

DESCRIPTION

TITLE OF THE INVENTION: RESIN AND PHOTSENSITIVE RESIN

COMPOSITION

TECHNICAL FIELD

[0001]

The present invention relates to a resin which contains a specific structure. More specifically, the present invention relates to a resin suitable for use in a surface protective film or an interlayer dielectric film for a semiconductor device, a dielectric layer for an organic electroluminescent element, and the like, and a photosensitive resin composition containing the resin.

BACKGROUND ART

[0002]

Polyimide resins are highly heat resistant and highly electrically insulative and have excellent mechanical characteristics, and thus are widely used in surface protective films and interlayer dielectric films for semiconductor devices, dielectric layers for organic electroluminescent elements, and the like.

[0003]

In the case where a polyimide is used as a surface protective film or an interlayer dielectric film, one way to

form a through hole or the like is etching which uses a positive photoresist. However, this method has a problem in that the process involves applying and removing the photoresist and thus is complicated. In view of this, a study has been done on a photosensitive heat-resistant material in an attempt to streamline the operation process.

[0004]

Moreover, with the reduced size of devices, and higher density, higher speed, and larger capacity of packages in recent years, there has been an increasing demand for an interlayer dielectric film that is useable in multilayer wiring. Therefore, there has been a requirement for a photosensitive resin composition that has a high sensitivity and a high residual film rate and is capable of processing a film having a larger thickness than known resin compositions.

[0005]

For example, in regard to a positive photosensitive heat-resistant composition that can be developed with an alkaline aqueous solution, the following have been reported a composition containing a phenolic hydroxyl-containing polyamide acid ester and an o-quinonediazide compound (Patent Document 1); a composition containing a cyclized polyimide soluble in a solvent and a naphthoquinonediazide compound; and a composition containing a polybenzoxazole precursor and a naphthoquinonediazide compound (Patent Document 2). However,

in the case where a polyimide that is poorly transparent is used in such compositions, there is a problem in that a photosensitizer has a poor photoreactive efficiency in the portion exposed to light and especially the composition in the form of a thick film has a low sensitivity.

[0006]

In order to satisfy such a requirement, there has been proposed a photosensitive resin composition which achieves a high sensitivity by using a highly transparent polyimide containing a tetracarboxylic anhydride having an alicyclic structure (for example, refer to Patent Documents 3 and 4).

[0007]

Moreover, there has been proposed a polyimide resin which contains a hexafluoropropyl group and a tetracarboxylic anhydride having an alicyclic structure (for example, refer to Patent Document 5).

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0008]

Patent Document 1: Japanese Patent Laid-open Publication No. 4-204945

Patent Document 2: Japanese Patent Laid-open Publication No. 1-46862

Patent Document 3: International Publication No.

00/73853

Patent Document 4: Japanese Patent Laid-open Publication
No. 2010-196041

Patent Document 5: Japanese Patent Laid-open Publication
No. 2007-183388

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0009]

However, the known polyimide resins containing a tetracarboxylic anhydride having an alicyclic structure are too soluble in an alkaline developer and thus cannot easily form a thick film structure. Furthermore, the polyimide resin containing a hexafluoropropyl group and a tetracarboxylic anhydride having an alicyclic structure is very poor in residual film rate and thus cannot easily form a highly sensitive thick film structure.

[0010]

In consideration of the problems of the above-described known techniques, it is an object of the present invention to provide a resin that has a high sensitivity and a high residual film rate when used in a photosensitive resin composition.

SOLUTIONS TO THE PROBLEMS

[0011]

The inventors of the present invention studied hard to attain the above object and found the present invention.

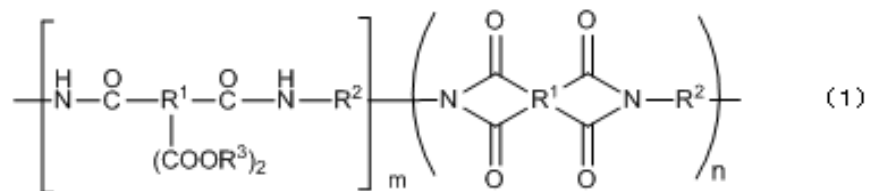
Specifically, the present invention has the following arrangements.

(1) A resin having a polyamide structure, a polyimide precursor structure, or a polyimide structure each of which contains an acid and/or an anhydride of the acid in an amount of 5 to 95 mol% assuming that the total amount of acids and/or anhydrides thereof is 100 mol%, the acid having a C6-C40 alicyclic structure or having a C6-C40 semi-alicyclic structure which has both an alicyclic structure and an aromatic ring.

(2) A resin having a structure represented by General Formula (1):

[0012]

[Chemical formula 1]



[0013]

(where each R¹ independently contains at least one organic group, which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together

directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic ring, in an amount of 5 to 95 mol% assuming that the total amount of R¹ is 100 mol%; each R² independently represents a C2-C40 divalent organic group; R³ represents hydrogen or a C1-C20 monovalent organic group; m and n each represent 0 to 100,000; and m + n > 2.)

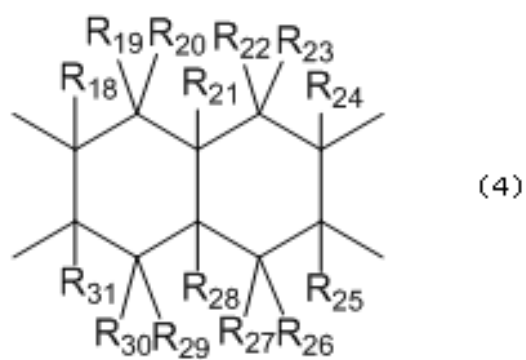
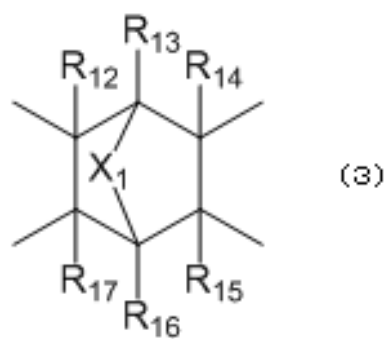
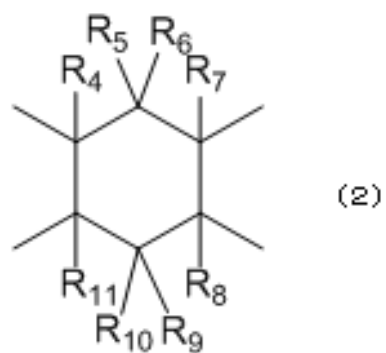
(3) The resin described in (2), wherein the structure represented by General Formula (1) has a fluorine component.

(4) The resin described in (2) or (3), wherein the structure represented by General Formula (1) has a phenolic hydroxyl group.

(5) The resin described in any of (2) to (4), wherein R¹ in General Formula (1) contains at least one organic group selected from the following General Formulas (2) to (7):

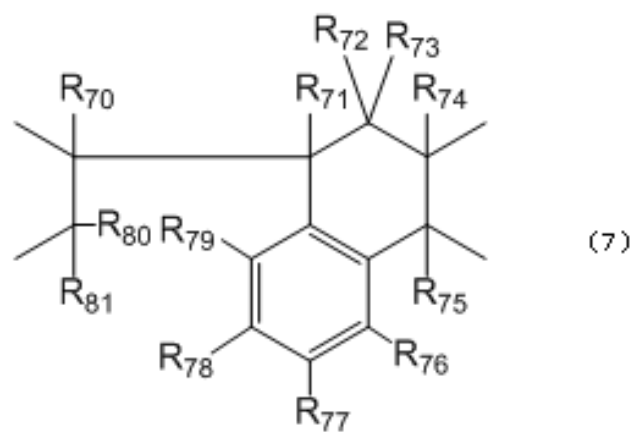
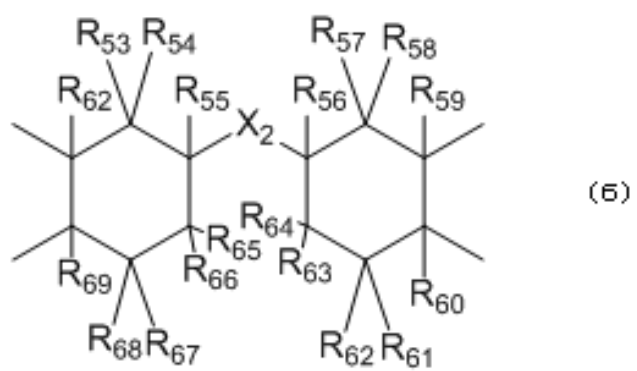
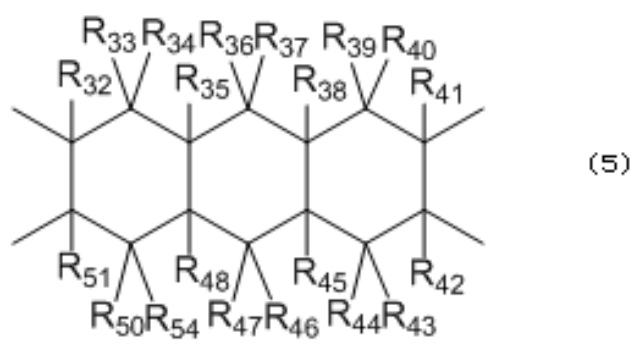
[0014]

[Chemical formula 2]



[0015]

【 Chemical formula 3】



[0016]

(where R_4 to R_{81} in General Formulas (2) to (7) each independently represent a hydrogen atom, a halogen atom, or a C1-C3 monovalent organic group, X_1 in General Formula (3) represents an oxygen atom, a sulfur atom, a sulfonyl group, a C1-C3 divalent organic group, or a divalent crosslink formed of two or more C1-C3 divalent organic groups bound together, and X_2 in General Formula (6) represents a direct bond, an oxygen atom, a sulfur atom, or a divalent crosslink formed of two or more organic groups selected from a sulfonyl group, C1-C3 divalent organic groups, and an arylene group bound together.)

(6) The resin described in any of (2) to (5), wherein a fluorine-atom-containing organic group is contained in an amount of 30 mol% or more assuming that the total amount of R^1 and R^2 is 100 mol%.

(7) The resin described in any of (2) to (6), wherein, in General Formula (1), each R^1 independently contains at least one organic group which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic ring, in an amount of 25 to 80 mol% assuming that the total amount of R^1 is 100 mol%.

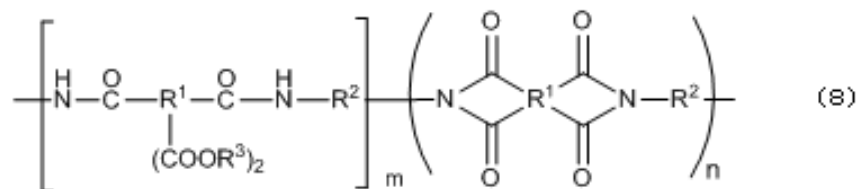
(8) The resin described in any of (2) to (6), wherein, in General Formula (1), each R^1 independently contains at least one organic group which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic ring, in an amount of 40 to 70 mol% assuming that the total amount of R^1 is 100 mol%.

(9) A photosensitive resin composition containing the resin described in any of (1) to (8).

(10) A photosensitive resin composition containing: (a) a resin containing as a main component a structure represented by General Formula (8); (b) a photo acid generator; and (c) a solvent, the photosensitive resin composition having a positive photosensitivity:

[0017]

[Chemical formula 4]



[0018]

(where each R^1 independently contains at least one organic group

which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic ring, in an amount of 5 to 95 mol% assuming that the total amount of R¹ is 100 mol%; each R² independently represents a C2-C40 divalent organic group; R³ represents hydrogen or a C1-C20 monovalent organic group; m and n each represent 0 to 100,000; and m + n > 2, with the proviso that the structure represented by General Formula (8) essentially has a fluorine component and a phenolic hydroxyl group.)

(11) The photosensitive resin composition described in (9) or (10), wherein R² in General Formula (1) or (8) further contains an aliphatic organic group.

(12) The photosensitive resin composition described in (11), wherein the aliphatic organic group is an organic group containing an aliphatic alkyl group.

(13) A method of producing a heat-resistant resin film from the photosensitive resin composition described in any of (9) to (12), including: applying the photosensitive resin composition to a support substrate and drying the photosensitive resin composition to obtain a photosensitive resin film; exposing the

photosensitive resin film obtained in the step to light;
developing the exposed photosensitive resin film by using an
alkaline aqueous solution; and treating the developed
photosensitive resin film with heat.

(14) An interlayer dielectric film which is obtained by the
method described in (13).

(15) An interlayer dielectric film for a multilayer wiring
structure, which has a total thickness of 10 μm or more and 50
 μm or less and which is obtained by the method described in (13).

(16) A surface protective film which is obtained by the method
described in (13).

(17) An electronic component including the interlayer
dielectric film described in (14) or the surface protective film
described in (16).

(18) A dielectric layer for an organic electroluminescent
element, which is obtained by the method described in (13).

EFFECTS OF THE INVENTION

[0019]

According to the present invention, it is possible to
obtain a resin that has a high sensitivity and a high residual
film rate when used in a photosensitive resin composition.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

Fig. 1 is a cross-sectional view of a pad portion of a semiconductor device in Examples of the present invention.

Fig. 2 shows cross-sectional views of a production process of a semiconductor device in Examples of the present invention.

EMBODIMENTS OF THE INVENTION

[0021]

The present invention is a resin having a polyamide structure, a polyimide precursor structure, or a polyimide structure each of which contains an acid and/or an anhydride of the acid in an amount of 5 to 95 mol% assuming that the total amount of acids and/or anhydrides thereof is 100 mol%, the acid having a C6-C40 alicyclic structure or having a C6-C40 semi-alicyclic structure which has both an alicyclic structure and an aromatic ring.

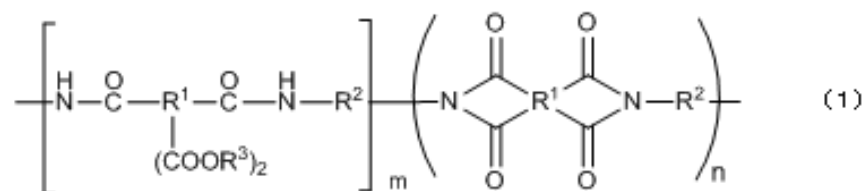
Alternatively, a resin of the present invention has a structure represented by the following General Formula (1). The resin having a structure represented by General Formula (1) is a polyimide precursor that will become a highly heat-resistant, highly solvent-resistant polyimide by cyclizing with heat, a polyimide that has been cyclized with heat, or a polyimide precursor in which the resin has been partially cyclized and imidized with heat.

[0022]

According to another aspect, the present invention is a photosensitive resin composition which contains a resin having a structure represented by General Formula (1).

[0023]

[Chemical formula 5]



[0024]

(where each R^1 independently contains at least one organic group, which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic ring, in an amount of 5 to 95 mol% assuming that the total amount of R^1 is 100 mol%; each R^2 independently represents a C2-C40 divalent organic group; R^3 represents hydrogen or a C1-C20 organic group; m and n each represent 0 to 100,000; and $m + n > 2$.)

The structure represented by General Formula (1) is a polyimide when $m = 0$ and is a polyimide precursor when $n = 0$. The structure is a polyimide precursor which has been partially

cyclized and imidized with heat when $m > 0$ and $n > 0$.

[0025]

The resin having a structure represented by General Formula (1) of the present invention may be a copolymer of the structure represented by General Formula (1) and a resin that has a structure other than the structure represented by General Formula (1).

[0026]

In General Formula (1), each R^1 independently contains at least one organic group which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic ring, in an amount of 5 to 95 mol% assuming that the total amount of R^1 is 100 mol%; each R^2 independently represents a C2-C40 divalent organic group; R^3 represents hydrogen or a C1-C20 organic group; m and n each represent 0 to 100,000; and $m + n > 2$. When the resin contains a monocyclic, fused polycyclic, or semi-alicyclic structure, the resin has a low absorbency. Therefore, it is possible to obtain a photosensitive resin composition that provides a high sensitivity even in the form of a thick film.

[0027]

However, a polyimide-based resin in which each R^1 is an alicyclic structure is too soluble in an alkaline developer and therefore the developed film dissolves and the residual film rate decreases. Since the film readily takes in the alkaline developer, tackiness occurs and residues are left.

Furthermore, a polyimide resin containing an alicyclic structure with less than 6 carbon atoms or an alicyclic structure with 41 or more carbon atoms has a problem in that it is not soluble enough in the alkaline developer and therefore sensitivity is not high enough and residues are left in patterns after development.

[0028]

Furthermore, when the structure represented by General Formula (1) contains a fluorine component, the resin has water repellency and, during alkali development, penetration into the surface of a film is reduced. Therefore, such a structure is preferable because it is possible to obtain a resin film having a high residual film rate in which there is no tackiness in the unexposed portion and no development residues remain in the obtained pattern.

[0029]

Furthermore, when the structure represented by General Formula (1) contains a phenolic hydroxyl group, the resin is adequately soluble in the alkaline developer, which contributes

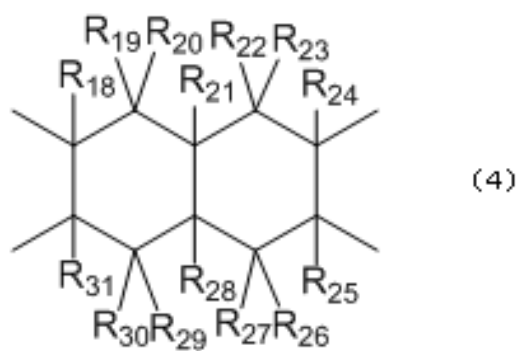
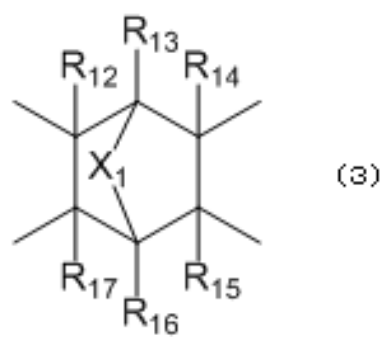
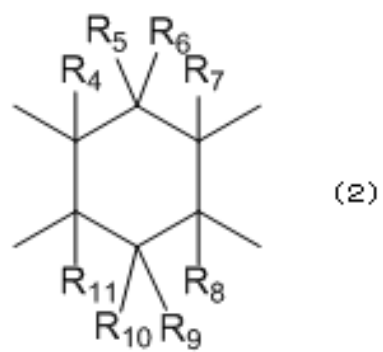
to an interaction with a photosensitizer. Therefore, such a structure is preferable because it is possible to obtain a resin film that has an improved residual film rate and a high sensitivity. Furthermore, the phenolic hydroxyl group also contributes to the reaction with a crosslinking agent. Therefore, such a structure is preferable also in view of high mechanical characteristics and high chemical resistance.

[0030]

It is preferable that R^1 in General Formula (1) be at least one selected from the following General Formulas (2) to (7):

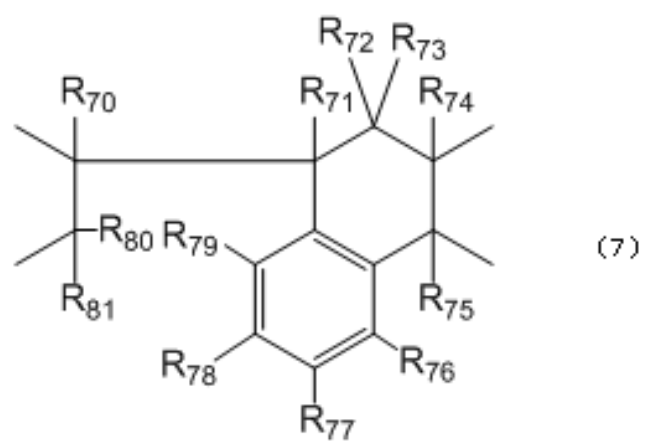
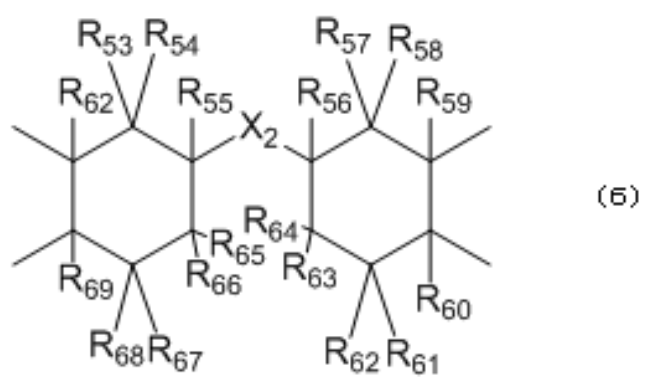
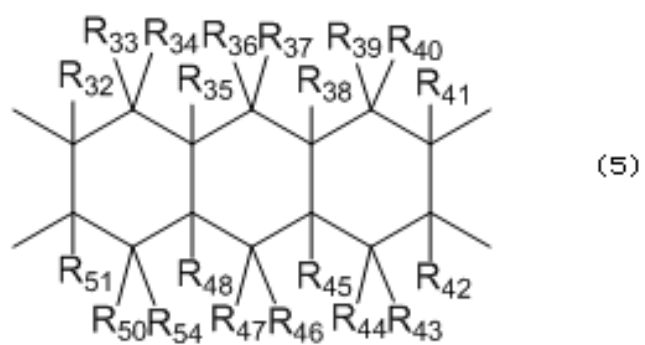
[0031]

[Chemical formula 6]



[0032]

[Chemical formula 7]



[0033]

R₄ to R₈₁ in General Formulas (2) to (7) each independently represent a hydrogen atom, a halogen atom, or a C1-C3 monovalent organic group. In the C1-C3 monovalent organic group, a hydrogen atom may be substituted by a halogen atom. X₁ in General Formula (3) represents an oxygen atom, a sulfur atom, a sulfonyl group, a C1-C3 divalent organic group, or a divalent crosslink formed of two or more C1-C3 divalent organic groups bound together. In the C1-C3 divalent organic group, a hydrogen atom may be substituted by a halogen atom. X₂ in General Formula (6) represents a direct bond, an oxygen atom, a sulfur atom, or a divalent crosslink formed of two or more selected from a sulfonyl group, C1-C3 divalent organic groups, and an arylene group. In the C1-C3 divalent organic group and arylene group, a hydrogen atom contained in the organic group may be substituted by a halogen atom.

[0034]

In General Formula (1), R¹ is a structure derived from an acid dianhydride. Specific examples of an acid dianhydride containing a C6-C40 tetravalent organic group having a monocyclic or fused polycyclic alicyclic structure, a C6-C40 tetravalent organic group formed of organic groups having a monocyclic alicyclic structure bound together directly or by a crosslink, and/or a C6-C40 tetravalent organic group having a semi-alicyclic structure having both an alicyclic structure

and an aromatic ring for use in the present invention include alicyclic tetracarboxylic dianhydrides such as 1,2-dimethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,2,3,4-tetramethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,2,4,5-cyclohexanetetracarboxylic dianhydride, 3,4-dicarboxy-1,2,3,4-tetrahydro-1-naphthalenesuccinic dianhydride, 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic dianhydride, 2,3,5-tricarboxy-2-cyclopentane acetic dianhydride, bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride, 2,3,4,5-tetrahydrofuran tetracarboxylic dianhydride, and 3,5,6-tricarboxy-2-norbornane acetic dianhydride, compounds obtained by substituting aromatic rings of these dianhydrides with alkyl groups or halogen atoms, semi-alicyclic tetracarboxylic dianhydrides such as 1,3,3a,4,5,9b-hexahydro-5(tetrahydro-2,5-dioxo-3-furanyl)naphtho[1,2-c]furan-1,3-dione, and compounds obtained by substituting hydrogen atoms of aromatic rings of these dianhydrides with alkyl groups or halogen atoms.

[0035]

When such an acid anhydride is contained in amount of 5 mol% to 95 mol% with respect to 100 mol% of R¹ in the structure represented by General Formula (1), the resin has a low absorbency and thus it is possible to obtain a photosensitive

resin composition that has a high sensitivity even in the form of a thick film.

[0036]

It is preferable that a pattern obtained from the photosensitive resin composition of the present invention have a high resolution. The resolution denotes the smallest size that can be obtained when a pattern is formed by using the photosensitive resin composition. Being able to form a smaller pattern means a higher resolution.

[0037]

A photosensitive resin composition obtained from a resin having a very low absorbency has a too high light collection rate and thus tends to form a pattern width larger than desired. The resulting pattern has a low resolution. Therefore, in view of the ability to obtain a pattern of a desired size during pattern formation, the content of the acid dianhydride with respect to 100 mol% of R¹ in the structure represented by General Formula (1) is more preferably 25 mol% or more, even more preferably 40 mol% or more.

[0038]

Furthermore, in the case where the content of the alicyclic structure is small, the light collection rate is low and a small opening cannot be patterned, and therefore the obtained pattern has a low resolution. Therefore, in view of the ability to increase light collection rate and the ability

to pattern a small opening, the content of the acid dianhydride with respect to 100 mol% of R^1 in the structure represented by General Formula (1) is more preferably 80 mol% or less, even more preferably 70 mol% or less.

[0039]

When the content of the acid dianhydride is within the above-described range, it is possible to obtain a high-resolution pattern.

[0040]

The resin that has a structure represented by General Formula (1) preferably has a fluorine component. It is preferable that, in General Formula (1), at least one of R^1 and R^2 be an organic group that has a fluorine atom. When a fluorine atom is contained, water repellency is given to the surface of a film during alkali development, and penetration into the surface can be reduced. Therefore, it is possible to obtain a photosensitive resin film having a high residual film rate in which there are no tackiness in the unexposed portion and no development residues in the formed pattern. For prevention of penetration through interfaces and adequate dissolution rate, it is preferable that, in General Formula (1), the amount of the organic group having a fluorine atom be 30 mol% or more assuming that the total amount of R^1 and R^2 is 100 mol%. Such a structure is introduced by using a fluorine-atom-containing monomer in an amount of 30 mol% with respect to the amount of

a monomer component for introducing R^1 and R^2 . Furthermore, for the adhesion to a substrate, it is preferable that the amount of the fluorine-atom-containing monomer be 90 mol% or less.

[0041]

Specific examples of a compound having a fluorine atom include aromatic acid dianhydrides such as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, compounds obtained by substituting aromatic rings of the dianhydride with alkyl groups or halogen atoms, and acid dianhydrides having an amide group, aromatic di-amines such as bis(3-amino-4-hydroxyphenyl)hexafluoropropane and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl, and compounds obtained by partially substituting hydrogen atoms of aromatic rings of these di-amines with C1-C10 alkyl groups, fluoroalkyl groups, halogen atoms, or the like. The resin having a structure represented by General Formula (1) is preferably a resin that contains a structure derived from any of these compounds.

[0042]

Furthermore, the resin having a structure represented by General Formula (1) preferably has a phenolic hydroxyl component. It is preferable that, in General Formula (1), at least one of R^1 and R^2 be an organic group that has a phenolic hydroxyl group. Phenolic hydroxyl groups provide adequate solubility in alkaline developers and interact with a

photosensitizer to prevent or reduce the solubility of unexposed portions. Therefore, it is possible to improve the residual film rate and increase sensitivity. In addition, since the phenolic hydroxyl groups also contribute to the reaction with crosslinking agents, the resin containing a phenolic hydroxyl component is preferable also in terms of high mechanical characteristics and high chemical resistance.

[0043]

Specific examples of a compound that has a phenolic hydroxyl group include aromatic acid dianhydrides such as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, compounds obtained by substituting aromatic rings of the dianhydride with alkyl groups or halogen atoms, and acid dianhydrides having an amide group, hydroxyl-containing di-amines such as bis(3-amino-4-hydroxyphenyl) hexafluoropropane, bis(3-amino-4-hydroxyphenyl) sulfone, bis(3-amino-4-hydroxyphenyl) propane, bis(3-amino-4-hydroxyphenyl) methylene, bis(3-amino-4-hydroxyphenyl) ether, bis(3-amino-4-hydroxy) biphenyl, and bis(3-amino-4-hydroxyphenyl) fluorene, and compounds obtained by partially substituting hydrogen atoms of aromatic rings of these di-amines with C1-C10 alkyl groups, fluoroalkyl groups, halogen atoms, or the like. It is preferable that the resin having a structure represented by General Formula (1) be a resin that contains a structure derived

from any of these compounds.

[0044]

With the use of the above-described acid dianhydride that contains a C6-C40 alicyclic structure or semi-alicyclic structure, the above-described compound that has a phenolic hydroxyl group, and the above-described compound that has a fluorine atom in adequate amounts, it is possible to obtain a highly photosensitive resin composition having a high residual film rate that leaves no tackiness or development residues after development.

[0045]

In General Formula (1), R^1 may further have a structure derived from an acid dianhydride other than the above-described acid dianhydrides.

[0046]

Specific examples of acid dianhydrides include aromatic acid anhydrides including aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, 2,3,3',4'-biphenyl tetracarboxylic dianhydride, 2,2',3,3'-biphenyl tetracarboxylic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 2,2',3,3'-benzophenone tetracarboxylic dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride,

1,1-bis(3,4-dicarboxyphenyl)ethane dianhydride,
1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride,
bis(3,4-dicarboxyphenyl)methane dianhydride,
bis(2,3-dicarboxyphenyl)methane dianhydride,
1,2,5,6-naphthalenetetracarboxylic dianhydride,
2,3,6,7-naphthalenetetracarboxylic dianhydride,
2,3,5,6-pyridinetetracarboxylic dianhydride, and
3,4,9,10-perylenetetracarboxylic dianhydride,
bis(3,4-dicarboxyphenyl)sulfone dianhydride,
bis(3,4-dicarboxyphenyl)ether dianhydride,
2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride,
compounds obtained by substituting aromatic rings of these
compounds with alkyl groups or halogen atoms, and acid
anhydrides having an amide group. Two or more of these acid
dianhydrides may be used in combination with an acid dianhydride
that contains a C6-C40 alicyclic structure or semi-alicyclic
structure.

[0047]

Furthermore, in General Formula (1), R^2 may further have
a structure derived from a di-amine other than the
above-described di-amines.

[0048]

An aliphatic di-amine denotes a di-amine that has no
aromatic rings, and examples include aliphatic alkyl di-amines
containing an alkylene ether group such as a polyalkyl group,

a polyethylene ether group, a polyoxypropylene group, or a tetramethylene ether group; alicyclic di-amines; and aliphatic di-amines having a siloxane structure. Specific examples of aliphatic alkyl di-amines include polyalkyl di-amines such as tetramethylenediamine, hexamethylenediamine, octamethylenediamine, decamethylenediamine, and dodecamethylenediamine; di-amines containing a polyethylene ether group such as JEFFAMINE KH-511, JEFFAMINE ED-600, JEFFAMINE ED-900, JEFFAMINE ED-2003, JEFFAMINE EDR-148, and JEFFAMINE EDR-176; polyoxypropylene di-amines such as D-200, D-400, D-2000, D-4000, RP-409, and RP-2009; di-amines containing a tetramethylene ether group such as RT-1000 and HT-1100; amino-group-containing alkylether di-amines such as HT-1000 and HE-1000 (those listed above are the names of products available from Huntsman Corporation). Specific examples of alicyclic di-amines include cyclohexyl di-amine and methylenebis cyclohexyl amine. Specific examples of aliphatic di-amines having a siloxane structure include bis(3-aminopropyl)tetramethyl disiloxane and bis(p-aminophenyl)octamethyl pentasiloxane. Especially the use of an aliphatic alkyl di-amine is preferable because softness is imparted and thus elongation at break improves, and elastic modulus decreases and thus warpage of a wafer is reduced. These characteristics are effective for multiple layers and thick films. When an aliphatic alkyl di-amine is employed, it

is preferable that the residues derived from aliphatic alkyl di-amines account for 10 mol% or more of the entire di-amine residues. In view of heat resistance, 50 mol% or less is preferable.

[0049]

Furthermore, in the case where an aliphatic group having a siloxane structure is copolymerized without reducing heat resistance, it is possible to improve the adhesion to the substrate. A copolymer containing 1 to 15 mol% of such an aliphatic group is preferable.

[0050]

Other examples include hydroxyl-containing di-amines such as bis(3-amino-4-hydroxyphenyl) hexafluoropropane, bis(3-amino-4-hydroxyphenyl) sulfone, bis(3-amino-4-hydroxyphenyl) propane, bis(3-amino-4-hydroxyphenyl) methylene, bis(3-amino-4-hydroxyphenyl) ether, bis(3-amino-4-hydroxy) biphenyl, and bis(3-amino-4-hydroxyphenyl) fluorene; sulfonic acid-containing di-amines such as 3-sulfonic acid-4,4'-diaminodiphenyl ether; thiol-containing di-amines such as dimercapto-phenylenediamine; and aromatic di-amines such as 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl methane, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfide, 4,4'-diaminodiphenyl

sulfide, 1,4-bis(4-aminophenoxy) benzene, benzine, m-phenylenediamine, p-phenylenediamine, 1,5-naphthalenediamine, 2,6-naphthalenediamine, bis(4-aminophenoxyphenyl) sulfone, bis(3-aminophenoxyphenyl) sulfone, bis(4-aminophenoxy) biphenyl, bis{4-(4-aminophenoxy)phenyl} ether, 1,4-bis(4-aminophenoxy) benzene, 2,2'-dimethyl-4,4'-diaminobiphenyl, 2,2'-diethyl-4,4'-diaminobiphenyl, 3,3'-dimethyl-4,4'-diaminobiphenyl, 3,3'-diethyl-4,4'-diaminobiphenyl, 2,2',3,3'-tetramethyl-4,4'-diaminobiphenyl, 3,3',4,4'-tetramethyl-4,4'-diaminobiphenyl, and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl; and compounds obtained by partially substituting hydrogen atoms of aromatic rings of these di-amines with C1-C10 alkyl groups, fluoroalkyl groups, halogen atoms, or the like. These di-amines may be used without changes or may be used as corresponding diisocyanate compounds or trimethylsilylated di-amines. Two or more of these di-amine components may be used in combination. For the use that requires heat resistance, it is preferable to use an aromatic di-amine in an amount of 50 mol% or more with respect to the total amount of di-amines.

[0051]

Preferred among those listed above are

3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether,

3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone,
3,4'-diaminodiphenyl sulfide, 4,4'-diaminodiphenyl sulfide,
bis(4-aminophenoxyphenyl) sulfone, bis(3-aminophenoxyphenyl)
sulfone, bis(4-aminophenoxy) biphenyl,
bis{4-(4-aminophenoxy)phenyl} ether, 1,4-bis(4-aminophenoxy)
benzene, 1,3-bis(4-aminophenoxy) benzene,
2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane,
2,2-bis[4-(4-aminophenoxy)phenyl] propane,
2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane, and
compounds obtained by substituting aromatic rings of those
listed above with alkyl groups or halogen atoms, and di-amines
having an amide group described below. These may be used
individually or two or more of these may be used in combination.
[0052]

The resin having a structure represented by General
Formula (1) of the present invention may further contain a
sulfonic acid group, a thiol group, or the like. The use of
a resin having an appropriate amount of sulfonic acid group
and/or thiol group provides a positive photosensitive resin
composition that has an adequate alkali solubility.
[0053]

In General Formula (1), m and n each represent the number
of repeating units of the resin and represent 0 to 100,000, with
the proviso that $m + n > 2$. In view of an improvement in
extensibility of the resulting resin, it is preferable that m

+ n be 10 or more. On the other hand, in view of the solubility to an alkaline developer of a photosensitive resin composition containing the resulting resin, $m + n$ is 200,000 or less, preferably 1,000 or less, more preferably 100 or less.

[0054]

The weight-average molecular weight of the resin having a structure represented by General Formula (1) is preferably 3,000 to 80,000, more preferably 8,000 to 50,000, which are polystyrene-equivalent molecular weights obtained by gel permeation chromatography. Provided that the weight-average molecular weight is within this range, a thick film can be readily formed.

[0055]

A terminal of the resin having a structure represented by General Formula (1) may be blocked with a terminal blocking agent such as a monoamine, an acid anhydride, an acid chloride, and a monocarboxylic acid. By blocking the terminal of the resin with a terminal blocking agent that has a hydroxyl group, a carboxyl group, a sulfonic acid group, a thiol group, a vinyl group, an ethynyl group, or an allyl group, it is possible to readily control the rate of dissolution of the resin in the alkaline aqueous solution within a preferred range. The terminal blocking agent is used in an amount of preferably 0.1 to 60 mol%, more preferably 5 to 50 mol%, with respect to the total amount of amine components of the resin.

[0056]

The resin having a structure represented by General Formula (1) may be produced in accordance with a known method of producing a polyimide precursor. Examples of the method include (I) a method by which a tetracarboxylic dianhydride having an R^1 group, a di-amine compound having an R^2 group, and a monoamino compound which is a terminal blocking agent are reacted with each other at low temperature; (II) a method by which a diester is obtained from a tetracarboxylic dianhydride having an R^1 group and an alcohol and the diester is then reacted with a di-amine compound having an R^2 group and a monoamino compound which is a terminal blocking agent in the presence of a condensation agent; and (III) a method by which a diester is obtained from a tetracarboxylic dianhydride having an R^1 group and an alcohol, remaining two carboxyl groups are then converted into acid chlorides, and the resultant is reacted with a di-amine compound having an R^2 group and a monoamino compound which is a terminal blocking agent. The resin polymerized in the manner described above is preferably put in a large amount of water, a methanol/water mixture, or the like so as to precipitate, and filtered out, dried, and isolated. This precipitation operation removes unreacted monomers and oligomer components such as dimers and trimers to improve the characteristics of a heat-cured film. Furthermore, a cyclized polyimide obtained by imidizing a polyimide precursor may be

synthesized by a known method of imidizing the polyimide precursor obtained above.

[0057]

The following describes an example of a method of producing a polyimide precursor, which is a preferred example of the method (I). First, a di-amine compound having an R^2 group is dissolved in a polymerization solvent. A tetracarboxylic dianhydride having an R^1 group in substantially the same molar quantity as the di-amine compound is gradually added to the solution. The solution is stirred with the use of a mechanical stirrer at -20 to 100°C , preferably 10 to 50°C for 0.5 to 100 hours, more preferably 2 to 24 hours. In the case where a terminal blocking agent is used, the terminal blocking agent may be gradually added after the tetracarboxylic dianhydride is added and stirred at a desired temperature for a desired period of time, or may be added at one time and reacted.

[0058]

The polymerization solvent is not limited to a particular kind, provided that the polymerization solvent dissolves tetracarboxylic dianhydrides and di-amines which are raw monomers. Examples of the polymerization solvent include amides such as N,N -dimethylformamide, N,N -dimethylacetamide, and N -methyl-2-pyrrolidone; cyclic esters such as γ -butyrolactone, γ -valerolactone, δ -valerolactone, γ -caprolactone, ϵ -caprolactone, and α -methyl- γ -butyrolactone;

carbonates such as ethylene carbonate and propylene carbonate; glycols such as triethylene glycol; phenols such as m-cresol and p-cresol; acetophenone; 1,3-dimethyl-2-imidazolidinone; sulfolane; and dimethyl sulfoxide. It is preferable that the polymerization solvent be used in an amount of 100 to 1,900 parts by weight, more preferably 150 to 950 parts by weight, with respect to 100 parts by weight of the resulting resin.

[0059]

The photosensitive resin composition of the present invention may contain an alkali-soluble resin other than the resin having a structure represented by General Formula (1). Specific examples of the alkali-soluble resin include alkali-soluble polybenzoxazole, polybenzoxazole precursor, polyamide, acrylic polymer obtained by copolymerization of acrylic acid, novolac resin, resole resin, siloxane resin, polyhydroxystyrene resin, resins in which crosslink groups such as a methylol group, an alkoxymethyl group, or an epoxy group are introduced, and copolymers of these resins. These resins are soluble in an alkaline aqueous solution containing an alkali such as tetramethylammonium hydroxide, choline, triethylamine, dimethylaminopyridine, monoethanolamine, diethylaminoethanol, sodium hydroxide, potassium hydroxide, or sodium carbonate. The addition of any of these alkali-soluble resins makes it possible to impart the characteristics of this alkali-soluble resin while maintaining the adhesiveness and high sensitivity

of the heat-resistant resin film. It is preferable that the resin containing a structure represented by General Formula (1) account for 30 wt% or more of the resin contained in the photosensitive resin composition of the present invention.

[0060]

The following describes a photosensitive resin composition having a positive sensitivity of the present invention. However, the scope of the present invention is not limited to such a photosensitive resin composition. Also in regard to a photosensitive resin composition having a negative sensitivity in which the portion exposed to light is reacted by development, when a polyimide having a poor transparency is used, the photoreactive efficiency of the photosensitizer in the exposed portion decreases and thus the residual film rate decreases, resulting in difficulty of obtaining a thick film structure. Therefore, for a highly photosensitive resin composition, there is a demand for the development of a highly transparent polyimide as is the case with the positive type.

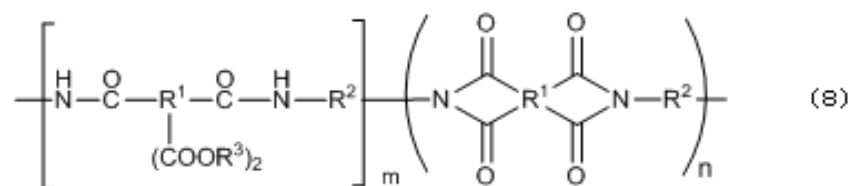
[0061]

The photosensitive resin composition having a positive photosensitivity of the present invention contains (a) a resin containing as a main component a structure represented by General Formula (8); (b) a photo acid generator; and (c) a solvent. As used herein, the main component means that the structure represented by General Formula (8) accounts for 50

mol% or more, preferably 70 mol% or more, even more preferably 90 mol% or more of the resin having the structure represented by General Formula (8).

[0062]

[Chemical formula 8]



[0063]

(In General Formula (8), each R^1 independently contains at least one organic group which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic ring, in an amount of 5 to 95 mol% assuming that the total amount of R^1 is 100 mol%; each R^2 independently represents a C2-C40 divalent organic group; R^3 represents hydrogen or a C1-C20 monovalent organic group; m and n each represent 0 to 100,000; and $m + n > 2$, with the proviso that

the structure represented by General Formula (8) essentially has a fluorine component and a phenolic hydroxyl group.)

The photosensitive resin composition having a positive photosensitivity of the present invention preferably contains a resin suitable for use in the earlier-mentioned photosensitive resin composition of the present invention, and may contain two or more of such resins.

[0064]

The photosensitive resin composition having a positive photosensitivity of the present invention may contain an alkali-soluble resin other than the resin containing as a main component a structure represented by General Formula (8). Specific examples include alkali-soluble polybenzoxazole, polybenzoxazole precursor, polyamide, acrylic polymer obtained by copolymerization of acrylic acid, novolac resin, resole resin, siloxane resin, polyhydroxystyrene resin, and resins in which crosslink groups such as methylol groups, alkoxymethyl groups, or epoxy groups are introduced, and copolymers of these resins. These resins are soluble in an alkaline aqueous solution containing an alkali such as tetramethylammonium hydroxide, choline, triethylamine, dimethylaminopyridine, monoethanolamine, diethylaminoethanol, sodium hydroxide, potassium hydroxide, or sodium carbonate. The addition of any of these alkali-soluble resins makes it possible to impart the characteristics of this alkali-soluble

resin while maintaining the adhesiveness and high sensitivity of the heat-resistant resin film.

[0065]

The photo acid generator which is the component (b) of the present invention is a compound that generates an acid upon irradiation with light and imparts the characteristics of increasing the solubility of the irradiated portion in an alkaline aqueous solution. Examples include quinonediazide compounds, sulfonium salts, phosphonium salts, diazonium salts, and iodonium salts.

[0066]

Examples of the quinonediazide compounds include compounds in which a quinonediazide sulfonic acid is bound to a polyhydroxy compound by an ester bond, compounds in which a quinonediazide sulfonic acid is bound to a polyamino compound by a sulfonamide bond, and compounds in which a quinonediazide sulfonic acid is bound to a polyhydroxypolyamino compound by an ester bond and/or a sulfonamide bond. Although not all the functional groups of these polyhydroxy compounds and polyamino compounds have to be substituted with quinonediazides, it is preferable that 50 mol% or more of all the functional groups be substituted with quinonediazides. If less than 50 mol% of the functional groups are substituted with quinonediazides, the solubility in an alkaline developer becomes too high, the contrast to the unexposed portion cannot be achieved, and a

desired pattern may not be obtained. The use of such a quinonediazide compound makes it possible to obtain a positive photosensitive resin composition which is sensitive to i-line (365 nm), h-line (405 nm), and g-line (436 nm) from a mercury lamp which are typical ultraviolet rays. These compounds may be used individually or a mixture of two or more of them may be used. Furthermore, the use of two photo acid generators makes it possible to increase the ratio of the dissolution rate of the exposed portion to that of the unexposed portion and, as a result, possible to obtain a highly photosensitive resin composition.

[0067]

Examples of the polyhydroxy compounds include, but are not limited to, Bis-Z, BisP-EZ, TekP-4HBPA, TrisP-HAP, TrisP-PA, TrisP-SA, TrisOCR-PA, BisOCHP-Z, BisP-MZ, BisP-PZ, BisP-IPZ, BisOCP-IPZ, BisP-CP, BisRS-2P, BisRS-3P, BisP-OCHP, methylene tris-FR-CR, BisRS-26X, DML-MBPC, DML-MBOC, DML-OCHP, DML-PCHP, DML-PC, DML-PTBP, DML-34X, DML-EP, DML-POP, dimethylol-BisOC-P, DML-PFP, DML-PSBP, DML-MTrisPC, TriML-P, TriML-35XL, TML-BP, TML-HQ, TML-pp-BPF, TML-BPA, TMOM-BP, HML-TPPHBA, HML-TPHAP (those listed above are the names of products available from Honshu Chemical Industry Co., Ltd.), BIR-OC, BIP-PC, BIR-PC, BIR-PTBP, BIR-PCHP, BIP-BIOC-F, 4PC, BIR-BIPC-F, TEP-BIP-A, 46DMOC, 46DMOEP, TM-BIP-A (those listed above are the names of products available from Asahi Organic

Chemicals Industry Co., Ltd.), 2,6-dimethoxymethyl-4-t-butyl phenol, 2,6-dimethoxymethyl-p-cresol, 2,6-diacetoxymethyl-p-cresol, naphthol, tetrahydroxy benzophenone, methyl gallate ester, bisphenol A, bisphenol E, methylene bisphenol, and BisP-AP (the name of a product available from Honshu Chemical Industry Co., Ltd.).

[0068]

Examples of the polyamino compounds include, but are not limited to, 1,4-phenylenediamine, 1,3-phenylenediamine, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl sulfone, and 4,4'-diaminodiphenyl sulfide.

[0069]

Examples of the polyhydroxy polyamino compounds include, but are not limited to, 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoro propane and 3,3'-dihydroxy benzidine.

[0070]

In the present invention, a preferred form of a quinonediazide may either be a 5-naphthoquinonediazide sulfonyl group or a 4-naphthoquinonediazide sulfonyl group. A 4-naphthoquinonediazide sulfonyl ester compound has an absorbency in the i-line region of the mercury lamp and thus is suitable for i-line exposure. A 5-naphthoquinonediazide sulfonyl ester compound has an absorbency that reaches the g-line region of the mercury lamp and thus is suitable for g-line

exposure. In the present invention, it is preferable to select a 4-naphthoquinonediazide sulfonyl ester compound or a 5-naphthoquinonediazide sulfonyl ester compound depending on the wavelength of the light for exposure. Furthermore, a naphthoquinonediazide sulfonyl ester compound that has both a 4-naphthoquinonediazide sulfonyl group and a 5-naphthoquinonediazide sulfonyl group per molecule may be obtained. Alternatively, a mixture of a 4-naphthoquinonediazide sulfonyl ester compound and a 5-naphthoquinonediazide sulfonyl ester compound may be used.

[0071]

In the case where the molecular weight of the quinonediazide compound is more than 5,000, the quinonediazide compound is not pyrolyzed sufficiently during the heat treatment performed afterwards. Thus, there may be a problem in that the heat resistance of the resulting film decreases, mechanical characteristics of the resulting film decrease, or the adhesiveness of the resulting film decreases. In view of this, the molecular weight of the quinonediazide compound is preferably 300 to 3,000, more preferably 350 to 1,500.

[0072]

The quinonediazide compound for use in the present invention is synthesized from a specific phenol compound by the following method. An example of the method is a method by which a 5-naphthoquinonediazide sulfonyl chloride and a phenolic

compound are reacted in the presence of triethylamine. The phenol compound is synthesized by, for example, a method by which an α -(hydroxyphenyl) styrene derivative is reacted with a polyhydric phenolic compound in the presence of an acid catalyst.

[0073]

The photo acid generator for use as the component (b) of the present invention is preferably a sulfonium salt, a phosphonium salt, or a diazonium salt which is a photo acid generator that moderately stabilizes the acid component generated by exposure to light. Since a resin composition obtained from the photosensitive resin composition of the present invention is used as a permanent film, the remaining phosphorus or the like is not preferred for environmental reasons. Further, the color tone of the film needs to be taken into consideration. Therefore, a sulfonium salt is preferred among those listed above. Especially preferred is a triarylsulfonium salt.

[0074]

Since the photosensitive resin composition of the present invention contains the photo acid generator (b), an acid is generated in the portion irradiated with light and the portion becomes more soluble in an alkaline aqueous solution. This makes it possible to obtain a positive pattern in which the portion irradiated with light becomes soluble.

[0075]

The amount of each photo acid generator for use as the component (b) in the present invention is preferably 0.01 to 50 parts by weight with respect to 100 parts by weight of the resin (a) which contains as a main component a structure represented by General Formula (8). Among these, a quinonediazide compound is preferably contained in an amount of 3 to 40 parts by weight. Furthermore, the total amount of a compound(s) selected from sulfonium salts, phosphonium salts, and diazonium salts is preferably 0.05 to 40 parts by weight, more preferably 0.1 to 30 parts by weight. When the amount of the photo acid generator (b) is within this range, a higher sensitivity is achieved. A sensitizer or the like may further be contained depending on need.

[0076]

Furthermore, for the purpose of improving the sensitivity of the photosensitive resin composition, a compound having a phenolic hydroxyl group may be contained if needed, provided that the shrinkage after curing is not reduced.

[0077]

Examples of the compound having a phenolic hydroxyl group include Bis-Z, BisOC-Z, BisOPP-Z, BisP-CP, Bis26X-Z, BisOTBP-Z, BisOCHP-Z, BisOCR-CP, BisP-MZ, BisP-EZ, Bis26X-CP, BisP-PZ, BisP-IPZ, BisCR-IPZ, BisOCP-IPZ, BisOIPP-CP, Bis26X-IPZ, BisOTBP-CP, TekP-4HBPA (tetrakisP-DO-BPA), TrisP-HAP,

TrisP-PA, TrisP-SA, TrisOCR-PA, BisOFP-Z, BisRS-2P, BisPG-26X, BisRS-3P, BisOC-OCHP, BisPC-OCHP, Bis25X-OCHP, Bis26X-OCHP, BisOCHP-OC, Bis236T-OCHP, methylenetris-FR-CR, BisRS-26X, BisRS-OCHP (those listed above are the names of products available from Honshu Chemical Industry Co., Ltd.), BIR-OC, BIP-PC, BIR-PC, BIR-PTBP, BIR-PCHP, BIP-BIOC-F, 4PC, BIR-BIPC-F, and TEP-BIP-A (those listed above are the names of products available from Asahi Organic Chemicals Industry Co., Ltd.).

[0078]

Among those listed above, a preferred compound having a phenolic hydroxyl group for use in the present invention is, for example, Bis-Z, BisP-EZ, TekP-4HBPA, TrisP-HAP, TrisP-PA, BisOCHP-Z, BisP-MZ, BisP-PZ, BisP-IPZ, BisOCP-IPZ, BisP-CP, BisRS-2P, BisRS-3P, BisP-OCHP, methylenetris-FR-CR, BisRS-26X, BIP-PC, BIR-PC, BIR-PTBP, BIR-BIPC-F, or the like. Among these, a particularly preferred compound having a phenolic hydroxyl group is, for example, Bis-Z, TekP-4HBPA, TrisP-HAP, TrisP-PA, BisRS-2P, BisRS-3P, BIR-PC, BIR-PTBP, or BIR-BIPC-F. Since the compound having a phenolic hydroxyl group is contained, the resulting resin composition does not dissolve in an alkaline developer much before exposure to light but readily dissolves in the alkaline developer upon exposure to light. Therefore, the loss of the film upon development is small and the development can be quickly and readily performed.

[0079]

The amount of such a compound having a phenolic hydroxyl group is preferably 1 to 50 parts by weight, more preferably 3 to 40 parts by weight, with respect to 100 parts by weight of the resin (a) which contains as a main component a structure represented by General Formula (8).

[0080]

The photosensitive resin composition having a positive photosensitivity of the present invention contains the solvent (c). Examples of the solvent include polar aprotic solvents such as N-methyl-2-pyrrolidone, γ -butyrolactone, N,N-dimethylformamide, N,N-dimethylacetamide, and dimethyl sulfoxide; ethers such as tetrahydrofuran, dioxane, and propylene glycol monomethyl ether; ketones such as acetone, methyl ethyl ketone, diisobutyl ketone, and diacetone alcohol; esters such as ethyl acetate, propylene glycol monomethyl ether acetate, 3-methoxymethyl propanoate, 3-ethoxyethyl propanoate, ethyl acetate, and ethyl lactate; and aromatic hydrocarbons such as toluene and xylene. Two or more of these may be contained. The amount of the solvent (c) is preferably 100 parts by weight or more and 1,500 parts by weight or less with respect to 100 parts by weight of the resin (a) which contains as a main component a structure represented by General Formula (8).

[0081]

The photosensitive resin composition having a positive sensitivity of the present invention may contain components other than the above-described (a) to (c), and preferably contains a compound having an alkoxymethyl group, a methylol group, or an epoxy group. Since the methylol group and alkoxymethyl group undergo a crosslinking reaction in the temperature region of 100°C or higher, a crosslink is formed by heat treatment and a heat-resistant resin film having high mechanical characteristics is obtained.

[0082]

Examples of a compound having an alkoxymethyl group or a methylol group include DML-PC, DML-PEP, DML-OC, DML-OEP, DML-34X, DML-PTBP, DML-PCHP, DML-OCHP, DML-PFP, DML-PSBP, DML-POP, DML-MBOC, DML-MBPC, DML-MTrisPC, DML-BisOC-Z, DML-BisOCHP-Z, DML-BPC, DML-BisOC-P, DMOM-PC, DMOM-PTBP, DMOM-MBPC, TriML-P, TriML-35XL, TML-HQ, TML-BP, TML-pp-BPF, TML-BPE, TML-BPA, TML-BPAF, TML-BPAP, TMOM-BP, TMOM-BPE, TMOM-BPA, TMOM-BPAF, TMOM-BPAP, HML-TPPHBA, HML-TPHAP, HMOM-TPPHBA, and HMOM-TPHAP (those listed above are the names of products available from Honshu Chemical Co., Ltd.), NIKALAC (registered trademark) MX-290, NIKALAC MX-280, NIKALAC MX-270, NIKALAC MX-279, NIKALAC MW-100LM and NIKALAC MX-750LM (those listed above are the names of products available from Sanwa Chemical Co., Ltd.). Among these, the addition of HMOM-TPHAP or MW-100LM containing many alkoxymethyl groups is preferable

because the crosslinking efficiency is good.

[0083]

Furthermore, since epoxy groups are thermally crosslinked with polymers at 200°C or lower and the crosslinking does not cause a dehydration reaction, the film does not shrink much and thus the epoxy groups are effective for achieving mechanical characteristics as well as low-temperature curing and reducing warpage. Examples of the compound having an epoxy group include silicones containing an epoxy group such as bisphenol A epoxy resin, bisphenol F epoxy resin, propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, and polymethyl(glycidyloxypropyl) siloxane. However, the present invention is not limited in any way by these examples. Specific examples include EPICLON 850-S, EPICLON HP-4032, EPICLON HP-7200, EPICLON HP-820, EPICLON HP-4700, EPICLON EXA-4710, EPICLON HP-4770, EPICLON EXA-859CRP, EPICLON EXA-1514, EPICLON EXA-4880, EPICLON EXA-4850-150, EPICLON EXA-4850-1000, EPICLON EXA-4816, and EPICLON EXA-4822 (those listed above are the names of products available from Dainippon Ink and Chemicals), RIKARESIN BEO-60E (the name of a product available from New Japan Chemical Co., Ltd.), EP-4003S and EP-4000S (ADEKA CORPORATION).

[0084]

Two or more of these compounds having an alkoxymethyl group, a methylol group, or an epoxy group may be contained.

[0085]

The amount of the compound having an alkoxymethyl group, a methylol group, or an epoxy group is 10 to 50 parts by weight, preferably 10 to 40 parts by weight, with respect to 100 parts by weight of the resin containing as a main component a structure represented by General Formula (8).

[0086]

The photosensitive resin composition of the present invention may further contain a silane compound. The addition of a silane compound improves the adhesiveness of the heat-resistant resin film. Specific examples of the silane compound include N-phenyl aminoethyl trimethoxysilane, N-phenyl aminoethyl triethoxysilane, N-phenyl aminopropyl trimethoxysilane, N-phenyl aminopropyl triethoxysilane, N-phenyl aminobutyl trimethoxysilane, N-phenyl aminobutyl triethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltrichlorosilane, vinyl-tris(β -methoxyethoxy)silane, 3-methacryloxypropyl trimethoxysilane, 3-acryloxypropyl trimethoxysilane, p-styryl trimethoxysilane, 3-methacryloxypropylmethyl dimethoxysilane, and 3-methacryloxypropylmethyl diethoxysilane. The amount of the silane compound is preferably 0.01 parts by weight or more and 15 parts by weight or less with respect to 100 parts by weight of the resin (a) which contains as a main component a structure represented by General Formula (8).

[0087]

Furthermore, for the purpose of improving wettability on a substrate, the photosensitive resin composition having a positive photosensitivity of the present invention may contain, depending on need, a surfactant; an ester such as ethyl lactate or propylene glycol monomethyl ether acetate; an alcohol such as ethanol; a ketone such as cyclohexanone or methyl isobutyl ketone; an ether such as tetrahydrofuran or dioxane, and/or the like. Furthermore, for the purpose of, for example, reducing thermal expansion coefficient, increasing dielectric constant, or reducing dielectric constant, the photosensitive resin composition may contain inorganic particles such as silicon dioxide or titanium dioxide or polyimide powder or the like.

[0088]

The following describes examples of a method of producing a photosensitive resin composition of the present invention. Examples include a method by which the components (a) to (c) described earlier and other components depending on need are put in a glass flask or a stainless steel vessel and stirred to dissolve with a mechanical stirrer or the like; a method by which the mixture is dissolved ultrasonically; and a method by which the mixture is stirred to dissolve with the use of a planetary mixing defoamer. The viscosity of the positive photosensitive resin composition is preferably 1 to 10,000 mPa·s. Furthermore, the photosensitive resin composition may be passed

through a filter having a pore size of 1 μm to 5 μm for removing impurities.

[0089]

The following describes a method of forming a pattern of a heat-resistant resin film from the photosensitive resin composition of the present invention.

[0090]

The photosensitive resin composition of the present invention may be made into a pattern of a polyimide through a process of applying the photosensitive resin composition on a support substrate and drying the photosensitive resin composition, a process of exposing the photosensitive resin composition to light, a process of developing the photosensitive resin composition, and a process of treating the photosensitive resin composition with heat.

[0091]

First, a photosensitive resin composition is applied on a substrate. The substrate is of, but not limited to, a silicon wafer, ceramics, gallium arsenide, metal, glass, metallic oxide dielectric film, silicon nitride, ITO, or the like. The photosensitive resin composition may be applied by spin coating using a spinner, spray application, roll coating, slit die coating, or the like. The photosensitive resin composition is usually applied so that the applied resin composition after drying will have a thickness of 0.1 to 150 μm , although the

thickness depends on the method of application and the solid content concentration, viscosity, or the like of the positive photosensitive resin composition.

[0092]

Next, the substrate which has the photosensitive resin composition thereon is dried to obtain a photosensitive resin film. The drying is performed preferably at a temperature of 50°C to 150°C for 1 minute to several hours with the use of an oven, hot plate, infrared rays, or the like.

[0093]

Next, the photosensitive resin film is irradiated with actinic rays through a mask in a desired pattern. Examples of the actinic rays for use for exposure include ultraviolet rays, visible rays, electron rays, and X rays. In the present invention, it is preferable to use i-line (365 nm), h-line (405 nm), or g-line (436 nm) of a mercury lamp.

[0094]

In order to form a pattern from the photosensitive resin film, it is only necessary to remove the exposed portion with the use of a developer after exposure. The developer is preferably an aqueous solution of an alkaline compound such as tetramethylammonium, diethanolamine, diethylaminoethanol, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, triethylamine, diethylamine, methylamine, dimethylamine, dimethylaminoethyl acetate,

dimethylaminoethanol, dimethylaminoethyl methacrylate, cyclohexylamine, ethylenediamine, or hexamethylenediamine. In some cases, these alkaline aqueous solutions may contain one or more of the following: polar solvents such as N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, γ -butyrolactone, and dimethylacrylamide; alcohols such as methanol, ethanol, and isopropanol; esters such as ethyl lactate and propylene glycol monomethyl ether acetate; ketones such as cyclopentanone, cyclohexanone, isobutyl ketone, and methyl isobutyl ketone; and the like. After the development, the photosensitive resin film is usually rinsed with water. In the process of rinsing, the water may contain one or more of the following: alcohols such as ethanol and isopropyl alcohol; esters such as ethyl lactate, propylene glycol monomethyl ether acetate, and 3-methoxymethyl propanoate; and the like.

[0095]

After the development, the photosensitive resin film is heated at a temperature of 150°C to 500°C to become a heat-resistant resin film. This heat treatment is performed preferably for 5 minutes to 5 hours while gradually raising the temperature to a selected temperature or sequentially raising the temperature within a selected temperature range. Examples include a method by which heat treatment is performed at 130°C for 30 minutes, 200°C for 30 minutes, and 350°C for 30 minutes;

and a method by which the temperature is raised linearly from room temperature to 320°C over 2 hours. The heat treatment is performed preferably at a temperature of 250°C or lower because otherwise the electric characteristics of the device may change and the warpage of the substrate may increase due to high-temperature heating or repeating of the high-temperature heating.

[0096]

The heat-resistant resin film formed from the photosensitive resin composition of the present invention may be used in an electronic component of a semiconductor device, a multilayer wiring board, or the like. Specifically, the heat-resistant resin film is suitable for use in the applications of a passivation film of a semiconductor, a surface protective film or an interlayer dielectric film of a semiconductor device, an interlayer dielectric film for high-density multilayer wiring, a dielectric layer for an organic electroluminescent element, or the like. However, this does not imply any limitation and the heat-resistant resin film may have a variety of structures.

[0097]

The following describes an application of a photosensitive resin composition of the present invention to a semiconductor device having a bump with reference to the drawings. Fig. 1 is an enlarged cross-sectional view of a pat

portion of a semiconductor device having a bump of the present invention. As illustrated in Fig. 1, a silicon wafer 1 has an Al pad 2 for input/output thereon that has a passivation film 3 thereon. The passivation film 3 has a via hole. On the passivation film 3, a pattern (dielectric film) 4 made of a photosensitive resin composition of the present invention is disposed and, on the pattern 4, a metal (Cr, Ti or the like) film 5 is disposed so as to be in contact with the Al pad 2. The metal film 5 etches around each solder bump 10 and insulates the bumps from each other. Each insulated pad has a barrier metal 8 and the solder bump 10. In the case where the photosensitive resin composition has a soft component, the wafer does not warp much and thus it is possible to perform light exposure and transport the wafer with high accuracy. Furthermore, since the polyimide resin is excellent also in mechanical characteristics, it is possible to reduce the stress from a sealing resin also when installed. Therefore, it is possible to prevent damage to a low-k layer and provide a highly reliable semiconductor device.

[0098]

The following describes a method of forming a semiconductor device in detail. As illustrated in 2c of Fig. 2, a metal wiring 6 in the form of a film is formed by plating. Next, as illustrated in 2d' of Fig. 2, a photosensitive resin composition of the present invention is applied and a

photolithography process is performed to form a pattern (dielectric film 7) illustrated in 2d of Fig. 2. In this step, the photosensitive resin composition in the dielectric film 7 is processed to have a large thickness in a scribe line 9. In the case where a multilayer wiring structure having three or more layers is to be formed, the above process may be repeated to form each layer. Since the multilayer wiring structure is formed by repeatedly forming a dielectric film in this way, the total thickness of the interlayer dielectric films is 10 μm or more. In view of the effects on warpage of a chip and the like, the total thickness is preferably 50 μm or less. The larger the number of layers of a multilayer wiring structure, the thicker film formation becomes required in a scribe line, and therefore it is preferable that the photosensitive resin composition be able to give a heat-resistant resin film that can be made into a pattern having a thickness of 10 μm or more. Furthermore, in order to form a highly dense multilayer wiring structure, it is also preferable that the photosensitive resin composition be able to give a high-resolution, heat-resistant resin film. Next, as illustrated in 2e and 2f of Fig. 2, the barrier metal 8 and the solder bump 10 are formed. Then, lastly, the film is cut along the scribe line 9 with a dicing machine into individual chips. In the case where the dielectric film 7 is not patterned in the scribe line 9 or in the case where the residue is remaining in the scribe line 9, cracks or the

like occur when cut with a dicing machine, which affects the reliability evaluation of the chip. Therefore, providing pattern processing excellent in thick film processing like the present invention is very preferred for high reliability of semiconductor devices.

EXAMPLES

[0099]

The following describes the present invention by using Examples and the like. However, the present invention is not limited to these examples. It should be noted that resins and photosensitive resin compositions of Examples were evaluated by the following methods.

[0100]

(Method of measuring film thickness)

A photosensitive resin composition was prebaked, and developed, and the thickness of the cured film was measured with the use of a Lambda Ace STM-602 available from Dainippon Screen Mfg. Co., Ltd., on the assumption that the refractive index was 1.629.

[0101]

(Preparation of developed film A)

Varnish was applied to an 8-inch silicon wafer by spin coating and then baked for 3 minutes with the use of a hot plate (a coater developer Act-8 available from Tokyo Electron Limited) at 120°C to obtain a prebaked film having a thickness

of 10 μm . This film was exposed to light with the use of an i-line stepper (NIKON NSR i9) at doses in the range of 0 to 1,000 mJ/cm^2 with a step of 10 mJ/cm^2 . After the exposure, the film was developed with a 2.38 wt% tetramethylammonium (TMAH) aqueous solution (ELM-D available from Mitsubishi Gas Chemical Co., Inc.) for 90 seconds, and then rinsed with pure water to obtain a developed film A having an isolated pattern of 10 μm .
[0102]

(1) Evaluation on sensitivity

In regard to the developed film A, the dose (represented as the minimum dose E_{th}) at which the exposed portion completely dissolved away after the exposure and development was used as a sensitivity. When the E_{th} is 400 mJ/cm^2 or less, the sensitivity is determined as high. A sensitivity of 300 mJ/cm^2 or less is more preferable.

[0103]

(2) Evaluation on residual film rate

The percentage of the thickness of the developed film with respect to that of the prebaked film is used as a residual film rate (residual film rate = (thickness of developed film)/(thickness of prebaked film) $\times$ 100)). A rate of 80% or more was determined as "pass".

[0104]

(3) Evaluation on pattern of developed film

In regard to the photosensitive resin composition film

formed by development, the surface was visually checked for tackiness in the unexposed portion and residues in the exposed portion. When the pattern of the developed film did not have any problems, the pattern was determined as good (O). When the pattern of the developed film had tackiness in the unexposed portion or a residue in the exposed portion, the pattern was determined as poor (X).

[0105]

(Preparation of heat-resistant resin film B)

Varnish was applied to an 8-inch silicon wafer by spin coating and then baked for 3 minutes with the use of a hot plate (a coater developer Act-8 available from Tokyo Electron Limited) at 120°C to obtain prebaked films having different thicknesses. Each film was exposed to light with the use of an i ray stepper (Nikon NSR i9) at a dose of 1,000 mJ/cm². After the exposure, the film was developed with a 2.38 wt% tetramethylammonium (TMAH) aqueous solution (ELM-D available from Mitsubishi Gas Chemical Co., Inc.) for 90 seconds, and then rinsed with pure water to obtain a developed film. The developed film was treated with heat at an oxygen concentration of 20 ppm or lower while raising the temperature to 250°C at 5°C/min. and at 250°C for 1 hour with the use of an inert oven CLH-21CD-S (available from Koyo Thermo Systems Co., Ltd.). The silicon wafer was removed from the oven when the temperature reached 50°C or lower, and the thickness of the heat-resistant

film on the silicon wafer was measured.

[0106]

(4) Evaluation on thick film formation

In regard to the heat-resistant resin film, the maximum thickness of the film at a point in time in which the exposed portion completely dissolved away and a pattern was formed (this is referred to as patternable) was evaluated. When a heat-resistant resin film was able to be patterned to have a thickness of 15 μm or more, then it was evaluated as excellent ($\odot$). When a heat-resistant resin film was able to be patterned to have a thickness of 10 μm or more and less than 15 μm , then it was evaluated as good ($\circ$), and when a heat-resistant resin film was able to be patterned to have a thickness less than 10 μm , then it was evaluated as poor ($\times$).

(5) Evaluation on resolution

In regard to a heat-resistant resin film having a thickness of 10 μm , the size of the smallest opening in the pattern was measured and used as a resolution. When the resolution was less than 3 μm , then it was evaluated as excellent ($\odot$). When the resolution was 3 μm or more and less than 7 μm , then it was evaluated as good ($\circ$). When the resolution was 7 μm or more and less than 10 μm , then it was evaluated as acceptable ($\triangle$). When the resolution was 10 μm or more or when a heat-resistant resin film having a thickness of 10 μm was not obtained, then it was evaluated as poor ($\times$).

[0107]

The following are the abbreviations of acid dianhydrides and di-amines in the following Examples and Comparative Examples.

PMDA-HH: 1S,2S,4R,5R-cyclohexane tetracarboxylic dianhydride

TDA100:

1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)naphtho[1,2-c]furan-1,3-dione

CBDA: cyclobutanetetracarboxylic dianhydride

6FDA: 4,4'-hexafluoroisopropylidenediphthalic dianhydride

ODPA: 3,3',4,4'-diphenylethertetracarboxylic dianhydride

SiDA: 1,1,3,3-tetramethyl-1,3-bis(3-aminopropyl) disiloxane

BAHF: 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane

APBS: bis(3-amino-4-hydroxyphenyl) sulfone

DAE: 4,4'-diaminodiphenyl ether

NMP: N-methyl-2-pyrrolidone

ED-600: JEFFAMINE ED-600 (name of a product available from HUNTSMAN Corporation)

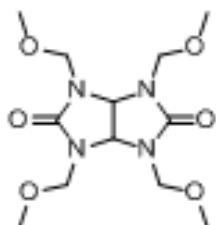
KBM-403: 3-glycidoxypropyltrimethoxysilane

[0108]

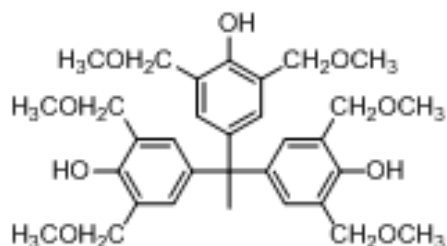
The following are thermal cross-linkable compounds used in Examples and Comparative Examples.

[0109]

【 Chemical formula 9】



MX-270



HMOM-TPHAP

[0110]

SYNTHESIS EXAMPLE 1 Synthesis of hydroxyl-containing di-amine compound (a)

BAHF in an amount of 18.3 g (0.05 mol) was dissolved in 100 mL of acetone and 17.4 g (0.3 mol) of propylene oxide and cooled to -15°C. To this mixture, a solution obtained by dissolving 20.4 g (0.11 mol) of 3-nitrobenzoyl chloride in 100 mL of acetone was dropped. After the dropping, the mixture was reacted at -15°C for 4 hours and then the temperature was changed to room temperature. The precipitated white solid material was separated by filtration and dried in vacuum at 50°C.

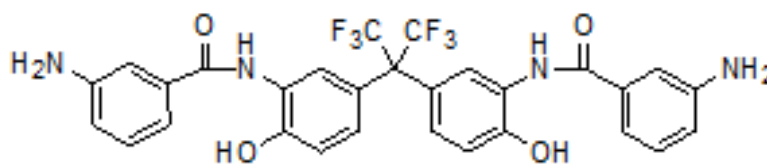
[0111]

The obtained white solid material in an amount of 30 g was put in a 300 mL stainless steel autoclave, and dispersed in 250 mL of methyl cellosolve, and 2 g of 5% palladium-carbon was added. Hydrogen was introduced here with a balloon and a

reducing reaction was performed at room temperature. After about 2 hours, it was confirmed that the balloon did not shrink anymore and the reaction was ended. After the reaction was ended, the resultant was passed through a filter to remove a palladium compound which was a catalyst, and concentrated with a rotary evaporator, to obtain a hydroxyl-containing di-amine compound (a) represented by the following formula. The obtained solid material was used without changes for a reaction.

[0112]

【 Chemical formula 10】



Hydroxyl-containing di-amine compound (a)

[0113]

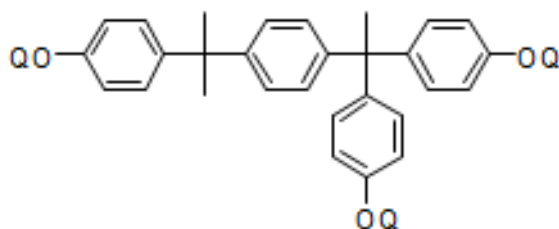
SYNTHESIS EXAMPLE 2 Synthesis of quinonediazide compound (b)

In a dry nitrogen gas flow, 21.22 g (0.05 mol) of TrisP-PA (name of a product available from HONSHU CHEMICAL INDUSTRY CO., LTD.), 26.86 g (0.10 mol) of 5-naphthoquinonediazide sulfonyl acid chloride, and 13.43 g (0.05 mol) of 4-naphthoquinonediazide sulfonyl acid chloride were dissolved in 50 g of 1,4-dioxane and the temperature was controlled to room temperature. To the obtained mixture, a mixture of 50 g of 1,4-dioxane and 15.18 g of triethylamine was dropped while

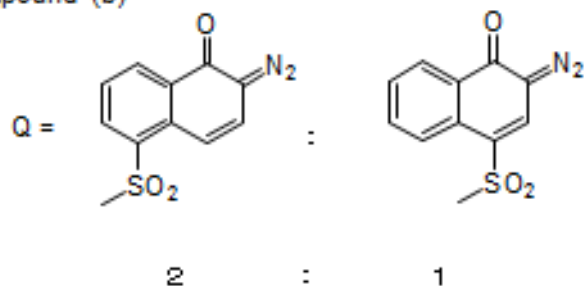
keeping the temperature inside the system lower than 35°C. After the dropping, the mixture was stirred at 30°C for 2 hours. The triethylamine salt was filtered out and the filtrate was put in water. After that, the separated precipitate was collected by filtration. The precipitate was dried with a vacuum dryer, to obtain a quinonediazide compound (b) represented by the following formula.

[0114]

【 Chemical formula 11】



Quinonediazide compound (b)



[0115]

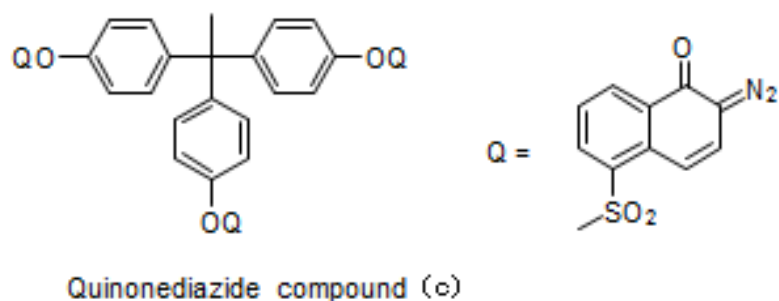
SYNTHESIS EXAMPLE 3 Synthesis of quinonediazide compound (c)

In a dry nitrogen gas flow, 15.31 g (0.05 mol) of TrisP-HAP (name of a product available from HONSHU CHEMICAL INDUSTRY CO., LTD.) and 40.28 g (0.15 mol) of 5-naphthoquinonediazide

sulfonyl acid chloride were dissolved in 450 g of 1,4-dioxane and the temperature was controlled to room temperature. With the use of a mixture of 50 g of 1,4-dioxane and 15.18 g of triethylamine, the same process as in Synthesis Example 2 was performed to obtain a quinonediazide compound (c) represented by the following formula.

[0116]

[Chemical formula 12]



[0117]

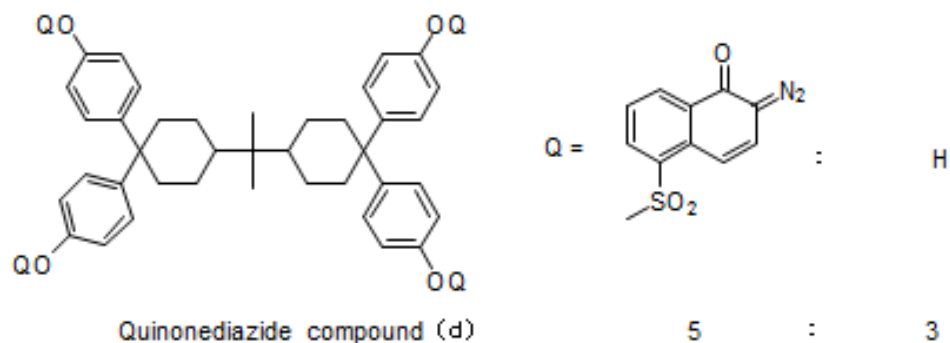
SYNTHESIS EXAMPLE 4 Synthesis of quinonediazide compound (d)

In a dry nitrogen gas flow, 28.83 g (0.05 mol) of TekP-4HBPA (name of a product available from HONSHU CHEMICAL INDUSTRY CO., LTD.) and 13.43 g (0.125 mol) of 5-naphthoquinonediazide sulfonyl acid chloride were dissolved in 450 g of 1,4-dioxane and the temperature was controlled to room temperature. With the use of a mixture of 50 g of 1,4-dioxane and 20.24 g of triethylamine, the same process as

in Synthesis Example 2 was performed to obtain a quinonediazide compound (d) represented by the following formula.

[0118]

[Chemical formula 13]



[0119]

SYNTHESIS EXAMPLE 5 Synthesis of acrylic resin (e)

To a 500 ml flask, 5 g of 2,2'-azobis(isobutyronitrile), 5 g of t-dodecanthiol, and 150 g of propylene glycol monomethyl ether acetate (hereinafter referred to as PGMEA for short) were introduced. After that, 30 g of methacrylic acid, 35 g of benzyl methacrylate, and 35 g of tricyclo[5.2.1.0^{2,6}]decan-8-yl methacrylate were introduced, and stirred at room temperature for a while, the air inside the flask was replaced with nitrogen, and the mixture was then stirred with heat at 70°C for 5 hours. Next, 15 g of glycidyl methacrylate, 1 g of dimethylbenzylamine, and 0.2 g of p-methoxyphenol were added to the obtained solution, stirred with heat at 90°C for 4 hours, to obtain a solution of an alkali-soluble acrylic resin (e). The solid content

concentration of the acrylic resin solution (e) was 43 wt%.

[0120]

SYNTHESIS EXAMPLE 6 Synthesis of novolac resin (f)

In a dry nitrogen gas flow, 70.2 g (0.65 mol) of m-cresol, 37.8 g (0.35 mol) of p-cresol, 75.5 g (0.93 mol of formaldehyde) of 37 wt% formaldehyde aqueous solution, 0.63 g (0.005 mol) of oxalic acid dihydrate, and 264 g of methyl isobutyl ketone were introduced, and then immersed in an oil bath, and the reaction liquid was subjected to a polycondensation reaction at reflux for 4 hours. After that, the temperature of the oil bath was raised over 3 hours, the pressure inside the flask was reduced to 40 to 67 hPa, a volatile component was removed, and the resin dissolved in the liquid was cooled to room temperature, to obtain an alkali-soluble novolac resin (f) in the form of a solid polymer. The Mw found by GPC was 3,500. To the obtained novolac resin (f), γ -butyrolactone (GBL) was added to obtain a solution of the novolac resin (f) having a solid content concentration of 43 wt%.

[0121]

SYNTHESIS EXAMPLE 7 Synthesis of polybenzoxazole precursor (g)

In a dry nitrogen gas flow, 18.3 g (0.05 mol) of BAHF was dissolved in 50 g of NMP and 26.4 g (0.3 mol) of glycidylmethyl ether, and the temperature of the solution was cooled to -15°C. To this solution, a solution obtained by dissolving 14.7 g of diphenyl ether dicarboxylic acid dichloride (0.050 mol,

available from NIHON NOHYAKU CO., LTD.) in 25 g of GBL was dropped while keeping the internal temperature to lower than 0°C. After the dropping, the solution was stirred at -15°C for another 6 hours. After the reaction finished, the solution was poured into 3 L of water containing 10 wt% of ethanol and white precipitate was deposited. The deposition was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain an alkali-soluble polybenzoxazole precursor (g). GBL was added to the obtained polybenzoxazole precursor (g) to obtain a solution of polybenzoxazole precursor (g) having a solid content concentration of 43 wt%.

[0122]

SYNTHESIS EXAMPLE 8 Synthesis of polyhydroxystyrene (h)

p-t-butoxystyrene and styrene in a total amount of 20 g at a molar ratio of 3 : 1 was added to a mixed solution of 500 ml of tetrahydrofuran and 0.01 mol of sec-butyllithium as an initiator and polymerized with stirring for 3 hours. A polymerization termination reaction was caused by adding 0.1 mol of methanol to the reaction liquid. Next, for purification of the polymer, the reaction mixture was poured into methanol and the precipitated polymer was dried, to obtain a white polymer. The polymer was further dissolved in 400 ml of acetone, a small amount of concentrated hydrochloric acid was added at 60°C, and the mixture was stirred for 7 hours. The mixture was

then poured into water, the polymer was precipitated, p-t-butoxystyrene was deprotected to give hydroxystyrene, and the resultant was washed and dried, to obtain a purified copolymer (h) of p-butoxystyrene and styrene.

[0123]

EXAMPLE 1

In a dry nitrogen gas flow, 15.57 g (0.04 mol) of BAHF and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 1.12 g (0.005 mol) of PMDA-HH, 19.99 g (0.045 mol) of 6FDA, and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (A) powder.

[0124]

17.5 g of the obtained resin (A), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g the acrylic resin (e) obtained in Synthesis Example 5, 3.0 g of a crosslink agent MX-270, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish A of a positive photosensitive resin composition. Using the obtained varnish A, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film

formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown in Table 2.

[0125]

EXAMPLE 2

In a dry nitrogen gas flow, 11.90 g (0.03 mol) of BAHF, 2.0 g (0.01 mol) of DAE, and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 10.09 g (0.045 mol) of PMDA-HH, 2.22 g (0.005 mol) of 6FDA, and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (B) powder.

[0126]

17.5 g of the obtained resin (B), 2.3 g of the quinonediazide compound (c) obtained in Synthesis Example 3, 16 g of the novolac resin (f) obtained in Synthesis Example 6, 3.0 g of a crosslink agent MX270, and 1.0 g of KBM403 were added to 50 g of GBL to obtain varnish B of a positive photosensitive resin composition. Using the obtained varnish B, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as

described earlier. The results of the evaluations are shown in Table 2.

[0127]

EXAMPLE 3

In a dry nitrogen gas flow, 25.68 g (0.04 mol) of the compound (a) obtained in Synthesis Example 1 and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 4.48 g (0.02 mol) of PMDA-HH, 9.31 g (0.03 mol) of ODPA, and 10 g of NMP were added and reacted at 40°C for 1 hour. After that, a solution obtained by diluting 13.10 g (0.11 mol) of N,N-dimethylformamide dimethyl acetal with 15 g of NMP was dropped over 10 minutes. After that, the solution was stirred at 40°C for 1 hour. After the reaction finished, the solution was poured into 2 L of water and solid precipitate was collected by filtration. The solid resin was dried with a vacuum dryer at 50°C for 72 hours, to obtain a polyimide precursor resin (C).

[0128]

17.5 g of the obtained resin (C), 2.3 g of the quinonediazide compound (d) obtained in Synthesis Example 4, 16 g of the polybenzoxazole resin (g) obtained in Synthesis Example 7, 3.0 g of a crosslink agent HMOM-TPHAP, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish C of a positive photosensitive resin composition. Using the obtained varnish C, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film

formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown in Table 2.

[0129]

EXAMPLE 4

In a dry nitrogen gas flow, 11.91 g (0.04 mol) of APBS and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 4.48 g (0.02 mol) of PMDA-HH, 13.33 g (0.03 mol) of 6FDA, and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (D) powder.

[0130]

17.5 g of the obtained resin (D), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the polyhydroxystyrene resin (h) obtained in Synthesis Example 8, 3.0 g of a crosslink agent MX-270, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish D of a positive photosensitive resin composition. Using the obtained varnish D, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as

described earlier. The results of the evaluations are shown in Table 2.

[0131]

EXAMPLE 5

In a dry nitrogen gas flow, 11.91 g (0.04 mol) of APBS and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 6.01 g (0.02 mol) of TDA-100, 13.33 g (0.03 mol) of 6FDA, and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (E) powder.

[0132]

17.5 g of the obtained resin (E), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the acrylic resin (e) obtained in Synthesis Example 5, 3.0 g of a crosslink agent HMOM-TPHAP, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish E of a positive photosensitive resin composition. Using the obtained varnish E, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown

in Table 2.

[0133]

EXAMPLE 6

In a dry nitrogen gas flow, 9.16 g (0.03 mol) of BAHF, 2.0 (0.01 mol) of DAE, 4.5 g (0.008 mol) of ED600, and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 6.01 g (0.02 mol) of TDA-100, 13.33 g (0.03 mol) of 6FDA, and 10 g of NMP were added and reacted at 40°C for 1 hour. After that, a solution obtained by diluting 13.10 g (0.11 mol) of N,N-dimethylformamide dimethyl acetal with 15 g of NMP was dropped over 10 minutes. After that, the solution was stirred at 40°C for 1 hour. After the reaction finished, the solution was poured into 2 L of water and solid precipitate was collected by filtration. The solid resin was dried with a vacuum dryer at 50°C for 72 hours, to obtain a polyimide precursor resin (F).

[0134]

17.5 g of the obtained resin (F), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the polyhydroxystyrene resin (h) obtained in Synthesis Example 8, 3.0 g of a crosslink agent HMOM-TPHAP, and 1.0 g of KBM403 were added to 50 g of GBL to obtain varnish F of a positive photosensitive resin composition. Using the obtained varnish F, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as

described earlier. The results of the evaluations are shown in Table 2.

[0135]

EXAMPLE 7

In a dry nitrogen gas flow, 9.16 g (0.03 mol) of BAHF, 2.0 (0.01 mol) of DAE, 4.5 g (0.008 mol) of ED600, and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 6.01 g (0.02 mol) of TDA-100, 9.31 g (0.03 mol) of ODPA, and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (G) powder.

[0136]

17.5 g of the obtained resin (G), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the novolac resin (f) obtained in Synthesis Example 6, 3.0 g of a crosslink agent MX-270, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish G of a positive photosensitive resin composition. Using the obtained varnish G, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as

described earlier. The results of the evaluations are shown in Table 2.

[0137]

EXAMPLE 8

In a dry nitrogen gas flow, 15.57 g (0.04 mol) of BAHF and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 6.01 g (0.02 mol) of TDA-100, 13.33 g (0.03 mol) of 6FDA, and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (M) powder.

[0138]

17.5 g of the obtained resin (M), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the polybenzoxazole resin (g) obtained in Synthesis Example 7, 3.0 g of a crosslink agent MX-270, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish M of a positive photosensitive resin composition. Using the obtained varnish M, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown

in Table 2.

[0139]

EXAMPLE 9

In a dry nitrogen gas flow, 9.16 g (0.03 mol) of BAHF, 2.0 (0.01 mol) of ED600, 9.0 g (0.015 mol) of ED600, and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 6.01 g (0.02 mol) of TDA-100, 13.33 g (0.03 mol) of 6FDA, and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (N) powder.

[0140]

17.5 g of the obtained resin (N), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the polyhydroxystyrene resin (h) obtained in Synthesis Example 8, 3.0 g of a crosslink agent HMOM-TPHAP, and 1.0 g of KBM403 were added to 50 g of GBL to obtain varnish N of a positive photosensitive resin composition. Using the obtained varnish F, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown

in Table 2.

[0141]

EXAMPLE 10

In a dry nitrogen gas flow, 9.16 g (0.03 mol) of BAHF, 9.0 g (0.015 mol) of ED600, and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 8.97 g (0.05 mol) of PMDA-HH, 4.44 g (0.01 mol) of 6FDA, and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (O) powder.

[0142]

17.5 g of the obtained resin (O), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the acrylic resin (e) obtained in Synthesis Example 5, 3.0 g of a crosslink agent HMOM-TPHAP, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish O of a positive photosensitive resin composition. Using the obtained varnish O, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown in Table 2.

[0143]

EXAMPLE 11

In a dry nitrogen gas flow, 9.16 g (0.03 mol) of BAHF, 9.0 (0.015 mol) of ED600, and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 2.80 g (0.013 mol) of PMDA-HH, 16.66 g (0.037 mol) of 6FDA, and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (P) powder.

[0144]

17.5 g of the obtained resin (P), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the novolac resin (f) obtained in Synthesis Example 6, 3.0 g of a crosslink agent HMOM-TPHAP, and 1.0 g of KBM403 were added to 50 g of GBL to obtain varnish N of a positive photosensitive resin composition. Using the obtained varnish N, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown in Table 2.

[0145]

COMPARATIVE EXAMPLE 1

In a dry nitrogen gas flow, 15.57 g (0.04 mol) of BAHF and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 22.21 g (0.05 mol) of 6FDA and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (H) powder.

[0146]

17.5 g of the obtained resin (H), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the acrylic resin (e) obtained in Synthesis Example 5, 3.0 g of a crosslink agent MX-270, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish H of a positive photosensitive resin composition. Using the obtained varnish H, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown in Table 2.

[0147]

COMPARATIVE EXAMPLE 2

In a dry nitrogen gas flow, 15.57 g (0.04 mol) of BAHF

and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 9.81 g (0.05 mol) of CBDA and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (I) powder.

[0148]

17.5 g of the obtained resin (I), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the acrylic resin (e) obtained in Synthesis Example 5, 3.0 g of a crosslink agent MX-270, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish I of a positive photosensitive resin composition. Using the obtained varnish I, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown in Table 2.

[0149]

COMPARATIVE EXAMPLE 3

In a dry nitrogen gas flow, 8.5 g (0.04 mol) of DAE and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 11.21 g (0.05 mol) of PMDA-HH and 10 g of NMP

were added and reacted at 40°C for 1 hour. After that, a solution obtained by diluting 13.10 g (0.11 mol) of N,N-dimethylformamide dimethyl acetal with 15 g of NMP was dropped over 10 minutes. After that, the solution was stirred at 40°C for 1 hour. After the reaction finished, the solution was poured into 2 L of water and solid precipitate was collected by filtration. The solid resin was dried with a vacuum dryer at 50°C for 72 hours, to obtain a polyimide precursor resin (J).

17.5 g of the obtained resin (J), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the acrylic resin (e) obtained in Synthesis Example 5, 3.0 g of a crosslink agent MX-270, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish J of a positive photosensitive resin composition. Using the obtained varnish J, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown in Table 2.

[0150]

COMPARATIVE EXAMPLE 4

In a dry nitrogen gas flow, 15.57 g (0.04 mol) of BAHF and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 11.21 g (0.05 mol) of PMDA-HH and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at

180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (K) powder.

[0151]

17.5 g of the obtained resin (K), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the acrylic resin (e) obtained in Synthesis Example 5, 3.0 g of a crosslink agent MX-270, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish K of a positive photosensitive resin composition. Using the obtained varnish K, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown in Table 2.

[0152]

COMPARATIVE EXAMPLE 5

In a dry nitrogen gas flow, 11.91 g (0.04 mol) of APBS and 0.62 g (0.003 mol) of SiDA were dissolved in 100 g of NMP. To this solution, 15.01 g (0.05 mol) of TDA-100 and 10 g of NMP were added and reacted at 60°C for 1 hour, and then stirred at 180°C for 4 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate.

The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum dryer at 50°C for 72 hours, to obtain a cyclized polyimide resin (L) powder.

[0153]

17.5 g of the obtained resin (L), 2.3 g of the quinonediazide compound (b) obtained in Synthesis Example 2, 16 g of the acrylic resin (e) obtained in Synthesis Example 5, 3.0 g of a crosslink agent MX-270, and 1.0 g of KBM-403 were added to 50 g of GBL to obtain varnish L of a positive photosensitive resin composition. Using the obtained varnish L, the sensitivity evaluation, residual film rate evaluation, evaluation on developed film pattern, evaluation on thick film formation, and resolution evaluation were performed as described earlier. The results of the evaluations are shown in Table 2.

[0154]

[Table 1]

	Resin												Percentage of monomers containing fluorine (mol%)	Other resin	Photosensitizer
	Resin	Acid component (molar ratio)					Di-amine component (molar ratio)								
		PMDA-HH	TDA 100	CBDA	6FDA	ODPA	BAHF	(a)	APBS	DAE	ED600	SiDA			
Example 1	A	10			90		85					5	92	e	b
Example 2	B	90			10		65			20		5	39	f	c
Example 3	C	40				60		85				5	45	g	d
Example 4	D	40			60				85			5	32	h	b
Example 5	E		40		60				85			5	32	e	b
Example 6	F		40		60		50			20	15	5	58	h	b
Example 7	G		40			60	50			20	15	5	26	f	b
Example 8	M		40		60		85					5	76	g	b
Example 9	N		70		30		50				30	5	43	h	b
Example 10	O	80			20		50				30	5	38	e	b
Example 11	P	25			75		50				30	5	68	f	b
Comparative Example 1	H				100		85					5	97	e	b
Comparative Example 2	I			100			85					5	45	e	b
Comparative Example 3	J	100								85		5	0	e	b
Comparative Example 4	K	100					85					5	45	e	b
Comparative Example 5	L		100						85			5	0	e	b

[0155]

[Table 2]

	Varnish	Sensitivity Eth (mJ/cm ²)	Residual film rate evaluation	Evaluation on developed film pattern		Evaluation on thick film formation	Resolution
				Tackiness	Residue		
Example 1	A	290	91%	○	○	○	△
Example 2	B	280	91%	○	○	⊙	△
Example 3	C	250	93%	○	○	⊙	⊙
Example 4	D	300	88%	○	○	○	⊙
Example 5	E	290	85%	○	○	○	⊙
Example 6	F	280	88%	○	○	⊙	⊙
Example 7	G	380	83%	○	○	○	⊙
Example 8	M	250	85%	○	○	⊙	⊙
Example 9	N	250	91%	○	○	⊙	⊙
Example 10	O	280	88%	○	○	○	○
Example 11	P	300	91%	○	○	○	○
Comparative Example 1	H	600	94%	○	○	×	×
Comparative Example 2	I	550	93%	○	×	×	×
Comparative Example 3	J	>1000	98%	×	×	×	×
Comparative Example 4	K	—	0%	—	—	×	×
Comparative Example 5	L	—	0%	—	—	×	×

INDUSTRIAL APPLICABILITY

[0156]

According to the present invention, it is possible to obtain a resin that has a high sensitivity and high residual film rate when used in a photosensitive resin composition.

DESCRIPTION OF REFERENCE SIGNS

[0157]

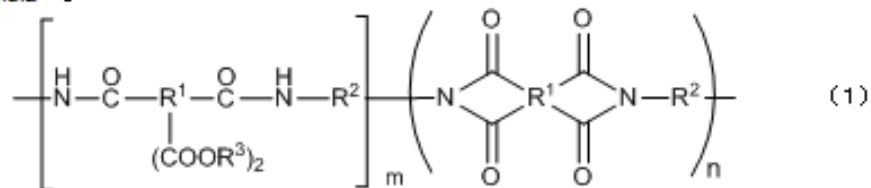
- 1: Silicon wafer
- 2: Al pad
- 3: Passivation film
- 4: Dielectric film
- 5: Metal (Cr, Ti, or the like) film
- 6: Wiring (Al, Cu, or the like)
- 7: Dielectric film
- 8: Barrier metal
- 9: Scribe line
- 10: Solder bump

CLAIMS

1. A resin comprising a polyamide structure, a polyimide precursor structure, or a polyimide structure each of which contains an acid and/or an anhydride of the acid in an amount of 5 to 95 mol% assuming that a total amount of acids and/or anhydrides thereof is 100 mol%, the acid having a C6-C40 alicyclic structure or having a C6-C40 semi-alicyclic structure which has both an alicyclic structure and an aromatic ring.

2. A resin comprising a structure represented by General Formula (1):

【 Chemical formula 1】



(where each R¹ independently contains at least one organic group, which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic ring, in an amount of 5 to 95 mol% assuming that a total amount of R¹ is 100 mol%; each

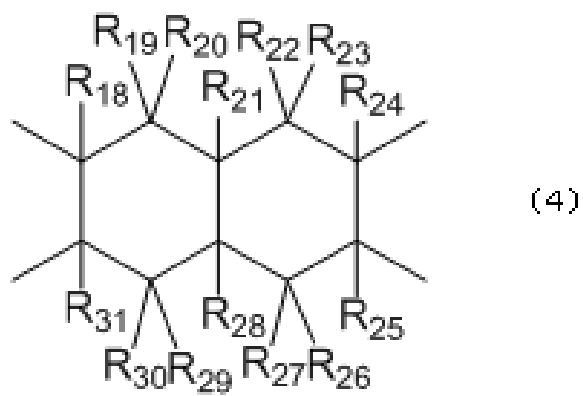
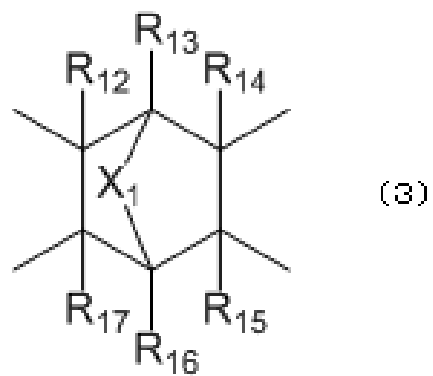
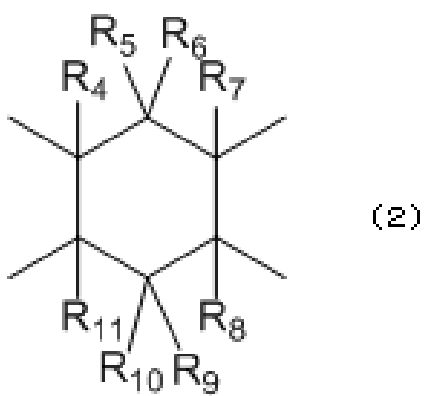
R^2 independently represents a C2-C40 divalent organic group;
 R^3 represents hydrogen or a C1-C20 monovalent organic group;
m and n each represent 0 to 100,000; and $m + n > 2$.)

3. The resin according to claim 2, wherein the structure represented by General Formula (1) has a fluorine component.

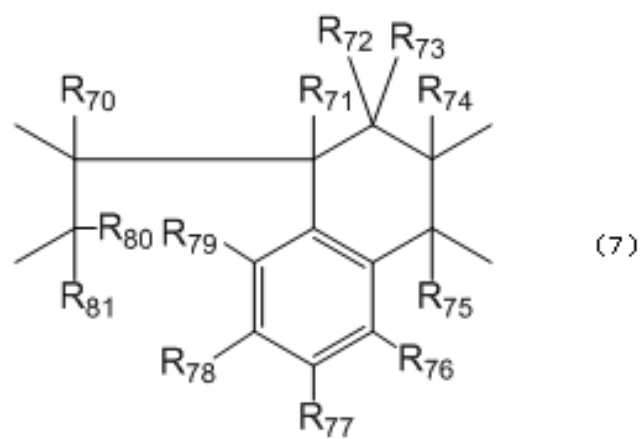
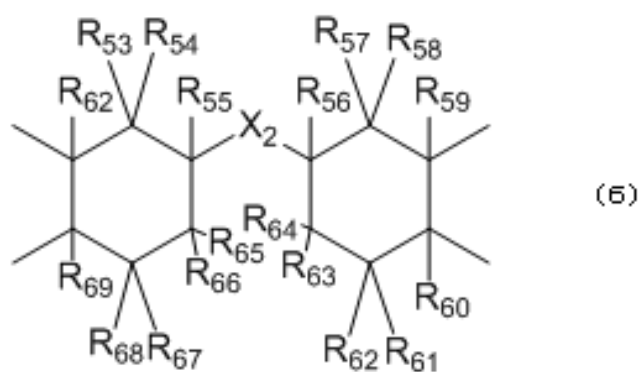
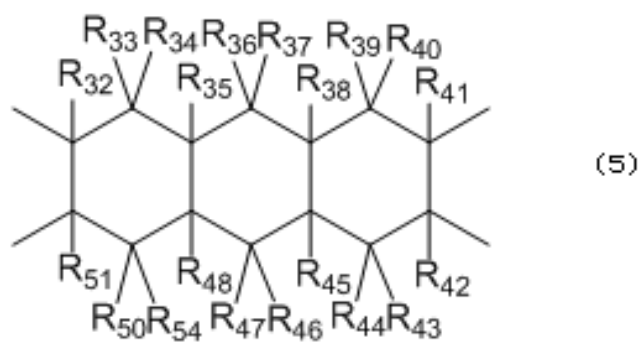
4. The resin according to claim 2 or 3, wherein the structure represented by General Formula (1) has a phenolic hydroxyl group.

5. The resin according to any of claims 2 to 4, wherein R^1 in General Formula (1) contains at least one organic group selected from the following General Formulas (2) to (7):

[Chemical formula 2]



[Chemical formula 3]



(where R_4 to R_{81} in General Formulas (2) to (7) each independently represent a hydrogen atom, a halogen atom, or a C1-C3 monovalent organic group, X_1 in General Formula (3) represents an oxygen atom, a sulfur atom, a sulfonyl group, a C1-C3 divalent organic group, or a divalent crosslink formed of two or more C1-C3 divalent organic groups bound together, and X_2 in General Formula (6) represents a direct bond, an oxygen atom, a sulfur atom, a sulfonyl group, C1-C3 divalent organic groups, or a divalent crosslink formed of two or more organic groups selected from an arylene group bound together.)

6. The resin according to any of claims 2 to 5, wherein a fluorine-atom-containing organic group is contained in an amount of 30 mol% or more assuming that a total amount of R^1 and R^2 is 100 mol%.

7. The resin according to any of claims 2 to 6, wherein, in General Formula (1), each R^1 independently contains at least one organic group which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic

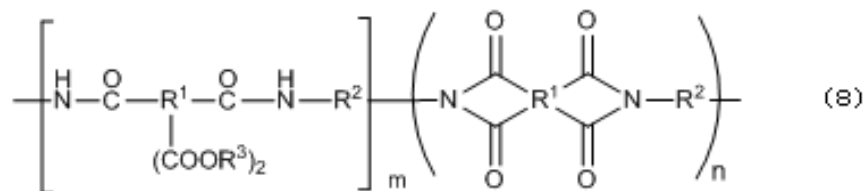
ring, in an amount of 25 to 80 mol% assuming that the total amount of R¹ is 100 mol%.

8. The resin according to any of claims 2 to 6, wherein, in General Formula (1), each R¹ independently contains at least one organic group which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic ring, in an amount of 40 to 70 mol% assuming that the total amount of R¹ is 100 mol%.

9. A photosensitive resin composition comprising the resin according to any of claims 1 to 8.

10. A photosensitive resin composition comprising: (a) a resin containing as a main component a structure represented by General Formula (8); (b) a photo acid generator; and (c) a solvent, the photosensitive resin composition having a positive photosensitivity:

【 Chemical formula 4】



(where each R¹ independently contains at least one organic group which is selected from C6-C40 tetravalent organic groups having a monocyclic or fused polycyclic alicyclic structure, C6-C40 tetravalent organic groups each formed of organic groups having a monocyclic alicyclic structure which are bound together directly or by a crosslink, and C6-C40 tetravalent organic groups having a semi-alicyclic structure having both an alicyclic structure and an aromatic ring, in an amount of 5 to 95 mol% assuming that a total amount of R¹ is 100 mol%; each R² independently represents a C2-C40 divalent organic group; R³ represents hydrogen or a C1-C20 monovalent organic group; m and n each represent 0 to 100,000; and m + n > 2, with the proviso that the structure represented by General Formula (8) essentially has a fluorine component and a phenolic hydroxyl group.)

11. The photosensitive resin composition according to claim 9 or 10, wherein R² in General Formula (1) or (8) further contains an aliphatic organic group.

12. The photosensitive resin composition according to claim 11, wherein the aliphatic organic group is an organic group containing an aliphatic alkyl group.

13. A method of producing a heat-resistant resin film from the photosensitive resin composition according to any of claims 9 to 12, comprising:

applying the photosensitive resin composition to a support substrate and drying the photosensitive resin composition to obtain a photosensitive resin film;

exposing the photosensitive resin film obtained in the step to light;

developing the exposed photosensitive resin film by using an alkaline aqueous solution; and

treating the developed photosensitive resin film with heat.

14. An interlayer dielectric film which is obtained by the method according to claim 13.

15. An interlayer dielectric film for a multilayer wiring structure, which has a total thickness of 10 μm or more and 50 μm or less and which is obtained by the method according to claim 13.

16. A surface protective film which is obtained by the method according to claim 13.

17. An electronic component comprising the interlayer dielectric film according to claim 14 or the surface protective film according to claim 16.

18. A dielectric layer for an organic electroluminescent element, which is obtained by the method according to claim 13.