maintained. The naphthalene ring can also have a substituent such as a C<sub>1</sub> to C<sub>6</sub> straight or branched alkyl group, a hydroxyl
- 10   group, or a C<sub>1</sub> to C<sub>6</sub> straight or branched alkoxy group. The structure derived from the naphthalene ring can be monovalent (free valency of 1), and can also be divalent (free valency of 2) or more, and monovalent is more preferred (however, at this point, the portion bonded to the substituent is removed to calculate the free valency). The number of the naphthalene ring is preferably 1 to 3.
- 15   **[0087]** The cation portion of onium salt having a naphthalene ring is preferably a

structure represented by formula (C-4) below:



In formula (C-4), at least one of  $\text{W}^{14}$  to  $\text{W}^{16}$  represents a group represented by formula (C-4a) below, and the rest represent a  $\text{C}_1$  to  $\text{C}_6$  straight or branched alkyl group, a phenyl group that can have a substituent, a hydroxyl group, or a  $\text{C}_1$  to  $\text{C}_6$  straight or branched alkoxy group. Or, one of  $\text{W}^{14}$  to  $\text{W}^{16}$  is a group represented by formula (C-4a) below, and the other two are respectively independently a  $\text{C}_1$  to  $\text{C}_6$  straight or branched alkylene group, and the ends of the alkylene group can be bonded to form a ring.



formula (C-4a)

In formula (C-4a),  $\text{W}^{17}$  and  $\text{W}^{18}$  respectively independently represent a hydroxyl group, a  $\text{C}_1$  to  $\text{C}_6$  straight or branched alkoxy group, or a  $\text{C}_1$  to  $\text{C}_6$  straight or branched alkyl group, and  $\text{W}^{19}$  represents a single bond or a  $\text{C}_1$  to  $\text{C}_6$  straight or branched alkylene group that can have a substituent.  $l$  and  $m$  respectively independently represent an integer of 0 to 2, and  $l+m$  is 3 or less. When a plurality of  $\text{W}^{17}$  exists, the  $\text{W}^{17}$ 's can be the same or different. When a plurality of  $\text{W}^{18}$  exists, the  $\text{W}^{18}$ 's can be the same or different.

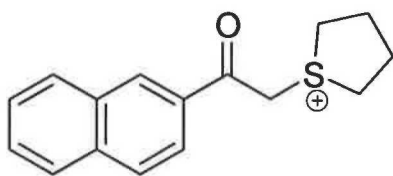
**[0088]** The number of the group represented by formula (C-4a) in  $\text{W}^{14}$  to  $\text{W}^{16}$  is preferably 1 from the stability viewpoint of the compound, the rest are  $\text{C}_1$  to  $\text{C}_6$  straight

or branched alkylene groups, and the ends of the alkylene groups can be bonded to form a ring. At this point, the 2 alkylene groups can contain a sulfur atom to form a 3- to 9-membered ring. The number of the atoms (containing sulfur atoms) forming the ring is preferably 5 to 6.

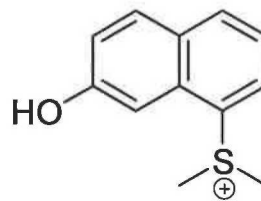
5 [0089] Moreover, the substituent that may be included in the alkylene group can be, for instance, an oxygen atom (here, a carbonyl group is formed by the oxygen atom with a carbon atom forming the alkylene group) or a hydroxyl group.

[0090] Moreover, the substituent for the phenyl group can include, for instance, a hydroxyl group, a C<sub>1</sub> to C<sub>6</sub> straight or branched alkoxy group, or a C<sub>1</sub> to C<sub>6</sub> straight or  
10 branched alkyl group.

[0091] Suitable cation portions can include formulas (C-4b) and (C-4c) below, in particular the structure represented by formula (C-4c) below.



formula (C-4b)



formula (C-4c)

15 [0092] The cation portion can be iodised salt or sulfonium salt; and sulfonium salt is preferred from the perspective of, for instance, acid generation efficiency.

[0093] Therefore, the anion portion having onium salt of a naphthalene ring is preferably an anion that can form sulfonium salt.

[0094] The anion portion used as such an acid generator is a fluoroalkylsulfonic acid  
20 ion or aryl sulfonic acid ion for which some or all of the hydrogen atoms are fluorinated.

[0095] The alkyl group in the fluoroalkylsulfonic acid ion can be C<sub>1</sub> to C<sub>20</sub> and

straight, branched, or cyclic, and based on the volume of the resulting acid and the diffusion distance thereof, C<sub>1</sub> to C<sub>10</sub> is preferred. In particular, branches or rings are preferred due to short diffusion distance. Moreover, in terms of affordable synthesis, a methyl group, an ethyl group, a propyl group, a butyl group, or an octyl group...etc. is preferred.

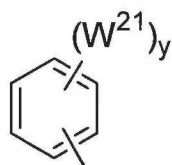
[0096] The aryl group in the aryl sulfonic acid ion is a C<sub>6</sub> to C<sub>20</sub> aryl group, and can include a phenyl group or a naphthyl group that can be substituted by an alkyl group or a halogen atom. In particular, in terms of affordable synthesis, a C<sub>6</sub> to C<sub>10</sub> aryl group is preferred. Preferred specific examples can include, for instance, a phenyl group, a toluenesulfonyl group, an ethylphenyl group, a naphthyl group, or a methyl naphthyl group.

[0097] In the fluoroalkylsulfonic acid ion or aryl sulfonic acid ion, the fluorination rate when some or all of the hydrogen atoms are fluorinated is preferably 10% to 100%, more preferably 50% to 100%, and preferably, all of the hydrogen atoms are substituted by fluorine atoms from increased acid strength. Among these, trifluoromethanesulfonate, perfluorobutanesulfonate, perfluorooctanesulfonate, or perfluorobenzenesulfonate...etc. can specifically be used.

[0098] Among these, a preferred anion portion can include formula (C-4d) below:



In formula (C-4d), W<sup>20</sup> is a group represented by formulas (C-4e), (C-4f), and (C-4g) below.



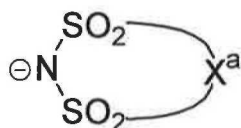
formula (C-4f)



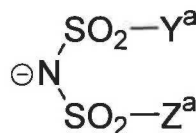
formula (C-4g)

5 In formula (C-4e),  $x$  represents an integer of 1 to 4. In formula (C-4f),  $\text{W}^{21}$  represents a hydrogen atom, a hydroxyl group, a  $\text{C}_1$  to  $\text{C}_6$  straight or branched alkyl group, or a  $\text{C}_1$  to  $\text{C}_6$  straight or branched alkoxy group, and  $y$  represents an integer of 1 to 3. Among these, from the safety perspective, trifluoromethanesulfonate or perfluorobutanesulfonate is preferred.

10 **[0099]** Moreover, the anion portion can also include formula (C-4h) or formula (C-4i) containing nitrogen below.



formula (C-4h)



formula (C-4i)

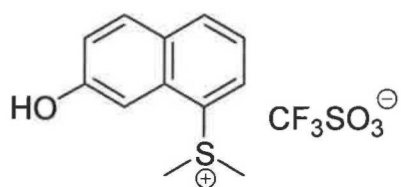
In formula (C-4h) and formula (C-4i),  $\text{X}^a$  represents a straight or branched alkylene group for which at least 1 hydrogen atom is substituted by a fluorine atom, and the alkylene group is  $\text{C}_2$  to  $\text{C}_6$ , preferably  $\text{C}_3$  to  $\text{C}_5$ , and most preferably  $\text{C}_3$ . Moreover,  $\text{Y}^a$  and  $\text{Z}^a$  respectively independently represent a straight or branched alkyl group for which at least 1 hydrogen atom is substituted by a fluorine atom, and the alkyl group is  $\text{C}_1$  to  $\text{C}_{10}$ , preferably  $\text{C}_1$  to  $\text{C}_7$ , and more preferably  $\text{C}_1$  to  $\text{C}_3$ .

**[0100]** The less carbon atoms the alkylene group of  $\text{X}^a$  has or the less carbon atoms the alkyl group of  $\text{Y}^a$  and  $\text{Z}^a$  has, the better the solubility of the organic solvent, which is

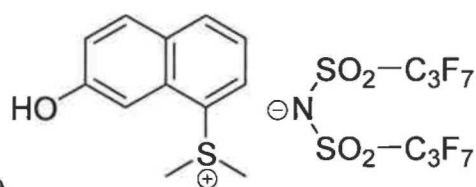
preferred.

[0101] Moreover, in the alkylene group of  $X^a$  or the alkyl group of  $Y^a$  and  $Z^a$ , a greater number of hydrogen atoms substituted by fluorine atoms results in greater acid strength, which is preferred. The ratio of fluorine atoms in the alkylene group or alkyl group, i.e., the fluorination rate, is preferably 70% to 100%, more preferably 90% to 100%, and a perfluoroalkyl group or a perfluoroalkyl group for which all of the hydrogen atoms are substituted by fluorine atoms is most preferred.

[0102] The onium salt having a naphthalene ring suitable for the cation portion can include compounds represented by formula (C-4j) and formula (C-4k) below:



formula (C-4j)



formula (C-4k)

[0103] Moreover, the fifth form of the photoacid generator (C) can include, for instance, dicarboxyl diazomethane such as bis(p-toluenesulfonyl)diazomethane, bis(1,1-dimethylethylsulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane, or bis(2,4-dimethylphenylsulfonyl)diazomethane; a methyl nitrobenzyl derivative such as methyl 2-nitrobenzyl p-toluenesulfonate, methyl 2,6-dinitrobenzyl p-toluenesulfonate, methyl nitrobenzene tosylate, methyl dinitrobenzene tosylate, methyl nitrobenzene sulfonate, methyl nitrobenzyl carbonate, or methyl dinitrobenzyl carbonate; sulfonate such as pyrogallol trifluoromethanesulfonate, pyrogallol trimethyl tosylate, phenylmethyl toluenesulfonate, benzyl sulfonate, N-methanesulfonyl oxysuccinimide, N-trichloromethylsulfoxysuccinimide, N-phenylsulfonyloxy maleimide, or N-methane-



sulfonyloxypthalimide; trifluoromethanesulfonate such as N-hydroxylphthalimide or N-hydroxynaphthyl imide; onium salt such as diphenylphosphonium hexafluorophosphate, (4-methoxyphenyl)phenyl trifluoromethanesulfonate, bis(p-tert-butylphenyl)iodonium triflate, triphenylphosphonium hexafluorophosphate, (4-methoxy-  
5 phenyl)diphenylphosphonium trifluoromethanesulfonate, or (p-tert-butylphenyl) diphenyl sulfonium trifluoromethanesulfonate; benzoin toluene sulfonate such as benzoin toluene sulfonate or  $\alpha$ -methyl benzoin toluene sulfonate; diphenyliodonium salt, triphenyl sulfonium salt, phenyl diazonium salt, or methyl phenyl carbonate.

[0104] The photoacid generator (C) can be used alone, and can also be used in a  
10 combination of 2 or more. Moreover, based on a total amount of 100 parts by weight of the resin (A), the amount of the photoacid generator (C) is 0.5 parts by weight to 5 parts by weight, preferably 0.6 parts by weight to 4.5 parts by weight, and more preferably 0.7 parts by weight to 4 parts by weight.

## 15 Solvent (D)

[0105] The type of the solvent (D) is not particularly limited as long as the scope of the objects of the invention is not affected, and a suitable organic solvent commonly used in a positive photosensitive resin composition can be used.

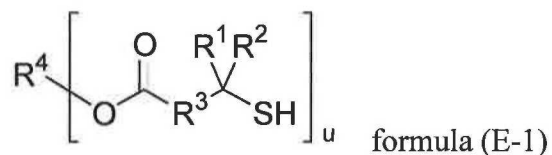
[0106] Specific examples of the solvent (D) can include, for instance, ketone such as  
20 monomethyl ether, monoethyl ether, monopropyl ether, monobutyl ether, or monophenyl ether of acetone, methyl ethyl ketone, cyclohexanone, methyl isopentyl ketone, or 2-heptanone; polyol and the derivative thereof such as ethylene glycol, ethylene glycol monoacetate, diethylene glycol, diethylene glycol monoacetate,

propylene glycol, propylene glycol monoacetate, dipropylene glycol, diethylene glycol dimethyl ether, or dipropylene glycol monoacetate; cyclic ether such as dioxane; ester such as ethyl formate, methyl lactate, ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, methyl acetoacetate, ethyl acetoacetate, ethyl pyruvate, ethyl ethoxyacetate, methyl methoxypropionate, ethyl 3-ethoxypropionate, methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, ethyl 2-hydroxy-2-methylpropionate, methyl 2-hydroxy-3-methylbutanoate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, or propylene glycol monomethyl ether acetate; aromatic hydrocarbon such as toluene or xylene. These can be used alone and can also be used in a mixture of 2 or more.

[0107] Based on a total amount of 100 parts by weight of the resin (A), the amount of the solvent (D) is 30 parts by weight to 360 parts by weight, preferably 40 parts by weight to 300 parts by weight, and more preferably 50 parts by weight to 240 parts by weight.

#### Thiol compound (E)

[0108] The thiol compound (E) has a structure represented by formula (E-1) below:



in formula (E-1),  $\text{R}^1$  and  $\text{R}^2$  each independently represent a hydrogen atom or a  $\text{C}_1$  to  $\text{C}_4$  alkyl group,  $\text{R}^3$  represents a single bond or a  $\text{C}_1$  to  $\text{C}_{10}$  alkylene group, and  $\text{R}^4$  represents a u-valence organic group; and u represents an integer of 2 to 6.

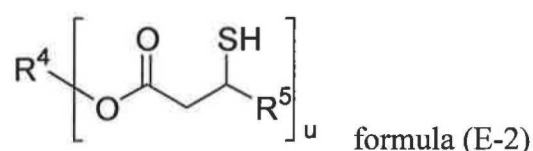
[0109] When  $\text{R}^1$  and  $\text{R}^2$  are alkyl groups, the alkyl groups can be straight or branched,

preferably straight. When  $R^1$  and  $R^2$  are alkyl groups, the alkyl groups are preferably  $C_1$  to  $C_4$ , more preferably  $C_1$  or  $C_2$ , and most preferably  $C_1$ . The combination of  $R^1$  and  $R^2$  is preferably a hydrogen atom and an alkyl group, more preferably a hydrogen atom and a methyl group.

5 [0110] When  $R^3$  is an alkylene group, the alkylene group can be straight or branched, preferably straight. When  $R^3$  is an alkylene group, the alkylene group is preferably  $C_1$  to  $C_{10}$ , more preferably  $C_1$  to  $C_5$ , still more preferably  $C_1$  or  $C_2$ , and most preferably  $C_1$ .

[0111] The u-valence organic group defined by  $R^4$  is specifically a 2- to 6-valence aliphatic group that can contain an atom other than carbon. Atoms in  $R^4$  other than  
10 carbon can include, for instance, a nitrogen atom, an oxygen atom, a sulfur atom, a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. The structure of the aliphatic group of  $R^4$  can be straight, branched, or cyclic, and can also be a structure formed by the combination of such structures.

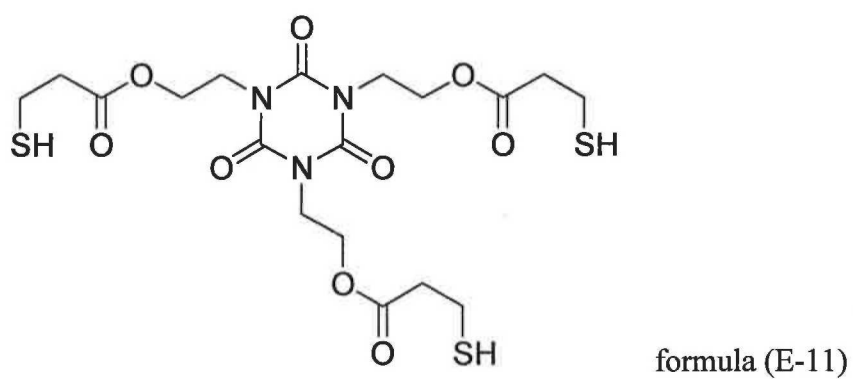
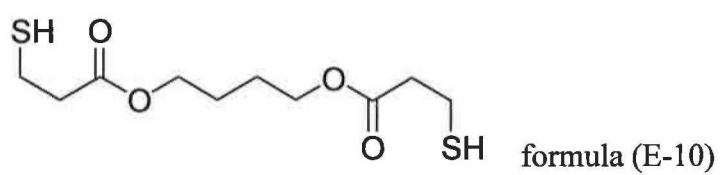
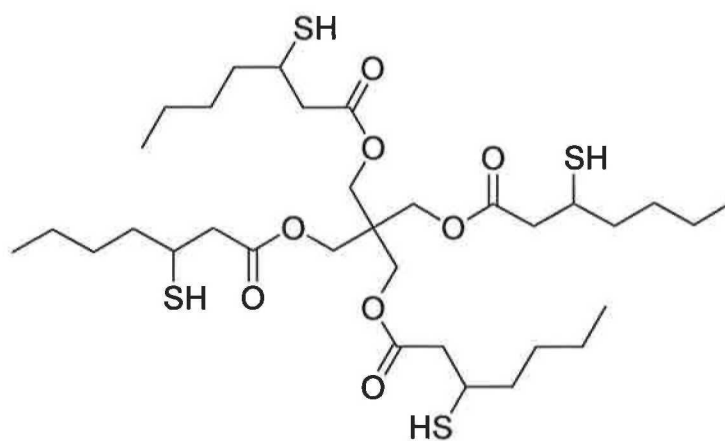
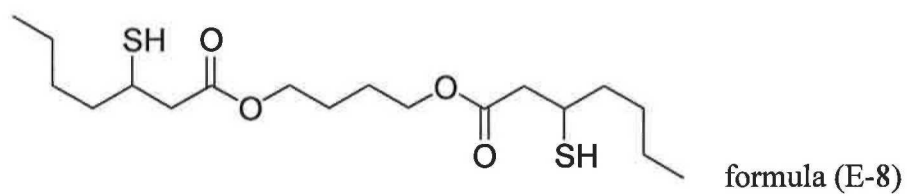
[0112] In the thiol compound (E) represented by formula (E-1), the compound  
15 represented by formula (E-2) below is more preferred:

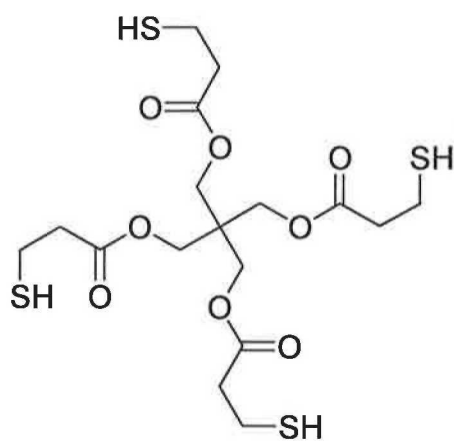


In formula (E-2), the definitions of  $R^4$  and  $u$  are the same as formula (E-1), and  $R^5$  is a hydrogen atom or a  $C_1$  to  $C_4$  alkyl group.

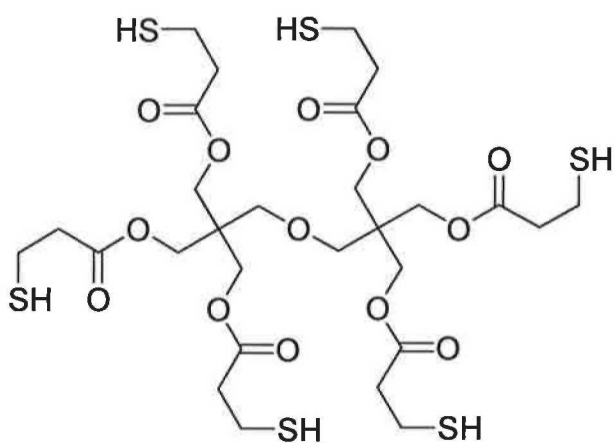
[0113] Specific examples of the thiol compound (E) can include formula (E-3) to  
20 formula (E-16), but are not limited to these specific examples:



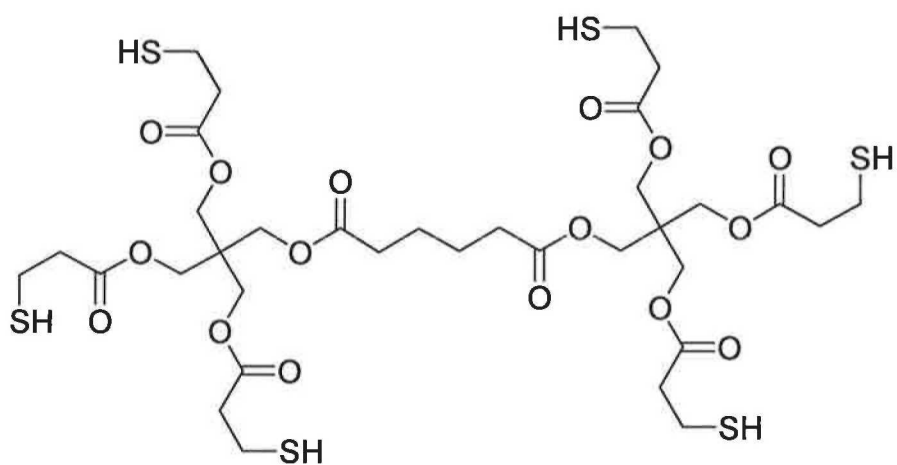




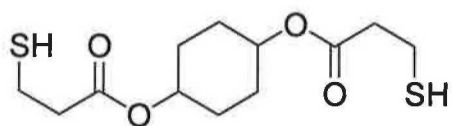
formula (E-12)



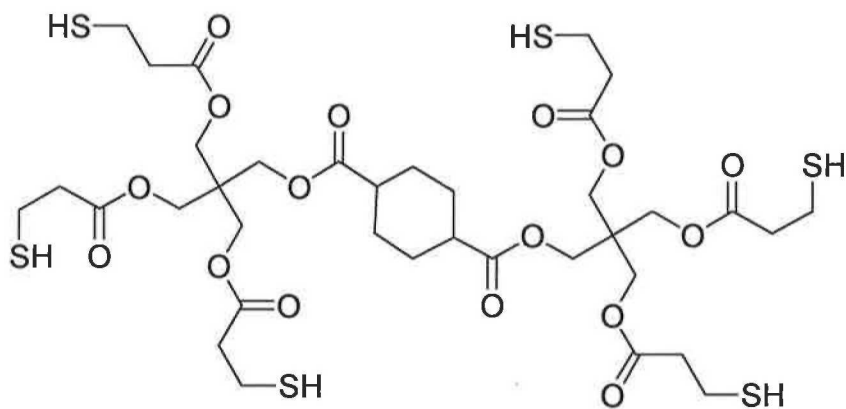
formula (E-13)



formula (E-14)



formula (E-15)



formula (E-16)

[0114] Based on a total amount of 100 parts by weight of the resin (A), the amount of the thiol compound (E) is 0.3 parts by weight to 3 parts by weight, preferably 0.4 parts by weight to 2.8 parts by weight, and more preferably 0.5 parts by weight to 2.5 parts by weight.

[0115] When the chemically-amplified positive photosensitive resin composition includes the thiol compound (E), the rectangularity of the chemically-amplified positive photosensitive resin composition can be further improved.

## 10 Anthracene compound (F)

[0116] Specific examples of the anthracene compound (F) can include, but are not limited to, the following compounds: anthracene, 9,10-dibutoxyanthracene, 9,10-dimethoxyanthracene, 2-ethyl-9,10-dimethoxyanthracene, 2-tert-butyl-9,10-dimethoxyanthracene, 2,3-dimethyl-9,10-dimethoxyanthracene, 9-methoxy-10-methylanthracene, 9,10-diethoxyanthracene, 2-ethyl-9,10-diethoxyanthracene, 2-tert-butyl-9,10-diethoxyanthracene, 2,3-dimethyl-9,10-diethoxyanthracene, 9-ethoxy-10-methylanthracene, 9,10-dipropoxyanthracene, 9,10-diisopropoxyanthracene, 2-ethyl-9,10-dipropoxyanthracene, 2-tert-butyl-9,10-dipropoxyanthracene, 2,3-dimethyl-9,10-

dipropoxyanthracene, 9-isopropoxy-10-methylanthracene, 9,10-dimethylphenoxyanthracene, 2-ethyl-9,10-dimethylphenoxyanthracene, 2-tert-butyl-9,10-dimethylphenoxyanthracene, 2,3-dimethyl-9,10-dimethylphenoxyanthracene, 9-tolyloxy-10-methylanthracene, 9,10-di- $\alpha$ -methyltoluoyloxyanthracene, 2-ethyl-9,10-di- $\alpha$ -methyltoluoyloxyanthracene, 2-tert-butyl-9,10-di- $\alpha$ -methyltoluoyloxyanthracene, 2,3-dimethyl-9,10-di- $\alpha$ -methyltoluoyloxyanthracene, 9-( $\alpha$ -methyltoluoxoxy)-10-methylanthracene, 9,10-diphenylanthracene, 9-methoxyanthracene, 9-ethoxyanthracene, 9-methylanthracene, 9-bromoanthracene, 9-methylthioanthracene, or 9-ethylthioanthracene.

[0117] Based on a total amount of 100 parts by weight of the resin (A), the amount of the anthracene compound (F) is 0.2 parts by weight to 1.5 parts by weight, preferably 0.25 parts by weight to 1.3 parts by weight, and more preferably 0.3 parts by weight to 1.1 parts by weight.

[0118] When the chemically-amplified positive photosensitive resin composition includes the anthracene compound (F), the sensitivity of the chemically-amplified positive photosensitive resin composition can be further improved.

#### **Additive (G)**

[0119] In the chemically-amplified positive photosensitive resin composition, an additive (G) can be further included as long as the effects of the invention are not affected, and the additive (G) can be used alone or in multiple combinations as decided based on actual need. The specific content of the additive (G) is described below.

[0120] In the chemically-amplified positive photosensitive resin composition, to improve plasticity, a polyethylene resin can also be further included as the additive (G).



Specific examples of the polyethylene resin can include, for instance, polyvinyl chloride, polystyrene, polyhydroxystyrene, polyvinyl acetate, polyvinyl benzoic acid, polyvinyl ether, polyethylene ether, polyvinyl alcohol, polyvinylpyrrolidone, polyphenol, and copolymers thereof. The polyethylene resin is preferably polyvinyl ether due to lower glass transition temperature.

[0121] Moreover, in the chemically-amplified positive photosensitive resin composition, to improve the bonding of the template formed by the photosensitive resin composition and the metal substrate, a bonding auxiliary can also be included as the additive (G).

10 [0122] Specific examples of the bonding auxiliary can include products made by CYTEC with the model number Cymel-300 or Cymel-303; melamine compound products with the model number MW-30MH, MW-30, MS-11, MS-001, MX-750, or MX-706 made by Sanwa Chemical; a silane compound such as vinyl trimethoxysilane, vinyl triethoxysilane, 3-methacryloyloxypropyltrimethoxysilane, 3-propenyloxypropyl-  
15 trimethoxysilane, vinyl tris(2-methoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyl dimethyl methoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-chloropropyl-methyldimethoxysilane, 3-chloropropyltrimethoxysilane, 3-mercaptopropyl-  
20 trimethoxysilane, or bis-1,2-(trimethoxysilyl)ethane.

[0123] Moreover, in the chemically-amplified positive photosensitive resin composition, to improve, for instance, coatability, defoaming properties, and uniformity, a surfactant can also be included as the additive (G). Specific examples of the

surfactant can include, for instance, commercial fluoride surfactants such as BM-1000 and BM-1100 (both made by BM Chemie), MEGAFACE F142D, MEGAFACE F172, MEGAFACE F173, MEGAFACE F183 (all made by DIC), FLUORAD FC-135, FLUORAD FC-170C, FLUORAD FC-430, FLUORAD FC-431 (all made by Sumitomo  
5 3M), SURFLON S-112, SURFLON S-113, SURFLON S-131, SURFLON S-141, SURFLON S-145 (all made by Asahi Glass), and SH-28PA, SH-190, SH-193, SZ-6032, SF-8428 (all made by Toray Silicone), but are not limited thereto.

[0124] Moreover, in the chemically-amplified positive photosensitive resin composition, to perform microadjustments on the solubility of the developing solution, a  
10 solvent containing acid, anhydride, or a high-boiling point solvent can be further added as the additive (G).

[0125] Specific examples of the acid and anhydride can include, for instance, monocarboxylic acid such as acetic acid, propionic acid, n-butyric acid, isobutyric acid, n-valeric acid, isovaleric acid, benzoic acid, or cinnamic acid; hydroxyl monocarboxylic  
15 acid such as lactic acid, 2-hydroxybutyric acid, 3-hydroxybutyric acid, salicylic acid, m-hydroxybenzoic acid, p-hydroxybenzoic acid, 2-hydroxyl cinnamic acid, 3-hydroxyl cinnamic acid, 4-hydroxyl cinnamic acid, 5-hydroxyisophthalic acid, or syringic acid; polycarboxylic acid such as oxalic acid, succinic acid, glutaric acid, adipic acid, maleic acid, itaconic acid, hexahydrophthalic acid, phthalic acid, isophthalic acid, terephthalic  
20 acid, 1,2-cyclohexanedicarboxylic acid, 1,2,4-cyclohexane tricarboxylic acid, butane tetracarboxylic acid, trimellitic acid, benzenetetracarboxylic acid, cyclopentane tetracarboxylic acid, butane tetracarboxylic acid, or 1,2,5,8-naphthalene tetracarboxylic acid; anhydride such as itaconic anhydride, succinic anhydride, citraconic anhydride,

dodecene succinic anhydride, propane tricarboxylic anhydride, maleic anhydride, hexahydrophthalic anhydride, methyl tetrahydrophthalic anhydride, humic anhydride, 1,2,3,4-butanetetracarboxylic anhydride, cyclopentane tetracarboxylic dianhydride, phthalic anhydride, pyromellitic anhydride, trimellitic anhydride, benzophenone  
5 tetracarboxylic anhydride, ethylene glycol bis-trimellitic anhydride, or glycerol tris-trimellitic anhydride.

[0126] Moreover, specific examples of the high-boiling point solvent can include, for instance, N-methylformamide, N,N-dimethylformamide, N-methyl toluidine, N-methylacetamide, N,N-dimethylacetamide, N-methylpyrrolidone, dimethyl sulfoxide,  
10 benzyl ether, dihexyl ether, acetylacetone, isophorone, hexanoic acid, caprylic acid, 1-octanol, 1-nonanol, benzyl alcohol, benzyl acetate, ethyl benzoate, diethyl oxalate, diethyl maleate,  $\gamma$ -butyrolactone, vinyl carbonate, propylene carbonate, phenyl sorsulfide.  
[0127] Moreover, in the chemically-amplified positive photosensitive resin composition, to improve sensitivity, a sensitizer can further be included as the additive  
15 (G).

**<Manufacturing method of chemically-amplified positive photosensitive resin composition>**

[0128] The manufacturing method of the chemically-amplified positive photosensitive  
20 resin composition is not particularly limited, and the chemically-amplified positive photosensitive resin composition can be obtained by mixing and stirring each component above via a regular method. The device mixing and stirring each of the components can include, for instance, a dissolving machine, a homogenizer, or a

three-roller mill. After each component was evenly mixed, the resulting mixture can also be further filtered using, for instance, a screen or a membrane filter.

**<Manufacturing method of substrate with casting mold>**

5 [0129] The method of forming the photoresist pattern for forming the casting mold of the electroplated molded article on the metal surface of the substrate using the chemically-amplified positive photosensitive resin composition is not particularly limited.

[0130] A preferred method can contain, for instance: a lamination step, laminating a  
10 photosensitive resin layer formed by the chemically-amplified positive photosensitive resin composition on the metal surface of a substrate, an exposure step, irradiating actinic ray or radiation on the photosensitive resin layer, and an developing step, developing the photosensitive resin layer after exposure to form a casting mold forming an electroplated molded article.

15 [0131] The substrate for laminating a photosensitive resin layer is not particularly limited, and a known substrate for electronic components or a substrate having a wiring pattern...etc. can be used. The substrate has a metal surface; and the metal forming the metal surface is preferably copper, gold, or aluminum, more preferably copper.

[0132] The photosensitive resin layer is laminated on the substrate by, for instance,  
20 the following method. A liquid chemically-amplified positive photosensitive resin composition is coated on the substrate, and then the solvent is removed to form a photosensitive resin layer having the desired thickness. The thickness of the photosensitive resin layer is not particularly limited as long as the photoresist pattern

used as the template can be formed at the desired film thickness. The film thickness of the photosensitive resin layer is not particularly limited, and is preferably 10  $\mu\text{m}$  or more, more preferably 10  $\mu\text{m}$  to 150  $\mu\text{m}$ , still more preferably 20  $\mu\text{m}$  to 120  $\mu\text{m}$ , and most preferably 20  $\mu\text{m}$  to 100  $\mu\text{m}$ .

- 5    **[0133]** The coating method for the photosensitive resin composition on the substrate can include, for instance, a spin coating method, slit coating method, roll coating method, screen printing method, or spreading method. Preferably, the photosensitive resin layer is pre-baked. The pre-bake conditions differ based on, for instance, the type of each component in the photosensitive resin composition, the mixing ratio, and the
- 10   coating film thickness, and are generally 70  $^{\circ}\text{C}$  to 150  $^{\circ}\text{C}$ , preferably 80  $^{\circ}\text{C}$  to 140  $^{\circ}\text{C}$ , and about 2 minutes to 60 minutes.

**[0134]** An actinic ray or radiation is selectively irradiated (exposure) on the resulting photosensitive resin layer with a mask having a predetermined pattern in between, such as UV or visible light having a wavelength of, for instance, 300 nm to 500 nm.

- 15   **[0135]** The ray source of the radiation can include, for instance, a low-pressure mercury lamp, a high-pressure mercury lamp, an ultra high-pressure mercury lamp, a metal halide lamp, or an argon laser. Moreover, the radiation contains, for instance, microwave, infrared, visible light, UV, X-ray,  $\gamma$ -ray, electron beam, proton beam, neutron beam, or ion beam. The amount of radiation differs based on, for instance, the
- 20   composition of the photosensitive resin composition or the film thickness of the photosensitive resin layer. For instance, when an ultra-high pressure mercury lamp is used, the amount of radiation is 100  $\text{mJ}/\text{cm}^2$  to 10000  $\text{mJ}/\text{cm}^2$ . Moreover, the radiation contains light activating the photoacid generator (C) to generate acid.

[0136] After exposure, the photosensitive resin layer is heated using a known method to promote acid diffusion, and the exposed portion in the photosensitive resin film results in change in the alkali solubility of the photosensitive resin layer.

[0137] Next, the exposed photosensitive resin layer is developed by a known method,  
5 and the soluble portion is dissolved and removed to form a predetermined photoresist pattern. At this point, the developing solution is an alkaline aqueous solution.

[0138] The developing solution can include, for instance, an alkali aqueous solution such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, ammonia water, ethylamine, n-propylamine, diethylamine, di-n-propylamine,  
10 triethylamine, methyldiamine, dimethylethanolamine, triethanolamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, pyrrole, piperidine, 1,8-diazabicyclo[5,4,0]-7-undecene, or 1,5-diazabicyclo[4,3,0]-5-nonane. Moreover, an aqueous solution formed by adding a water-soluble organic solvent such as methanol or ethanol or a surfactant in the alkali aqueous solution in a suitable amount can also be  
15 used as a developing solution.

[0139] The developing time differs from the composition of the photosensitive resin composition or the film thickness of the photosensitive resin layer, and is generally 1 minute to 30 minutes. The developing method can be any of a puddle method, dipping method, paddle method, or injection developing method.

20 [0140] After developing, washing is performed with running water for 30 seconds to 90 seconds, and drying is performed using, for instance, an air gun or an oven. As a result, the metal surface of a substrate with a casting mold used as a photoresist pattern can be formed.

### **<Manufacturing method of electroplated molded article>**

[0141] A conductor such as metal is embedded in the non-photoresist portion (the portion removed by the developing solution) in the casting mold of the substrate formed  
5 by the above method via electroplating to form an electroplated molded article such as a connection terminal such as a bump or a metal column. Moreover, the electroplating treatment method is not particularly limited, and various known methods can be used. The electroplating solution preferably includes solder paste, copper electroplating, gold electroplating, or nickel electroplating solution. The remaining casting mold is lastly  
10 removed by a common method using, for instance, a stripping solution.

[0142] According to the above method, a photoresist pattern that can inhibit undercutting and be used as the casting mold at the same time can be formed. By using the resulting substrate with a casting mold that can inhibit undercutting, an electroplated molded article having good adhesion with the substrate can be formed.

15 [0143] Examples are provided below to describe the invention in detail, but the invention is not limited to the contents disclosed in the examples.

### **<Examples>**

#### **Synthesis examples of rein (A)**

20 [0144] Synthesis examples A-1 to A-10 of the resin (A) are described below:

#### **[0145] Synthesis example A-1**

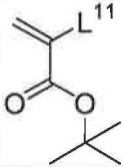
A nitrogen inlet, stirrer, heater, condenser, and thermometer were provided

in a 1000-mL four-necked flask. Next, 50 parts by weight of diethylene glycol dimethyl ether was added, and the temperature of the oil bath was increased to 70 °C. Next, 15 parts by weight of the compound represented by formula (A-1-26) (a11), 10 parts by weight of methacrylic acid (a41), 10 parts by weight of 2-hydroxyethyl methacrylate (a43), 35 parts by weight of isobonyl methacrylate (a44), 30 parts by weight of benzyl methacrylate (a46), and 3.5 parts by weight of 2,2'-azobis-2-methyl butyronitrile (AMBN) were added in the four-necked flask, and the mixture was slowly stirred. The reaction temperature of the entire polymerization process was kept at 70 °C, and the polymerization was maintained for 6 hours. After the polymerization was complete, the polymerization product was removed from the four-necked flask, and the solvent was removed to obtain the resin (A-1).

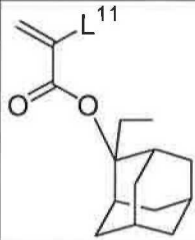
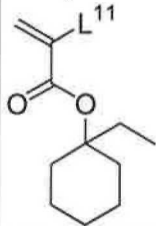
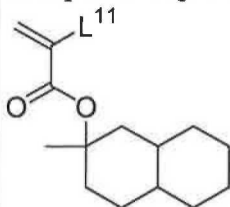
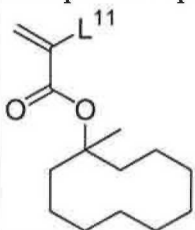
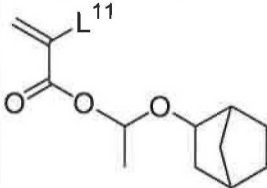
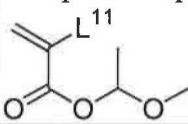
**[0146]** Synthesis examples A-2 to A-10

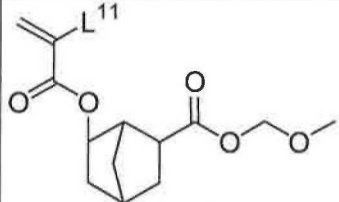
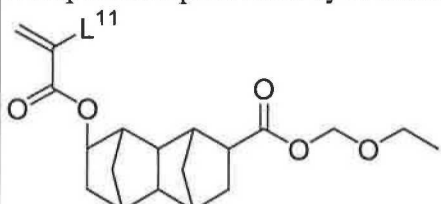
In synthesis examples A-2 to A-10, resins (A-2) to (A-10) were prepared with the same steps as synthesis example A-1, and the difference is: the reaction temperature, reaction time, and component types and amounts were changed, as shown in detail in Table 1.

**[0147]** Moreover, the compounds corresponding to the abbreviations in the following synthesis examples A-1 to A-10 are as shown below.

| Abbreviation | Compound                                                                                                                                                           |
|--------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| a11          | Compound represented by formula (A-1-26), L <sup>11</sup> is a methyl group<br> |
| a12          | Compound represented by formula (A-1-5), L <sup>11</sup> is a methyl group                                                                                         |



|     |                                                                                                                                                                        |
|-----|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|     |                                                                                       |
| a13 | <p>Compound represented by formula (A-1-1), L<sup>11</sup> is a methyl group</p>      |
| a14 | <p>Compound represented by formula (A-1-10), L<sup>11</sup> is a hydrogen atom</p>    |
| a15 | <p>Compound represented by formula (A-1-21), L<sup>11</sup> is a hydrogen atom</p>  |
| a21 | 3-methacryloyloxy methyl oxetane                                                                                                                                       |
| a22 | 3-acryloyloxy-2-trifluoromethyl oxetane                                                                                                                                |
| a23 | 2-methacryloyloxymethyl-3-phenyl oxetane                                                                                                                               |
| a24 | Tetrahydrofurfuryl acrylate                                                                                                                                            |
| a25 | (Tetrahydropyran-2-yl)methyl methacrylate                                                                                                                              |
| a31 | <p>Compound represented by formula (A-1-2), L<sup>11</sup> is a methyl group</p>    |
| a32 | <p>Compound represented by formula (A-2-21), L<sup>11</sup> is a hydrogen atom</p>  |
| a33 | Compound represented by formula (A-3-1), L <sup>11</sup> is a methyl group                                                                                             |

|         |                                                                                                                                                                     |
|---------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|         |                                                                                    |
| a34     | <p>Compound represented by formula (A-3-8), L<sup>11</sup> is a hydrogen atom</p>  |
| a41     | Methacrylic acid                                                                                                                                                    |
| a42     | Cyclohexyl acrylate                                                                                                                                                 |
| a43     | 2-hydroxyethyl methacrylate                                                                                                                                         |
| a44     | Isobonyl methacrylate                                                                                                                                               |
| a45     | Methyl methacrylate                                                                                                                                                 |
| a46     | Benzyl methacrylate                                                                                                                                                 |
| ADVN    | 2,2'-azobis(2,4-dimethylvaleronitrile)                                                                                                                              |
| AMBN    | 2,2'-azobis(2-methylbutyronitrile)                                                                                                                                  |
| Diglyme | Diethylene glycol dimethyl ether                                                                                                                                    |
| PGMEA   | Propylene glycol monomethyl ether acetate                                                                                                                           |

[0148] [Table 1]

| Preparation examples          |         |     | A-1 | A-2 | A-3 | A-4 | A-5 | A-6 | A-7 | A-8 | A-9 | A-10 |
|-------------------------------|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| Monomer (parts by weight)     | (a1)    | a11 | 15  | -   | -   | -   | -   | 20  | -   | -   | -   | -    |
|                               |         | a12 | -   | 10  | -   | -   | -   | 20  | -   | -   | -   | -    |
|                               |         | a13 | -   | -   | 20  | -   | -   | -   | 60  | -   | -   | -    |
|                               |         | a14 | -   | -   | -   | 30  | -   | -   | -   | -   | -   | -    |
|                               |         | a15 | -   | -   | -   | -   | 50  | -   | -   | -   | -   | -    |
|                               | (a2)    | a21 | -   | 30  | -   | -   | -   | -   | 10  | -   | -   | -    |
|                               |         | a22 | -   | -   | 25  | -   | -   | -   | -   | 15  | -   | -    |
|                               |         | a23 | -   | -   | -   | 15  | -   | -   | -   | -   | -   | -    |
|                               |         | a24 | -   | -   | -   | -   | 10  | -   | -   | -   | -   | -    |
|                               |         | a25 | -   | -   | -   | -   | -   | 5   | 10  | -   | -   | -    |
|                               | (a3)    | a31 | -   | 10  | -   | -   | -   | 5   | -   | -   | 15  | -    |
|                               |         | a32 | -   | -   | 10  | -   | -   | -   | -   | 35  | -   | 40   |
|                               |         | a33 | -   | -   | 5   | -   | -   | -   | -   | -   | 10  | -    |
|                               |         | a34 | -   | -   | -   | -   | 20  | -   | -   | -   | -   | -    |
|                               | (a4)    | a41 | 10  | -   | 15  | 15  | -   | 5   | 10  | -   | 20  | -    |
|                               |         | a42 | -   | 10  | -   | -   | -   | 10  | -   | -   | -   | -    |
|                               |         | a43 | 10  | 15  | -   | -   | 10  | -   | -   | 20  | -   | 25   |
|                               |         | a44 | 35  | -   | 25  | -   | -   | 35  | -   | -   | 20  | -    |
|                               |         | a45 | -   | 25  | -   | 20  | -   | -   | 10  | 30  | 35  | 20   |
|                               |         | a46 | 30  | -   | -   | 20  | 10  | -   | -   | -   | -   | 15   |
| Solvent (parts by weight)     | Diglyme | 50  | -   | 60  | -   | -   | -   | -   | -   | 60  | 20  | -    |
|                               | PGMEA   | -   | 55  | -   | 55  | 60  | 55  | 55  | 60  | -   | 35  | 55   |
| Catalyst (parts by weight)    | AMBN    | 3.5 | -   | -   | 3.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | -   | 4.5  |
|                               | ADV N   | -   | 4.0 | 3.0 | 0.5 | -   | -   | -   | -   | -   | 4.0 | -    |
| Reaction temperature (°C)     |         | 70  | 65  | 70  | 75  | 70  | 70  | 70  | 70  | 70  | 65  | 75   |
| Polycondensation time (hours) |         | 6   | 7   | 6   | 6   | 6   | 6   | 6   | 6   | 6   | 7   | 5    |

### Synthesis examples of novolac resin (B)

[0149] Synthesis examples B-1-1 to B-1-3 and B-2-1 to B-2-2 of the novolac resin (B)

5 are described below:

**[0150]** Synthesis example B-1-1

A nitrogen inlet, stirrer, heater, condenser tube, and thermometer were provided to a four-necked flask having a volume of 1000 mL. Nitrogen was introduced, and then 64.89 g (0.6 moles) of m-cresol, 43.26 g (0.4 moles) of p-cresol,  
5 0.5 g (0.0028 moles) of manganese acetate, and 48.70 g (0.6 moles) of a 37 wt% formaldehyde aqueous solution were added. The components were slowly stirred and polymerized for 3 hours. Next, 1.38 g (0.01 moles) of salicylic acid was added to adjust the pH to 3.5, and then drying was performed under a reduced pressure of 300 mmHg for 30 minutes. Next, the reaction solution was slowly heated to 150 °C to  
10 remove the solvent to obtain a high-ortho novolac resin (B-1-1).

The resulting high-ortho novolac resin (B-1-1) was measured for the number of bonds of the methylene group by carbon nuclear magnetic resonance ( $^{13}\text{C}$ -NMR), and the ratio of the methylene group of the novolac resin bonded in an ortho-ortho arrangement was calculated to be 18%.

15

**[0151]** Synthesis example B-1-2

A nitrogen inlet, stirrer, heater, condenser tube, and thermometer were provided to a four-necked flask having a volume of 1000 mL. Nitrogen was introduced, and then 5.40 g (0.05 moles) of o-cresol, 64.89 g (0.6 moles) of m-cresol,  
20 37.86 g (0.35 moles) of p-cresol, 0.5 g (0.0028 moles) of manganese acetate, and 52.75 g (0.65 moles) of a 37 wt% formaldehyde aqueous solution were added. The components were slowly stirred and polymerized for 3 hours. Next, 1.10 g (0.008 moles) of salicylic acid was added to adjust the pH to 4.0, and then drying was

performed under a reduced pressure of 300 mmHg for 30 minutes. Next, the reaction solution was slowly heated to 150 °C to remove the solvent to obtain a high-ortho novolac resin (B-1-2).

The resulting high-ortho novolac resin (B-1-2) was measured for the number  
5 of bonds of the methylene group by carbon nuclear magnetic resonance ( $^{13}\text{C}$ -NMR), and the ratio of the methylene group of the novolac resin bonded in an ortho-ortho arrangement was calculated to be 20%.

#### [0152] Synthesis example B-1-3

10 A nitrogen inlet, stirrer, heater, condenser tube, and thermometer were provided to a four-necked flask having a volume of 1000 mL. Nitrogen was introduced, and then 64.89 g (0.6 moles) of m-cresol, 43.26 g (0.4 moles) of p-cresol, 0.5 g (0.0028 moles) of manganese acetate, and 56.82 g (0.7 moles) of a 37 wt% formaldehyde aqueous solution were added. The components were slowly stirred and  
15 polymerized for 3 hours. Next, 0.37 g (0.003 moles) of benzoic acid was added to adjust the pH to 4.8, then drying was performed under a reduced pressure of 300 mmHg for 30 minutes, and then 0.03 g (0.0002 moles) of dimethyl sulfate was added. Next, the reaction solution was slowly heated to 150 °C to remove the solvent to obtain a high-ortho novolac resin (B-1-3).

20 The resulting high-ortho novolac resin (B-1-3) was measured for the number of bonds of the methylene group by carbon nuclear magnetic resonance ( $^{13}\text{C}$ -NMR), and the ratio of the methylene group of the novolac resin bonded in an ortho-ortho arrangement was calculated to be 25%.

**[0153]** Synthesis example B-2-1

A nitrogen inlet, stirrer, heater, condenser tube, and thermometer were provided to a four-necked flask having a volume of 1000 mL. Nitrogen was introduced, and then 64.89 g (0.6 moles) of m-cresol, 43.26 g (0.4 moles) of p-cresol, 1.80 g (0.02 moles) of oxalic acid, and 48.70 g (0.6 moles) of a 37 wt% formaldehyde aqueous solution were added. The components were slowly stirred and polymerized for 3 hours. Next, the reaction solution was heated to 150 °C to remove the solvent to obtain a novolac resin (B-2-1).

The resulting novolac resin (B-2-1) was measured for the number of bonds of the methylene group by carbon nuclear magnetic resonance ( $^{13}\text{C}$ -NMR), and the ratio of the methylene group of the novolac resin bonded in an ortho-ortho arrangement was calculated to be 16%.

**[0154]** Synthesis example B-2-2

A nitrogen inlet, stirrer, heater, condenser tube, and thermometer were provided to a four-necked flask having a volume of 1000 mL. Nitrogen was introduced, and then 64.89 g (0.6 moles) of m-cresol, 32.45 g (0.3 moles) of p-cresol, 12.22 g (0.1 moles) of 2,5-xyleneol, 0.90 g (0.01 moles) of oxalic acid, and 44.64 g (0.55 moles) of a 37 wt% formaldehyde aqueous solution were added. The components were slowly stirred and polymerized for 3 hours. Next, the reaction solution was heated to 150 °C to remove the solvent to obtain a novolac resin (B-2-2).

The resulting novolac resin (B-2-2) was measured for the number of bonds

of the methylene group by carbon nuclear magnetic resonance ( $^{13}\text{C}$ -NMR), and the ratio of the methylene group of the novolac resin bonded in an ortho-ortho arrangement was calculated to be 14%.

## 5 **Examples of chemically-amplified positive photosensitive resin composition**

[0155] Example 1 to example 14 and comparative example 1 to comparative example 4 of the chemically-amplified positive photosensitive resin composition are described below:

### 10 [0156] Example 1

100 parts by weight of the resin (A-1) obtained in synthesis example A-1, 35 parts by weight of the high-ortho novolac resin (B-1-1) obtained in synthesis example B-1-1, 0.2 parts by weight of the photoacid generator C-1 (hereinafter C-1), and 0.3 parts by weight of 2,4-bis(trichloromethyl)-6-piperonyl-1,3,5-triazine (hereinafter C-2) were added to 30 parts by weight of propylene glycol monomethyl ether acetate (hereinafter D-1), and then the components were dissolved and mixed by a shaking stirrer to obtain a chemically-amplified positive photosensitive resin composition. The chemically-amplified positive photosensitive resin composition was evaluated by each measurement method below, and the results are shown in Table 2.

### 20 [0157] Example 2 to example 14

In example 2 to example 14, the same operating method as the manufacturing method of the chemically-amplified positive photosensitive resin composition of example 1 was used, and the difference is that in example 2 to example

14, the type and amount of the raw materials of the chemically-amplified positive photosensitive resin composition were changed, and the formula and the following evaluation results are as shown in Table 2 and Table 3.

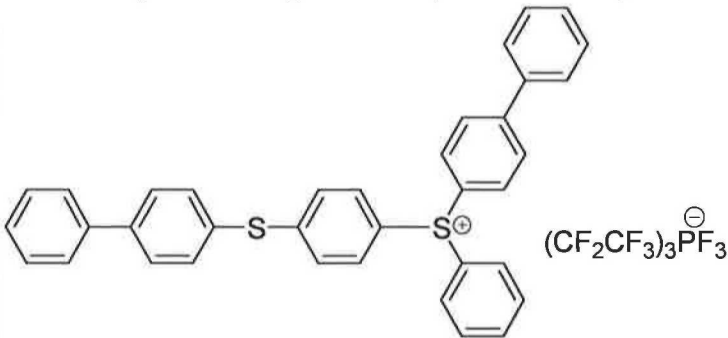
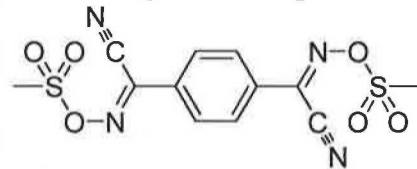
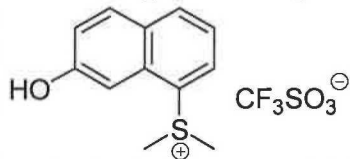
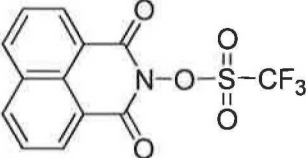
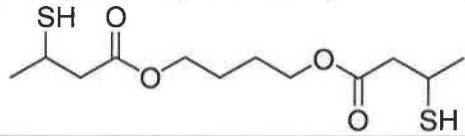
**[0158]** Comparative example 1 to comparative example 6

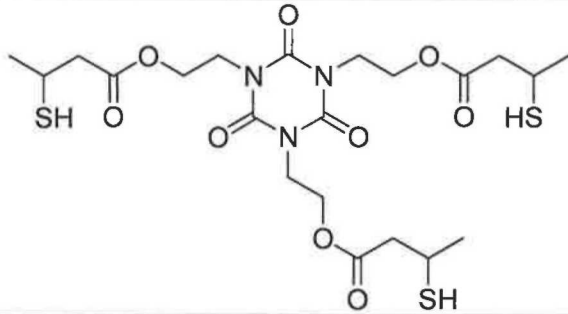
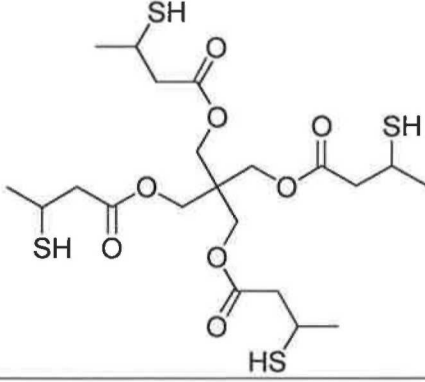
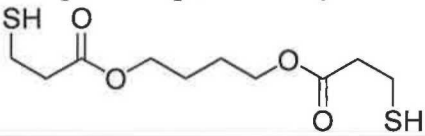
5 In comparative example 1 to comparative example 4, the same manufacturing method as the chemically-amplified positive photosensitive resin composition of example 1 was used, and the difference is that in comparative example 1 to comparative example 4, the type and amount of the raw materials of the chemically-amplified positive photosensitive resin composition were changed, and the  
10 formula and the following evaluation results are as shown in Table 3.

**[0159]** The compounds corresponding to the labels in Table 2 and Table 3 are as shown below.

| Abbreviation | Compound                                         |
|--------------|--------------------------------------------------|
| A-1          | Resin (A-1) of synthesis example A-1             |
| A-2          | Resin (A-2) of synthesis example A-2             |
| A-3          | Resin (A-3) of synthesis example A-3             |
| A-4          | Resin (A-4) of synthesis example A-4             |
| A-5          | Resin (A-5) of synthesis example A-5             |
| A-6          | Resin (A-6) of synthesis example A-6             |
| A-7          | Resin (A-7) of synthesis example A-7             |
| A-8          | Resin (A-8) of synthesis example A-8             |
| A-9          | Resin (A-9) of synthesis example A-9             |
| A-10         | Resin (A-10) of synthesis example A-10           |
| B-1-1        | Novolac resin (B-1-1) of synthesis example B-1-1 |
| B-1-2        | Novolac resin (B-1-2) of synthesis example B-1-2 |
| B-1-3        | Novolac resin (B-1-3) of synthesis example B-1-3 |



|       |                                                                                                                                                 |
|-------|-------------------------------------------------------------------------------------------------------------------------------------------------|
| B-2-1 | Novolac resin (B-2-1) of synthesis example B-2-1                                                                                                |
| B-2-2 | Novolac resin (B-2-2) of synthesis example B-2-2                                                                                                |
| C-1   | Photoacid generator represented by the following formula<br>  |
| C-2   | 2,4-bis(trichloromethyl)-6-piperonyl-1,3,5-triazine                                                                                             |
| C-3   | Photoacid generator represented by formula (C-3-1)<br>         |
| C-4   | Photoacid generator represented by formula (C-4j)<br>        |
| C-5   | Photoacid generator represented by the following formula<br> |
| D-1   | Propylene glycol methyl ether acetate                                                                                                           |
| D-2   | Diethylene glycol dimethyl ether                                                                                                                |
| D-3   | Ethyl 3-ethoxypropionate                                                                                                                        |
| E-1   | Compound represented by formula (E-3)<br>                    |
| E-2   | Compound represented by formula (E-4)                                                                                                           |

|     |                                                                                                                               |
|-----|-------------------------------------------------------------------------------------------------------------------------------|
|     |                                             |
| E-3 | Compound represented by formula (E-5)<br>    |
| E-4 | Compound represented by formula (E-10)<br> |
| F-1 | 9,10-dibutoxyanthracene                                                                                                       |
| F-2 | 2-tert-butyl-9,10-dimethoxyanthracene                                                                                         |
| F-3 | 2,3-dimethyl-9,10-diethoxyanthracene                                                                                          |
| F-4 | 9-isopropoxy-10-methylantracene                                                                                               |
| G-1 | SH-28PA (made by Toray Silicone)                                                                                              |
| G-2 | 3-glycidoxypropyltrimethoxysilane                                                                                             |

[0160] [Table 2]

| Component<br>(parts by weight) |       | Examples |     |     |     |     |     |     |     |     |
|--------------------------------|-------|----------|-----|-----|-----|-----|-----|-----|-----|-----|
|                                |       | 1        | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
| Resin (A)                      | A-1   | 100      | -   | -   | -   | -   | -   | -   | -   | -   |
|                                | A-2   | -        | 100 | -   | -   | -   | -   | -   | -   | -   |
|                                | A-3   | -        | -   | 100 | -   | -   | -   | -   | -   | -   |
|                                | A-4   | -        | -   | -   | 100 | -   | -   | -   | -   | -   |
|                                | A-5   | -        | -   | -   | -   | 50  | -   | -   | 50  | -   |
|                                | A-6   | -        | -   | -   | -   | 50  | -   | 80  | -   | -   |
|                                | A-7   | -        | -   | -   | -   | -   | 100 | -   | -   | -   |
|                                | A-8   | -        | -   | -   | -   | -   | -   | -   | -   | 100 |
|                                | A-9   | -        | -   | -   | -   | -   | -   | 20  | -   | -   |
|                                | A-10  | -        | -   | -   | -   | -   | -   | -   | 50  | -   |
| Novolac resin (B)              | B-1-1 | 35       | -   | -   | 60  | -   | -   | 50  | -   | 100 |
|                                | B-1-2 | -        | 20  | -   | -   | 70  | -   | 50  | -   | -   |
|                                | B-1-3 | -        | -   | 45  | -   | -   | 80  | -   | 90  | -   |
|                                | B-2-1 | -        | -   | -   | -   | -   | -   | -   | -   | 50  |
|                                | B-2-2 | -        | -   | -   | -   | -   | -   | -   | -   | -   |
| Photoacid generator (C)        | C-1   | 0.2      | -   | -   | -   | -   | 2.0 | -   | -   | -   |
|                                | C-2   | 0.3      | 0.8 | -   | -   | -   | -   | 3.0 | -   | -   |
|                                | C-3   | -        | -   | 1.0 | -   | -   | -   | -   | 4.0 | -   |
|                                | C-4   | -        | -   | -   | 1.3 | -   | -   | -   | -   | 5.0 |
|                                | C-5   | -        | -   | -   | -   | 1.5 | -   | -   | -   | -   |
| Solvent (D)                    | D-1   | 30       | -   | -   | 55  | -   | -   | 120 | -   | 60  |
|                                | D-2   | -        | 40  | -   | -   | 70  | -   | -   | 140 | -   |
|                                | D-3   | -        | -   | 45  | -   | -   | 100 | -   | -   | 100 |
| Thiol compound (E)             | E-1   | -        | 0.3 | -   | 0.2 | -   | 2.0 | -   | -   | -   |
|                                | E-2   | -        | -   | 1.0 | -   | -   | -   | -   | -   | -   |
|                                | E-3   | -        | -   | -   | 0.5 | -   | -   | -   | -   | -   |
|                                | E-4   | -        | -   | -   | -   | -   | -   | -   | 3.0 | -   |
| Anthracene compound (F)        | F-1   | -        | 0.5 | -   | -   | -   | -   | 0.3 | -   | -   |
|                                | F-2   | -        | -   | 0.2 | -   | -   | -   | -   | -   | -   |
|                                | F-3   | -        | -   | -   | -   | -   | 0.8 | -   | -   | -   |
|                                | F-4   | -        | -   | -   | -   | -   | -   | -   | 1.0 | -   |
| Additive (G)                   | G-1   | -        | -   | 0.3 | -   | -   | -   | -   | -   | -   |
|                                | G-2   | -        | -   | -   | -   | -   | -   | -   | -   | -   |
| Sensitivity evaluation         |       | ○        | ◎   | ◎   | ◎   | ◎   | ◎   | ◎   | ◎   | ◎   |
| Rectangularity evaluation      |       | ◎        | ◎   | ◎   | ◎   | ◎   | ◎   | ◎   | ◎   | ○   |

[0161] [Table 3]

| Component<br>(parts by weight) |       | Examples |     |     |     |     | Comparative examples |     |     |     |
|--------------------------------|-------|----------|-----|-----|-----|-----|----------------------|-----|-----|-----|
|                                |       | 10       | 11  | 12  | 13  | 14  | 1                    | 2   | 3   | 4   |
| Resin (A)                      | A-1   | -        | -   | -   | -   | -   | -                    | 100 | -   | -   |
|                                | A-2   | -        | -   | -   | -   | -   | -                    | -   | 100 | -   |
|                                | A-3   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
|                                | A-4   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
|                                | A-5   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
|                                | A-6   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
|                                | A-7   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
|                                | A-8   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
|                                | A-9   | 100      | -   | 100 | -   | 100 | -                    | -   | -   | -   |
|                                | A-10  | -        | 100 | -   | 100 | -   | -                    | -   | -   | -   |
| Novolac resin (B)              | B-1-1 | -        | -   | 50  | -   | -   | 100                  | -   | -   | -   |
|                                | B-1-2 | 120      | -   | -   | 30  | -   | -                    | -   | -   | -   |
|                                | B-1-3 | -        | 75  | -   | -   | 85  | -                    | -   | -   | -   |
|                                | B-2-1 | -        | -   | -   | -   | -   | -                    | 50  | -   | -   |
|                                | B-2-2 | -        | 25  | -   | -   | -   | -                    | -   | -   | 100 |
| Photoacid generator (C)        | C-1   | -        | 1.8 | -   | -   | -   | 2.0                  | -   | -   | -   |
|                                | C-2   | -        | -   | 1.2 | -   | -   | -                    | 3.0 | -   | -   |
|                                | C-3   | -        | -   | -   | 0.7 | -   | -                    | -   | 4.0 | -   |
|                                | C-4   | -        | -   | -   | -   | 2.8 | -                    | -   | -   | 2.5 |
|                                | C-5   | 2.3      | -   | -   | -   | -   | -                    | -   | -   | -   |
| Solvent (D)                    | D-1   | 360      | -   | -   | 160 | -   | 50                   | -   | -   | 80  |
|                                | D-2   | -        | 300 | -   | 160 | -   | -                    | 60  | -   | -   |
|                                | D-3   | -        | -   | 240 | -   | 280 | -                    | -   | 70  | -   |
| Thiol compound (E)             | E-1   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
|                                | E-2   | -        | -   | 0.5 | -   | -   | -                    | -   | -   | -   |
|                                | E-3   | -        | -   | -   | 1.5 | -   | -                    | -   | -   | -   |
|                                | E-4   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
| Anthracene compound (F)        | F-1   | -        | -   | -   | 1.3 | 1.0 | -                    | -   | -   | -   |
|                                | F-2   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
|                                | F-3   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
|                                | F-4   | -        | -   | -   | -   | 0.5 | -                    | -   | -   | -   |
| Additive (G)                   | G-1   | -        | -   | -   | -   | -   | -                    | -   | -   | -   |
|                                | G-2   | 1.0      | -   | -   | -   | -   | -                    | -   | -   | -   |
| Sensitivity evaluation         |       | ○        | ○   | ○   | ◎   | ◎   | X                    | ○   | ○   | X   |
| Rectangularity evaluation      |       | ○        | ○   | ◎   | ◎   | ○   | X                    | X   | X   | X   |

## Evaluation methods

### [0162] a. Ratio of methylene group ortho-ortho bond of novolac resin

The number of methylene group bonds of the novolac resin was measured using carbon nuclear magnetic resonance ( $^{13}\text{C}$ -NMR, made by Bruker, model: AV400), and the ortho-ortho bond ratio in the novolac resin was calculated according to the following formula.

$$\text{Ortho-ortho bond ratio (\%)} = \{(\text{ortho-ortho bond}) / [(\text{ortho-ortho bond}) + (\text{ortho-para bond}) + (\text{para-para bond})]\} \times 100\%$$

Ortho-ortho bond: number of bonds of methylene group in ortho-ortho arrangement

Ortho-para bond: number of bonds of methylene group in ortho-para arrangement

Para-para bond: number of bonds of methylene group in para-para arrangement

### [0163] b. Sensitivity

The chemically-amplified positive photosensitive resin compositions of the examples and comparative examples were each coated on a 6-in. copper substrate using a spin coating machine to form a 50- $\mu\text{m}$  photosensitive resin layer. Next, the photosensitive resin layer was pre-baked at 110  $^{\circ}\text{C}$  for 6 minutes. After pre-bake, pattern exposure was performed using a mask having a hole pattern and a diameter of 60

$\mu\text{m}$  and the exposure device Titan 2 (made by Ultratech) with g ray, h ray, and i ray, and the amount of exposure was changed stepwise. Next, the substrate was placed on a heating plate, and exposure was performed at  $100\text{ }^{\circ}\text{C}$  for 3 minutes, and then heating was performed (PEB). Next, 2.38% tetramethylammonium hydroxide (TMAH) aqueous solution was added dropwise to the photosensitive resin layer, then the photosensitive resin layer was left at  $23\text{ }^{\circ}\text{C}$  for 60 seconds to repeat the developing process 4 times. Next, washing was performed with running water, then nitrogen was blown to obtain a thick-film photoresist pattern having a via hole pattern and a diameter of  $50\text{ }\mu\text{m}$ .

Next, the amount of exposure for which pattern residue was not observed was obtained as the minimum amount of exposure needed to form the thick-film photoresist pattern as an indicator for sensitivity. The evaluation criteria are as follows:

⊙: amount of exposure  $< 100\text{ mJ/cm}^2$

○:  $100\text{ mJ/cm}^2 \leq \text{amount of exposure} < 150\text{ mJ/cm}^2$

△:  $150\text{ mJ/cm}^2 \leq \text{amount of exposure} < 200\text{ mJ/cm}^2$

×: amount of exposure  $\geq 200\text{ mJ/cm}^2$

#### [0164] c. Rectangularity

Referring to FIG. 1, FIG. 1 is a schematic of the measurement of the rectangularity of a photoresist pattern. After the photosensitive resin layer coated on a substrate 100 was exposed and developed, a photoresist pattern 120 having a photoresist portion 122 and a non-photoresist portion 124 was formed. The section shape of the

photoresist pattern having the optimal amount of exposure was observed, the values of a bottom width  $L_b$  and a top width  $L_t$  were measured, and  $L_t/L_b$  was calculated as an indicator for rectangularity. The evaluation criteria are as follows:

◎:  $0.9 < L_t/L_b < 1.1$

5 ○:  $0.85 < L_t/L_b \leq 0.9$ ;  $1.1 \leq L_t/L_b < 1.15$

△:  $0.75 < L_t/L_b \leq 0.85$ ;  $1.15 \leq L_t/L_b < 1.25$

✕:  $L_t/L_b < 0.75$ ;  $L_t/L_b > 1.25$

### Evaluation results

10 [0165] It can be known from Table 2 and Table 3 that, in comparison to the chemically-amplified positive photosensitive resin composition containing the high-ortho novolac resin (B-1) (examples 1 to 14), the rectangularity of the chemically-amplified positive photosensitive resin composition without the high-ortho novolac resin (B-1) (comparative examples 2 to 4) is poor; in comparison to the  
15 chemically-amplified positive photosensitive resin composition containing the resin (A) (examples 1 to 14), the sensitivity of the chemically-amplified positive photosensitive resin composition without the resin (A) (comparative examples 1 and 4) is poor.

[0166] At the same time, when the copolymerized monomer mixture used in the resin (A) contains the monomer (a1) having the structure represented by formula (A-1)  
20 (examples 1 to 7), the rectangularity performance thereof is better. Moreover, when the monomer mixture further includes the monomer (a2) containing a cyclic ether group (examples 2 to 8), the sensitivity performance thereof is better.

[0167] Moreover, when the chemically-amplified positive photosensitive resin

composition contains the thiol compound (E) (examples 2 to 4, 6, 8, 12, and 13), the rectangularity performance thereof is also better.

[0168] Moreover, when the chemically-amplified positive photosensitive resin composition contains the anthracene compound (F) (examples 2, 3, 6 to 8, 13, and 14),  
5 the sensitivity performance thereof is also better.

[0169] Based on the above, the chemically-amplified positive photosensitive resin composition of the invention contains the high-ortho novolac resin (B-1) in which 18% to 25% of a methylene group is bonded in an ortho-ortho arrangement, and therefore the issue of poor rectangularity can be alleviated.

10 [0170] Moreover, if the resin (A) in the chemically-amplified positive photosensitive resin composition of the invention is obtained by the copolymerization of a monomer mixture containing a specific monomer or the chemically-amplified positive photosensitive resin composition of the invention further contains the thiol compound (E), then the resulting photoresist pattern can further achieve better rectangularity.

15 [0171] Moreover, if the resin (A) in the chemically-amplified positive photosensitive resin composition of the invention is obtained by the copolymerization of a monomer mixture containing the specific monomer (a2) or the chemically-amplified positive photosensitive resin composition of the invention further contains the anthracene compound (F), then the resulting photoresist pattern can further achieve better  
20 sensitivity.

[0172] Although the invention has been described with reference to the above embodiments, it will be apparent to one of ordinary skill in the art that modifications to the described embodiments may be made without departing from the spirit of the



invention. Accordingly, the scope of the invention is defined by the attached claims not by the above detailed descriptions.

WHAT IS CLAIMED IS:

1. A chemically-amplified positive photosensitive resin composition, comprising:

a resin (A), wherein the resin (A) is obtained by copolymerizing a monomer

5 mixture and contains an acid-dissociated protecting group;

a novolac resin (B);

a photoacid generator (C); and

a solvent (D),

the novolac resin (B) comprises a high-ortho novolac resin (B-1) and the high-

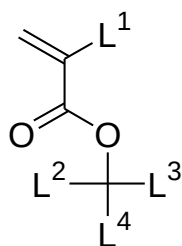
10 ortho novolac resin (B-1) has 18% to 25% of a methylene group bonded in an ortho-ortho arrangement,

wherein based on a total amount of 100 parts by weight of the resin (A), an amount of the high-ortho novolac resin (B-1) is 20 parts by weight to 120 parts by weight.

2. The chemically-amplified positive photosensitive resin composition of

15 claim 1, wherein the monomer mixture comprises a monomer (a1), and the monomer (a1)

has a structure represented by formula (A-1) below:



formula (A-1)

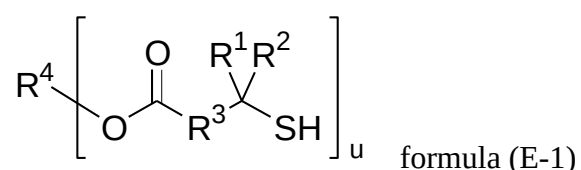
in formula (A-1), L<sup>1</sup> represents a hydrogen atom, a C<sub>1</sub> to C<sub>6</sub> straight or branched alkyl group, a fluorine atom, or a C<sub>1</sub> to C<sub>6</sub> straight or branched fluorinated alkyl

20 group; L<sup>2</sup>, L<sup>3</sup>, and L<sup>4</sup> respectively independently represent a C<sub>1</sub> to C<sub>6</sub> straight or branched alkyl group or a C<sub>1</sub> to C<sub>6</sub> straight or branched fluoroalkyl group, or L<sup>3</sup> and L<sup>4</sup> are bonded

to each other to form a C<sub>5</sub> to C<sub>20</sub> hydrocarbon ring.

3. The chemically-amplified positive photosensitive resin composition of claim 1, wherein the monomer mixture comprises a monomer (a2), and the monomer (a2) contains a cyclic ether group.

5 4. The chemically-amplified positive photosensitive resin composition of claim 1, further comprising a thiol compound (E), wherein the thiol compound (E) has a structure represented by formula (E-1) below:



10 in formula (E-1), R<sup>1</sup> and R<sup>2</sup> each independently represent a hydrogen atom or a C<sub>1</sub> to C<sub>4</sub> alkyl group, R<sup>3</sup> represents a single bond or a C<sub>1</sub> to C<sub>10</sub> alkylene group, and R<sup>4</sup> represents a u-valence organic group; and u represents an integer of 2 to 6.

5. The chemically-amplified positive photosensitive resin composition of claim 1, further comprising an anthracene compound (F).

15 6. The chemically-amplified positive photosensitive resin composition of claim 1, wherein based on a total amount of 100 parts by weight of the resin (A), an amount of the novolac resin (B) is 20 parts by weight to 150 parts by weight, an amount of the photoacid generator (C) is 0.5 parts by weight to 5 parts by weight, and an amount of the solvent (D) is 30 parts by weight to 360 parts by weight.

20 7. The chemically-amplified positive photosensitive resin composition of claim 2, wherein based on a total amount of 100 parts by weight of the monomer mixture, an amount of the monomer (a1) is 10 parts by weight to 60 parts by weight.

8. The chemically-amplified positive photosensitive resin composition of claim 3, wherein based on a total amount of 100 parts by weight of the monomer mixture, an amount

of the monomer (a2) is 5 parts by weight to 30 parts by weight.

9. The chemically-amplified positive photosensitive resin composition of claim 4, wherein based on a total amount of 100 parts by weight of the resin (A), an amount of the thiol compound (E) is 0.3 parts by weight to 3 parts by weight.

5           10. The chemically-amplified positive photosensitive resin composition of claim 5, wherein based on a total amount of 100 parts by weight of the resin (A), an amount of the anthracene compound (F) is 0.2 parts by weight to 1.5 parts by weight.

11. A manufacturing method of a substrate with a casting mold, comprising:

10           a laminate step, laminating a photosensitive resin layer formed by the chemically-amplified positive photosensitive resin composition of any one of claims 1 to 10 on a metal surface of a substrate;

            an exposure step, irradiating the photosensitive resin layer with an actinic ray or a radiation; and

15           a developing step, developing the photosensitive resin layer after exposure to form a casting mold for forming an electroplated molded article.

12. A manufacturing method of an electroplated molded article, comprising:

            a step of electroplating the substrate with the casting mold made by the manufacturing method of the substrate with the casting mold of claim 11 to form an electroplated molded article in the casting mold.