

DESCRIPTION

PHOTOSENSITIVE FILM

5 TECHNICAL FIELD

[0001]

The present invention relates to a photosensitive film. More specifically, the present invention relates to a photosensitive film suitable as a surface protective film on the surface of a semiconductor device, an interlayer insulating film, and an
10 insulating layer for an organic electroluminescent element.

BACKGROUND ART

[0002]

Resins typified by polyimide and polybenzoxazole are highly heat resistant and
15 highly electrically insulative, and thus are used in surface protective films and interlayer insulating films for semiconductor devices, insulating layers for organic electroluminescent elements, and the like. In recent years, microfabrication of semiconductor devices has demanded that surface protective films and interlayer insulating films have resolution of a few μm level. Owing to this, microfabricable
20 positive tone photosensitive polyimide resin compositions and positive tone photosensitive polybenzoxazole resin compositions are often used in such applications.

[0003]

In general semiconductor device production processes, a semiconductor device
25 is formed by forming a passivation film composed typically of Si and SiN on a substrate, forming a photosensitive layer on the passivation film, drying the resulting layered product by heating using a hot plate and the like, and forming a pattern on

the product by light exposure and development. After the pattern formation, the product is heat-treated at high temperature and cured to thereby form an insulating layer.

[0004]

5 For formation of semiconductor devices, circular substrates have conventionally been used, but in recent years, substrates have increased in size, resulting in using square substrates.

[0005]

Examples of methods of forming a photosensitive layer on a substrate include: a
10 method in which a resin composition is applied by spin coating; and a method in which a photosensitive film is laminated onto a substrate by thermal compression bonding. In a case where an insulating layer is formed on a large size square substrate, a common method is such that a photosensitive film is used for lamination in order to increase film thickness uniformity obtained after the formation.

15 [0006]

As positive tone photosensitive polyimides used as resin composition photosensitive films, those based on polyimide (for example, Patent Document 1), those based on polyhydroxystyrene (for example, Patent Document 2), and mixtures of polyimide and polyhydroxystyrene (for example, Patent Document 3) are known.

20 [0007]

In addition, a technology in which a phenol resin is used as a photosensitive film (for example, Patent Document 4) and a technology in which a polyimide having a low glass transition point is used (for example, Patent Document 5) are proposed.

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Citation List

Patent Documents

[0008]

Patent Document 1: JP2014-71374A

Patent Document 2: JP2006-154779A

Patent Document 3: JP2014-137523A

5 Patent Document 4: JP2015-19006A

Patent Document 5: WO 2011/059089

SUMMARY OF INVENTION

10 Technical Problem

[0009]

As above-mentioned, in a case where an insulating layer is formed on a large size square substrate, a common method is such that a photosensitive film is used for lamination in order to promote uniformity of film thickness obtained after the formation. The photosensitive film is required to be such that mechanical properties such as high elongation and high heat resistance can be imparted to the photosensitive film as a cured film, and besides, required to have not only good patterning property (high resolution) but also good adhesion to a substrate, in other words, lamination suitability.

20 [0010]

However, a film for which such a polyimide-based resin composition as disclosed in Patent Documents 1 to 3 is used has insufficient flexibility and insufficient lamination suitability which, for example, may cause the film to generate cracks when the film is laminated onto a substrate by thermal compression bonding. In Patent Document 4, a technology in which a phenol resin is used for the purpose of increasing flowability is disclosed, but has a problem in that the cured film has low heat resistance. In addition, a technology in which a polyimide having a low

glass transition point is used is disclosed in Patent Document 5, but has a problem in that the technology does not afford high heat resistance.

[0011]

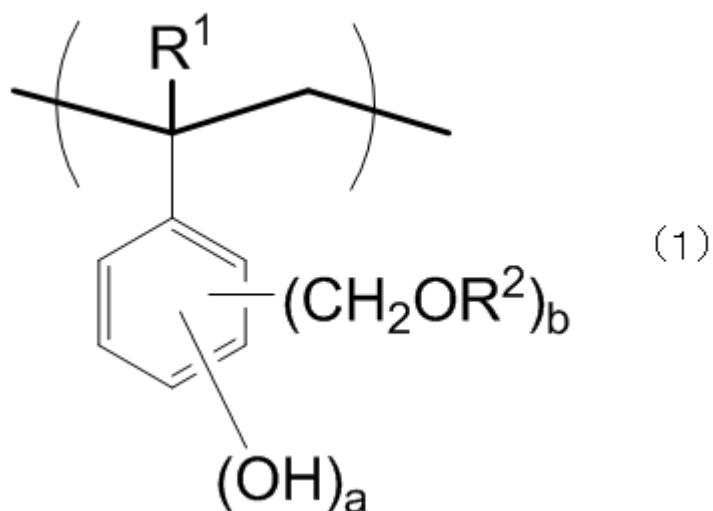
The present invention provides a photosensitive film that affords a cured film having high heat resistance and has good patterning property (high resolution) and good adhesion to a substrate, in other words, lamination suitability.

Solution to Problem

[0012]

In order to solve the above-mentioned problems, the photosensitive film according to the present invention has the following constitution: that is, a photosensitive film containing: (A1) an alkali soluble resin containing a structural unit represented by the general formula (1); (A2) an alkali soluble resin containing one or more selected from polyimides, polybenzoxazoles, polyamideimides, precursors of these, and copolymers of these; (B) a photo acid generator; and (C) a heat-crosslinker.

[0013]



[0014]

(wherein in the general formula (1), R^1 represents a hydrogen atom or a C_1 - C_5 alkyl group; a is an integer in a range of from 0 to 4; b is an integer in a range of from 1 to 3; and R^2 is a hydrogen atom, methyl group, ethyl group, or propyl group.)

5 Advantageous Effects of Invention

[0015]

The present invention affords a photosensitive film that has good patterning property (high resolution) and good adhesion to a substrate, in other words, lamination suitability. In addition, the photosensitive film according to the present
10 invention affords a cured film having high elongation and high heat resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0016]

15 Fig. 1 is an example of a schematic cross-sectional view of a semiconductor device using a photosensitive film according to the present invention.

Fig. 2 is an example of a cross-sectional view of the coil portion of an inductor using a photosensitive film according to the present invention.

20 Fig. 3 is an example of a cross-sectional view of the hollow portion of a surface acoustic wave device using a photosensitive film according to the present invention.

Fig. 4 is an example of a cross-sectional view of a semiconductor device using a photosensitive film according to the present invention and having a level difference on a substrate.

25 EMBODIMENTS OF INVENTION

[0017]

The present invention is a photosensitive film containing: (A1) an alkali soluble resin containing a structural unit represented by the general formula (1); (A2) an alkali soluble resin containing one or more selected from polyimides, polybenzoxazoles, polyamideimides, precursors of these, and copolymers of these; (B) a photo acid generator; and (C) a heat-crosslinker. Hereinafter, these may be referred to as the (A1) resin, the (A2) resin, the (B) component, and the (C) component respectively for short.

[0018]

The photosensitive film according to the present invention contains the (A1) alkali soluble resin containing a structural unit represented by the general formula (1). In the general formula (1), R^1 represents a hydrogen atom or a C_1 - C_5 alkyl group, a is an integer in a range of from 0 to 4, b is an integer in a range of from 1 to 3, R^2 represents a hydrogen atom, methyl group, ethyl group, or propyl group. Containing the (A1) resin allows the photosensitive film to have its photosensitivity enhanced.

[0019]

The structural unit represented by the general formula (1) can be obtained, for example, by using a known method (for example, the method described in JP5659259B2) to cause addition reaction by adding an alkoxy group to part of a polymer obtained by polymerizing, by a known method, one or more of: aromatic vinyl compounds having a phenolic hydroxyl group, such as p-hydroxystyrene, m-hydroxystyrene, o-hydroxystyrene, p-isopropenylphenol, m-isopropenylphenol and o-isopropenylphenol; and aromatic vinyl compounds such as styrene, o-methylstyrene, m-methylstyrene and p-methylstyrene.

[0020]

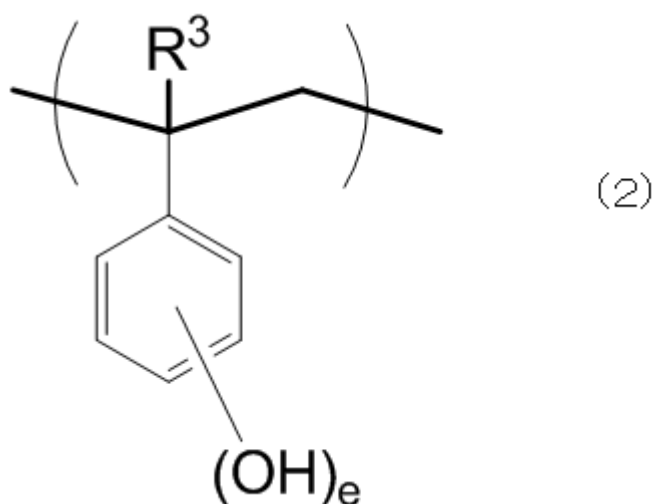
Examples of aromatic vinyl compounds having a phenolic hydroxyl group that are preferably used include p-hydroxystyrene and/or m-hydroxystyrene, and

examples of aromatic vinyl compounds that are preferably used include styrene.

[0021]

Preferably, the (A1) alkali soluble resin containing a structural unit represented by the general formula (1) further has at least any one of the structural units represented by the general formula (2) and the general formula (3), considering the convenience for enhancing photosensitivity and enabling solubility in an alkaline developing solution to be adjusted. Furthermore, the structural unit of the general formula (3) is preferably contained at 50 mol% or less from the viewpoint of solubility in an alkaline developing solution.

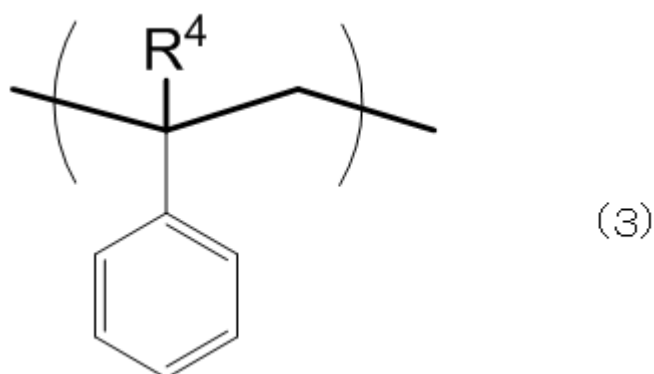
[0022]



[0023]

(wherein in the general formula (2), R^3 represents a hydrogen atom or a C_1 - C_5 alkyl group, and e represents an integer in a range of from 1 to 5.)

[0024]



[0025]

(wherein in the general formula (3), R^4 represents a hydrogen atom or a C_1 - C_5 alkyl group.)

5 The introduction rate of an alkoxy alkyl (CH_2OR^2) group in the (A1) resin is preferably 10 mol% or more per 1 mol of hydroxystyrene, more preferably 20 mol% or more, from the viewpoint of heat resistance achieved after curing. It is preferably 70 mol% or less, more preferably 50 mol% or less, with a view to enhancing resolution.

10 [0026]

The (A1) resin preferably has a weight-average molecular weight (M_w) of 3,000 or more in terms of polystyrene with a view to forming a pattern without dissolving its unexposed areas. In addition, it is preferably 60,000 or less, more preferably 25,000 or less, with a view to maintaining alkali solubility that enables the

15 residue of the exposed areas to be reduced.

[0027]

The weight-average molecular weight (M_w) in terms of polystyrene refers to a value calculated in terms of polystyrene using GPC (gel permeation chromatography) measurements.

20 [0028]

The photosensitive film according to the present invention contains (A2) an alkali soluble resin containing one or more selected from polyimides,

polybenzoxazoles, polyamideimides, precursors of these, and copolymers of these.
[0029]

The (A2) resin may contain any two or more of polyimides, polybenzoxazoles, polyamideimides, precursors of these, and copolymers of these, or may contain a
5 copolymer containing any two or more of these repeating units. In addition, the (A2) resin preferably has a substituent that reacts with an alkoxyalkyl group of the (A1) resin. An alkoxyalkyl group of the (A1) refers to an alkoxymethyl group in particular. The (A2) resin is not limited to a particular structure as long as it has a substituent that reacts with an alkoxyalkyl group, and preferably has, on the main
10 chain or end thereof, one or more groups selected from carboxyl group, phenolic hydroxyl group, sulfonic group, and thiol group.

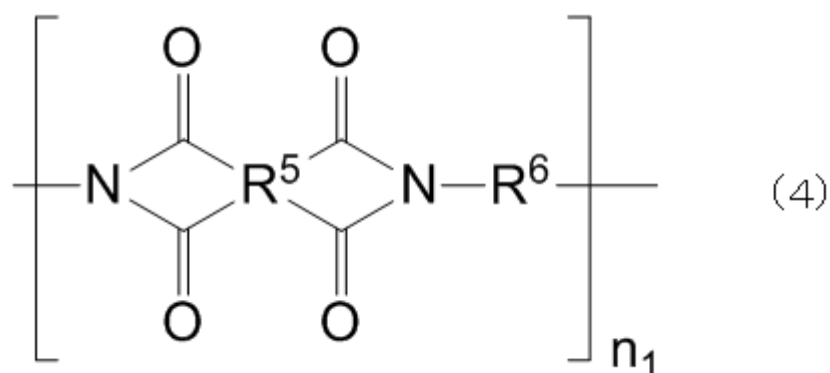
[0030]

The reaction between the alkoxyalkyl group of the (A1) resin and the (A2) resin in heat-curing allows the heat resistance and mechanical properties to be maintained
15 sufficiently and accordingly allows both the good patterning property of the (A1) resin and the high heat resistance and mechanical properties of the (A2) resin to be achieved. The (A2) resin content is preferably 5 parts by mass or more, more preferably 10 parts by mass or more, with respect to the total of the (A1) resin and the (A2) resin as 100 parts by mass, from a patterning property viewpoint. In
20 addition, the content is preferably 90 parts by mass or less, more preferably 70 parts by mass or less, from the viewpoints of heat resistance and mechanical properties.

[0031]

The (A2) resin preferably contains at least any one of the structural units represented by the general formulae (4) or (5).

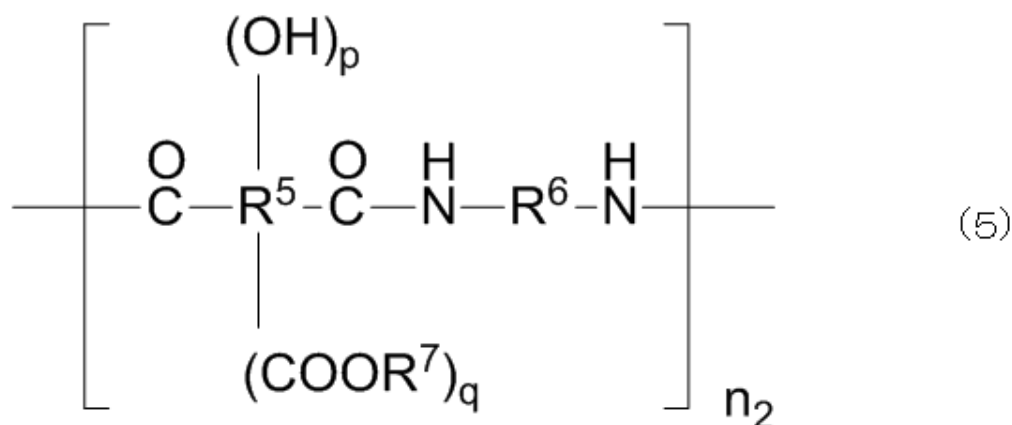
25 [0032]



[0033]

(wherein in the general formula (4), R⁵ represents a C₄-C₄₀ bivalent to
 tetravalent organic group; R⁶ represents a C₂₀-C₁₀₀ bivalent organic group; and n₁
 5 represents an integer in a range of from 10 to 100,000.)

[0034]



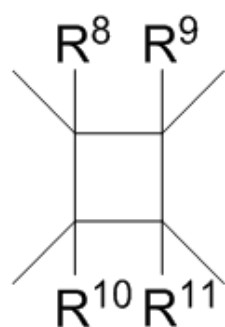
[0035]

(wherein in the general formula (5), R⁵ represents a C₄-C₄₀ bivalent to
 10 tetravalent organic group; R⁶ represents a C₂₀-C₁₀₀ bivalent organic group; R⁷
 represents hydrogen or a C₁-C₂₀ organic group; n₂ represents an integer in a range of
 from 10 to 100,000; and p and q each represent an integer satisfying 0 ≤ p + q ≤ 2.)

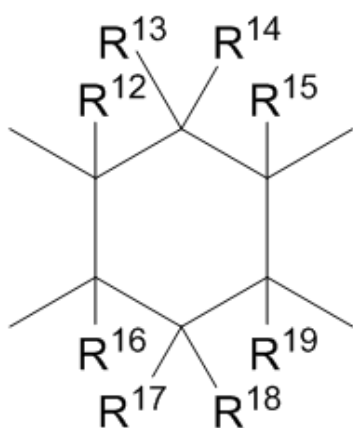
In the general formulae (4) and (5), R⁵ represents a C₄-C₄₀ bivalent to
 tetravalent organic group having an alicyclic structure of a monocyclic or condensed
 15 polycyclic type. The alicyclic structure of a monocyclic or condensed polycyclic

type in R^5 preferably contains one or more organic groups selected from the following general formulae (6) to (9).

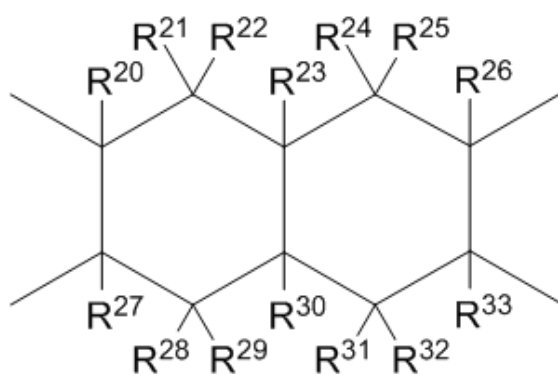
[0036]



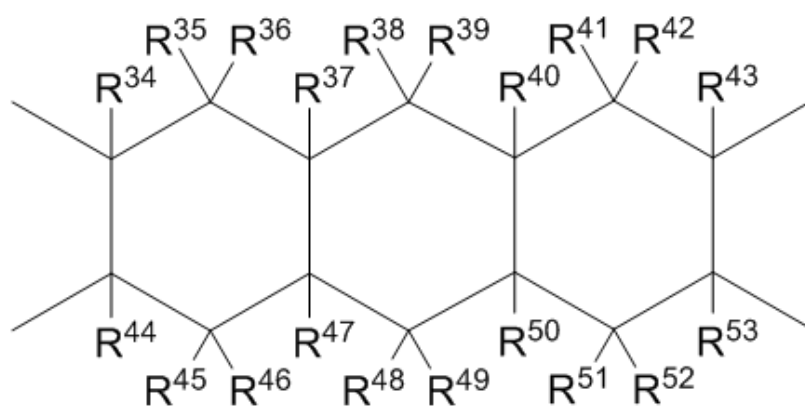
(6)



(7)



(8)



(9)

[0037]

(wherein in the general formulae (6) to (9), R^8 to R^{53} each independently

represent a hydrogen atom, a halogen atom, or a C₁-C₃ monovalent organic group; and a hydrogen atom contained in the C₁-C₃ monovalent organic group may be substituted with a halogen atom.)

In addition, R⁵ in the general formulae (4) and (5) is an organic group derived from an acid dianhydride that is used as a raw material of a resin.

[0038]

Specific examples of acid dianhydrides used in the present invention that contain a C₄-C₄₀ bivalent to tetravalent organic group having an alicyclic structure of a monocyclic or condensed polycyclic type can include compounds such as 1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,2-dimethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,2,3,4-tetramethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride, and 1,2,4,5-cyclohexanetetracarboxylic dianhydride.

[0039]

Examples of preferred structures of a C₄-C₄₀ bivalent to tetravalent organic group having 1 to 4 aromatic rings in R⁵ in the general formulae (4) and (5) include structures in which a carboxyl group is removed from an aromatic tetracarboxylic acid such as pyromellitic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,3,3',4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 3,3',4,4'-benzophenonetetracarboxylic acid, 2,2',3,3'-benzophenonetetracarboxylic acid, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane, 2,2-bis(2,3-dicarboxyphenyl)hexafluoropropane, 1,1-bis(3,4-dicarboxyphenyl)ethane, 1,1-bis(2,3-dicarboxyphenyl)ethane, bis(3,4-dicarboxyphenyl)methane, bis(2,3-dicarboxyphenyl)methane, bis(3,4-dicarboxyphenyl)sulfone, bis(3,4-dicarboxyphenyl)ether, 1,2,5,6-naphthalenetetracarboxylic acid, 2,3,6,7-naphthalenetetracarboxylic acid, 2,3,5,6-pyridinetetracarboxylic acid, or 3,4,9,10-perylenetetracarboxylic acid; and structures in which one to four hydrogen atoms of

the aromatic tetracarboxylic acid are partially substituted with a C₁-C₂₀ alkyl group, a fluoroalkyl group, an alkoxy group, an ester group, a nitro group, a cyano group, a fluorine atom, and a chlorine atom.

[0040]

5 The alicyclic structure of a monocyclic or condensed polycyclic type in R⁵ is contained at preferably 10 mol% or more, more preferably 30 mol% or more, with respect to R⁵ in the general formulae (4) and (5) taken as 100 mol%, from the viewpoint of achieving higher elongation and enhancing lamination suitability to a film substrate. It is preferably 80 mol% or less, more preferably 60 mol% or less,
10 from the viewpoint of attaining a suitable dissolution rate in a developing solution.

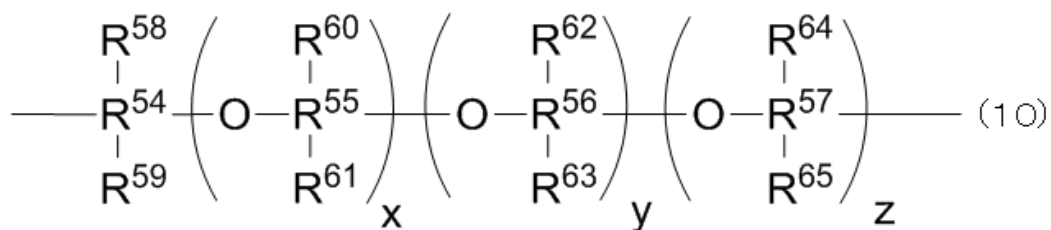
[0041]

For example, in a case where 70 mol% of R⁵s have an alicyclic structure of a monocyclic or condensed polycyclic type and 30 mol% thereof have a tetravalent organic group having an aromatic ring with respect to the total amount of the
15 repeating units of the general formulae (4) and (5) taken as 100 mol%, calculation assumes that the alicyclic structures of a monocyclic or condensed polycyclic type are present at 70 mol%. Here, if R⁵s have two or more alicyclic structures of a monocyclic or condensed polycyclic type, the amount of the structures is calculated at 70 mol%.

20 [0042]

In addition, R⁶ in the general formulae (4) and (5) preferably contains an organic group having a polyether structure represented by the following general formula (10):

[0043]



[0044]

(wherein, R⁵⁴ to R⁵⁷ independently represent a C₁-C₆ alkylene group; R⁵⁸ to R⁶⁵ independently represent hydrogen, fluorine, or a C₁-C₆ alkyl group, with the proviso that the structure represented in the parentheses of the repeating unit x and the structure represented in the parentheses of the repeating unit y are different, and with the proviso that the structure represented in the parentheses of the repeating unit z and the structure represented in the parentheses of the repeating unit y are different; x, y, and z independently represent an integer from 0 to 35.) In addition, R⁶ in the general formulae (4) and (5) is an organic group derived from a diamine that is used as a raw material of a resin.

[0045]

Specific examples of diamines used in the present invention that contain an organic group having a polyether structure include aliphatic diamines such as “JEFFAMINE” (registered trademark) HK-511, ED-600, ED-900, ED-2003, EDR-148, EDR-176, D-200, D-400, D-2000, D-4000, “ELASTAMINE” (registered trademark) RP-409, RP-2009, RT-1000, HT-1100, HE-1000, and HT-1700 (those listed above are the names of products made by HUNTSMAN Corporation). Having a polyether structure is preferable because it affords hydrophilicity and high temperature meltability and thus enhances lamination suitability to a substrate, that it affords flexibility and thus enhances the elongation, and that it reduces elastic modulus and thus suppresses the warpage of a wafer. These characteristics are effective with multiple layers and thick films. A polyether structure represented by the general formula (10) is preferably contained at 10 mol% or more with respect to

R^6 in the general formulae (4) and (5) taken as 100 mol% because it provides the resin with flexibility, low stressfulness, and lamination suitability to a substrate. In addition, it is preferably 80 mol% or less because it affords a suitable dissolution rate in a developing solution. The content is more preferably 20 mol% to 50 mol%.

5 [0046]

For example, in a case where 70 mol% of R^6 have an organic group derived from a diamine containing an organic group having a polyether structure and 30 mol% thereof have a bivalent organic group having an aromatic ring with respect to the total amount of the repeating units in the general formulae (4) and (5) taken as
10 100 mol%, calculation assumes that the organic groups derived from a diamine containing an organic group having a polyether structure are present at 70 mol%. Here, if R^6 has two or more organic groups derived from a diamine containing an organic group having a polyether structure, the amount of the groups is calculated at 70 mol%.

15 [0047]

In addition, further containing a fluorine-atom-containing organic group as R^5 in the general formulae (4) and (5) is preferable because it imparts water repellency to the resin and thus allows the resin to suppress permeation through the film surface during alkaline development. Suppressing permeation through the film surface
20 makes it possible to obtain a resin film which suffers less thickness loss after development and in which there is neither tackiness in the unexposed area nor development residue in the formed pattern. These characteristics are important in enabling thick films to be processed. The fluorine-atom-containing organic group is preferable because it can produce the effect of preventing permeation at an
25 interface at 20 mol% or more and afford a suitable dissolution rate into a developing solution at 90 mol% or less, with respect to the total amount of R^5 as 100 mol%, and is more preferably at 40 mol% to 60 mol%.

[0048]

Specific examples of compounds having a fluorine atom include aromatic acid dianhydrides such as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, compounds obtained by substituting an aromatic ring of the dianhydride with an alkyl group or a halogen atom, acid dianhydrides having an amide group, and the like. It is preferable that the (A2) resin contains a structure derived from any of these compounds.

[0049]

With the use of the above-described acid dianhydride having a C₄-C₄₀ alicyclic structure, a diamine having a C₂₀-C₁₀₀ polyether structure, and a compound containing a fluorine atom in the above-described ranges, it is possible to obtain a highly photosensitive film that has high elongation and low stressfulness and yet achieves a high residual film rate allowing no tackiness nor development residue after development.

[0050]

These characteristics are useful particularly in redistribution layer applications for semiconductor devices and noise filter applications for inductor devices, in both of which devices the photosensitive film is used in multiple layers as interlayer insulating films between metal wiring layers. The photosensitive film according to the present invention may also have a structure derived from another acid dianhydride and diamine in addition to the above-described acid dianhydride and diamine to the extent that the above-described characteristics are not impaired.

[0051]

Specific examples of other acid dianhydrides include: 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, 3,4,9,10-perylenetetracarboxylic dianhydride, bis(3,4-dicarboxyphenyl)sulfone dianhydride, 3,3',4,4'-diphenyl ether tetracarboxylic dianhydride, or compounds obtained by substituting a hydrogen atom of these compounds with an alkyl group or a halogen atom; alicyclic and semi-
 3-cyclohexene-1,2-dicarboxylic dianhydride, 2,3,5-tricarboxy-2-cyclopentaneacetic dianhydride, bicyclo[2.2.2]octo-7-ene-2,3,5,6-tetracarboxylic dianhydride, 2,3,4,5-tetrahydrofuran-tetracarboxylic dianhydride, 3,5,6-tricarboxy-2-norbornaneacetic dianhydride, 3,4-dicarboxy-1,2,3,4-tetrahydro-1-naphthalenesuccinic dianhydride, or compounds obtained by substituting a hydrogen atom of these compounds with an alkyl group or a halogen atom; acid dianhydrides having an amide group; and the like. These together with an acid dianhydride that has a C₄-C₄₀ alicyclic structure may be used in combination of two or more kinds thereof.

[0052]

Specific examples of other diamines include hydroxyl-containing diamines 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 diamines such as 3-sulfonic acid-4,4'-diaminodiphenyl ether; thiol-containing diamines such as dimercapto-phenylenediamine; and aromatic diamines

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, benzene, 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 diamines with C₁-C₁₀ alkyl groups, fluoroalkyl groups, halogen atoms, or the like; alicyclic diamines such as cyclohexyldiamine and methylenebiscyclohexylamine; and the like. These diamines may be used without changes or may be used as corresponding diisocyanate compounds or trimethylsilylated diamines. Two or more of these diamine components may be used in combination.

[0053]

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 diamines having an amide group. These are used singly or in combination of two or more kinds thereof.

5 [0054]

Furthermore, an aliphatic group having a siloxane structure may be incorporated into these components to the extent that the heat resistance is not reduced, thereby making it possible to improve the adhesion to a substrate. Specific examples include those copolymerized with a 1 to 15 mol% diamine component, such as bis(3-aminopropyl)tetramethyl disiloxane or bis(p-amino-phenyl)octamethyl pentasiloxane, with respect to R⁶ in the general formulae (4) and (5) as 100 mol%.

10

[0055]

For applications that require heat resistance, it is preferable to use an aromatic diamine in an amount of 50 mol% or more with respect to the total amount of diamines.

15

[0056]

Furthermore, the (A2) resin preferably has a phenolic hydroxyl group component. It is preferable that, in the general formulae (4) and (5), at least one of R⁵ and R⁶ is an organic group having a phenolic hydroxyl group. The presence of a phenolic hydroxyl group provides adequate solubility in an alkaline developing solution, and the group interacts with a photosensitizer and reduces the solubility of unexposed areas. Therefore, it is possible to improve the residual film rate and increase the photosensitivity. In addition, phenolic hydroxyl groups also contribute to the reaction with crosslinkers, and hence are preferable also with a view to achieving high mechanical properties and high chemical resistance.

20

25

[0057]

Specific examples of compounds having 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 diamines such as bis(3-amino-4-

5 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 diamines with C₁-C₁₀ alkyl groups, fluoroalkyl
10 groups, halogen atoms, or the like. It is preferable that the (A2) resin contains a structure derived from any of these compounds.

[0058]

In the general formulae (4) and (5), n_1 and n_2 represent a polymerization degree. Assuming that the molecular weight per unit in the general formulae (4) and (5) is M
15 and that the weight-average molecular weight of the alkali soluble resin is M_w , the polymerization degree n is determined in accordance with the equation $n = M_w / M$. The weight-average molecular weight of the alkali soluble resin can be determined by GPC (gel permeation chromatography) as described in Examples. The values, n_1 and n_2 , can easily be calculated with weight-average molecular weights (M_w)
20 measured by gel permeation chromatography (GPC), light scattering, small angle X-ray scattering, and the like. Assuming that the molecular weight of a repeating unit is M and that the weight-average molecular weight of a polymer is M_w , $n = M_w / M$ is given. The number of repeating units, n , in the present invention refers to a value calculated in terms of polystyrene using GPC (gel permeation chromatography)
25 measurements, which type of calculation is most convenient.

[0059]

The weight-average molecular weight of the (A2) resin is preferably in a range

of from 3,000 to 80,000, more preferably in a range of from 8,000 to 50,000, as determined in terms of polystyrene by gel permeation chromatography. These ranges enable a thick film to be easily formed.

[0060]

5 In addition, the (A2) resin may have an end capped with an end-capping agent such as a monoamine, an acid anhydride, an acid chloride, and a monocarboxylic acid. Capping the end of the resin with an end-capping agent having a hydroxyl group, a carboxyl group, a sulfonic group, a thiol group, a vinyl group, an ethynyl group, or an allyl group enables the dissolution rate of the resin in the alkaline
10 aqueous solution to be easily controlled within a preferred range. The end-capping 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.

[0061]

Specific examples of end-capping agents include: monoamines such as 3-
15 aminophenylacetylene, 4-aminophenylacetylene, and 3,5-diethynylaniline; monocarboxylic acids such as 3-ethynylbenzoic acid, 4-ethynylbenzoic acid, 3,4-diethynylbenzoic acid, and 3,5-diethynylbenzoic acid; acid anhydrides such as maleic anhydride and 5-norbornene-2,3-dicarboxylic anhydride; compounds resulting from the aforementioned monocarboxylic acids whose carboxyl group has
20 been made into an acid chloride, and compounds resulting from dicarboxylic acids, such as maleic acid, one of whose carboxyl groups has been made into an acid chloride; end-capping agents having an unsaturated bond, such as active ester compounds obtained by the reaction of a monoacid chloride compound with n-hydroxy-5-norbornene-2,3-dicarboxy imide; monoamines such as 5-amino-8-
25 hydroxyquinoline, 1-hydroxy-7-aminonaphthalene, 1-hydroxy-6-aminonaphthalene, 1-hydroxy-5-aminonaphthalene, 1-hydroxy-4-aminonaphthalene, 2-hydroxy-7-aminonaphthalene, 2-hydroxy-6-aminonaphthalene, 2-hydroxy-5-aminonaphthalene,

1-carboxy-7-aminonaphthalene, 1-carboxy-6-aminonaphthalene, 1-carboxy-5-aminonaphthalene, 2-carboxy-7-aminonaphthalene, 2-carboxy-6-aminonaphthalene, 2-carboxy-5-aminonaphthalene, 2-aminobenzoic acid, 3-aminobenzoic acid, 4-aminobenzoic acid, 4-aminosalicylic acid, 5-aminosalicylic acid, 6-aminosalicylic acid, 2-aminobenzenesulfonic acid, 3-aminobenzenesulfonic acid, 4-aminobenzenesulfonic acid, 3-amino-4,6-dihydroxy pyrimidine, 2-aminophenol, 3-aminophenol, 4-aminophenol, 2-aminothio phenol, 3-aminothio phenol, and 4-aminothio phenol; acid anhydrides such as phthalic anhydride, cyclohexanedicarboxylic anhydride, and 3-hydroxyphthalic anhydride; monocarboxylic acids such as 3-carboxyphenol, 4-carboxyphenol, 3-carboxythiophenol, 4-carboxythiophenol, 1-hydroxy-7-carboxynaphthalene, 1-hydroxy-6-carboxynaphthalene, 1-hydroxy-5-carboxynaphthalene, 1-mercapto-7-carboxynaphthalene, 1-mercapto-6-carboxynaphthalene, 1-mercapto-5-carboxynaphthalene, 3-carboxybenzenesulfonic acid, 4-carboxybenzenesulfonic acid, and monoacid chloride compounds resulting from these monocarboxylic acids whose carboxyl group has been made into an acid chloride; monoacid chloride compounds resulting from dicarboxylic acids, such as terephthalic acid, phthalic acid, cyclohexanedicarboxylic acid, 1,5-dicarboxynaphthalene, 1,6-dicarboxynaphthalene, 1,7-dicarboxynaphthalene, and 2,6-dicarboxynaphthalene, only one of whose carboxyl groups has been made into an acid chloride; and end-capping agents having no unsaturated bond, such as active ester compounds obtained by the reaction of a monoacid chloride compound with n-hydroxybenzotriazole. Alternatively, when a hydrogen bond of these end-capping agents having no unsaturated bond is substituted with a vinyl group, the agents can be used as end-capping agents having an unsaturated bond.

[0062]

The resin having at least any one of structural units represented by the general

formulae (4) and (5) may be produced in accordance with a known method of producing a polyimide or a polyimide precursor. Examples of the method include (I) a method by which a tetracarboxylic dianhydride having an R^5 group, a diamine compound having an R^6 group, and a monoamino compound which is an end-capping 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^5 group and an alcohol and the diester is then reacted with a diamine compound having an R^6 group and a monoamino compound which is an end-capping 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^5 group and an alcohol, remaining two carboxyl groups are then converted into acid chlorides, and the resultant is reacted with a diamine compound having an R^6 group and a monoamino compound which is an end-capping agent.

[0063]

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

[0064]

The following describes an example of a method of producing a polyimide precursor, which is a preferred example of the method (I). First, a diamine compound having an R^6 group is dissolved in a polymerization solvent. A tetracarboxylic dianhydride having an R^5 group in substantially the same molar quantity as the diamine 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 a case where an end-capping agent is used, the end-capping agent may be gradually added after the tetracarboxylic dianhydride is added and stirred at -20 to 100°C, preferably 10 to 50°C, for 0.1 to 24 hours, or may be added at one time and allowed to react.

[0065]

The polymerization solvent is not limited to a particular kind, provided that the polymerization solvent can dissolve tetracarboxylic dianhydrides and diamines which are raw monomers. Examples of polymerization solvents 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.

[0066]

The polymerization solvent is preferable at 100 parts by mass or more with respect to 100 parts by mass of the total of the tetracarboxylic dianhydride and diamine compound that are used for polymerization and the monoamino compound which is an end-capping agent because the reaction can be carried out without precipitation of the raw materials or resins, preferable at 1900 parts by mass or less because the reaction progresses rapidly, and more preferable at 150 to 950 parts by mass.

[0067]

Next, the photosensitive film according to the present invention will be described. The photosensitive film according to the present invention contains (B) a photo acid generator, thereby having photosensitivity. In other words, the (B)

photo acid generator has the characteristics because it generates an acid upon irradiation with light, resulting in increasing the solubility of the irradiated portion into an alkaline aqueous solution. Examples of (B) photo acid generators include a quinonediazide compound, a sulfonium salt, a phosphonium salt, a diazonium salt, and an iodonium salt. Among these, quinonediazide compounds are preferably used because they exhibit an excellent dissolution inhibition effect if used together with the (A1) alkali soluble resin containing a structural unit represented by the general formula (1) and the (A2) alkali soluble resin containing one or more selected from polyimides, polybenzoxazoles, polyamideimides, precursors of these, and copolymers of these.

[0068]

Examples of 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, compounds in which a quinonediazide sulfonic acid is bound to a polyhydroxypolyamino compound by an ester bond or a sulfonamide bond, compounds in which a quinonediazide sulfonic acid is bound to a polyhydroxypolyamino compound by an ester bond and a sulfonamide bond, and the like.

[0069]

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 are substituted with quinonediazides. If 50 mol% or more of the functional groups are substituted with quinonediazides, the solubility in an alkaline developing solution does not become too high, the contrast to the unexposed area can be achieved, and a desired pattern can be obtained. The use of such a quinonediazide compound makes it possible to

obtain a positive tone photosensitive film which is sensitive to the i-line (365 nm), h-line (405 nm), and g-line (436 nm) of a mercury lamp which are typical ultraviolet rays. These compounds may be used singly 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 area to that of the unexposed area and, as a result, possible to obtain a highly photosensitive film.

[0070]

Examples of 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 made by 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 made by 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, gallic acid methyl ester, bisphenol A, bisphenol E, methylene bisphenol, and BisP-AP (the name of a product made by Honshu Chemical Industry Co., Ltd.).

[0071]

Examples of 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.

[0072]

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

[0073]

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

[0074]

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
15 naphthoquinonediazide sulfonyl ester compound that has both a 4-naphthoquinonediazide sulfonyl group and a 5-naphthoquinonediazide sulfonyl group per molecule may be obtained, or a mixture of a 4-naphthoquinonediazide sulfonyl ester compound and a 5-naphthoquinonediazide sulfonyl ester compound may be used.

20 [0075]

The molecular weight of a quinonediazide compound according to the present invention is preferably in a range of from 300 to 3,000. In a 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
25 performed afterwards, and thus there may be problems in that the heat resistance of the resulting film decreases, mechanical properties of the resulting film decrease, or the adhesion of the resulting film decreases.

[0076]

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 in which a 5-naphthoquinonediazide sulfonyl chloride and a phenolic compound are allowed to react in the presence of triethylamine. The phenol compound is synthesized by, for example, a method in which an α -(hydroxyphenyl)styrene derivative is allowed to react with a polyhydric phenolic compound in the presence of an acid catalyst.

[0077]

Among the (B) photo acid generators used in the present invention, those which moderately stabilize an acid component generated by exposure to light are preferably a sulfonium salt, a phosphonium salt, or a diazonium salt. Since a photosensitive film according to the present invention is used as a permanent film, survival of 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. Particularly preferable examples include a triarylsulfonium salt, which can suppress change in the color tone of the film.

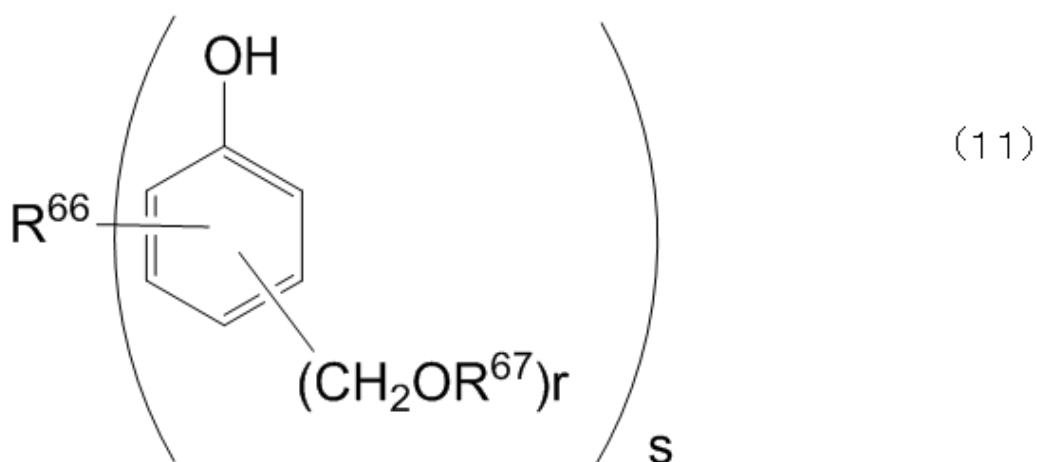
[0078]

The (B) photo acid generator content is preferably 0.01 to 50 parts by mass or more with respect to the total of the (A1) resin and the (A2) resin as 100 parts by mass. Among these, a quinonediazide compound is preferably contained in an amount of 3 to 40 parts by mass. 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 mass, more preferably 0.1 to 30 parts by mass. Having the (B) photo acid generator content in these ranges makes it possible to attempt to achieve higher photosensitivity. A sensitizer or the like may further be contained, if necessary.

[0079]

The photosensitive film according to the present invention contains (C) a heat-crosslinker. As the (C) heat-crosslinker, a compound containing an alkoxymethyl group is preferable, and in particular a compound represented by the general formula (11) is preferable.

[0080]



[0081]

(wherein in the general formula (11), R^{66} represents a monovalent to decavalent organic group; a plurality of R^{67} s, the same or different, represent a C_1 - C_4 alkyl group; r represents an integer from 1 to 5; and s represents an integer from 1 to 10.)

An alkoxymethyl group causes heat crosslinking reaction at 160°C or more. Accordingly, the group causes cross-linking reaction in a step of heat-curing a photosensitive film and affords a good pattern shape.

[0082]

In addition, the number of alkoxymethyl groups contained is preferably two or more because this enhances the density of cross-linking, and further, the number is more preferably four or more because this enhances chemical resistance. In addition, at least one compound having six or more alkoxymethyl groups is preferably contained as the (C) heat-crosslinker to reduce variation in the dimensions

of a pattern obtained after heat-curing.

[0083]

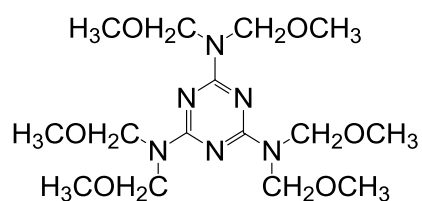
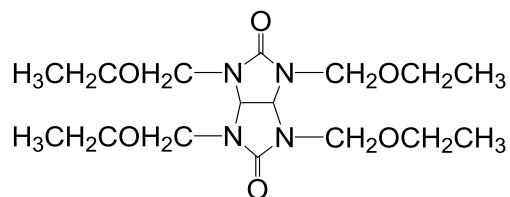
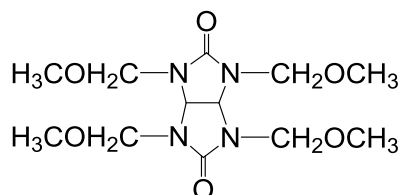
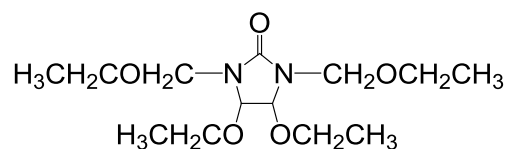
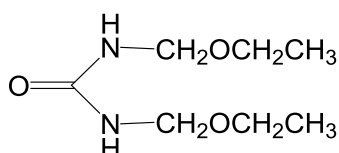
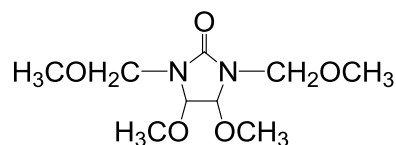
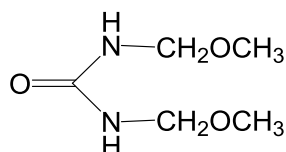
The compound represented by the general formula (11) functions as a thermoplasticizer at less than 160°C at which a heat crosslinking reaction is caused.

- 5 A lamination step is preferably carried out at a temperature of 150°C or less, and this is presumably because this temperature allows the photosensitive layer to be heat-melted, increases its contact area with the substrate, and thus enhances adhesion between them.

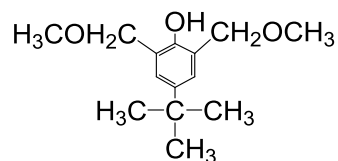
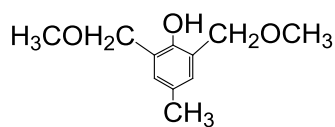
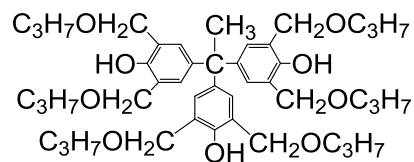
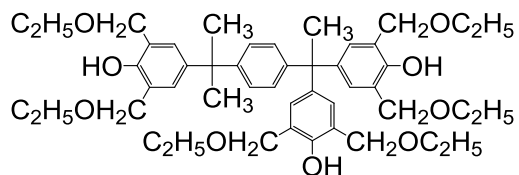
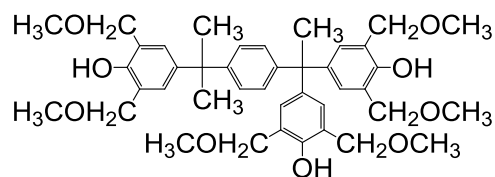
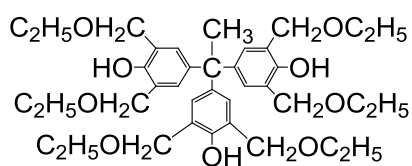
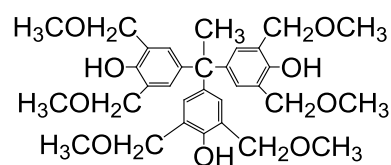
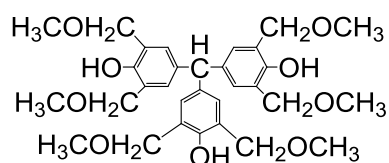
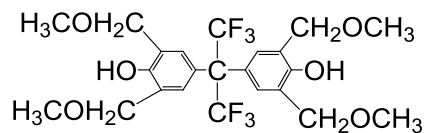
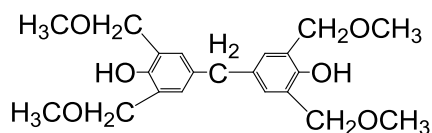
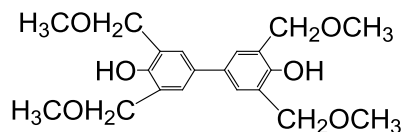
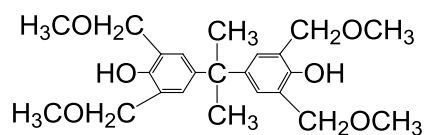
[0084]

- 10 Specific examples of (C) heat-crosslinkers include, but are not limited to, the below-mentioned compounds. Two or more of these may be contained.

[0085]



[0086]



[0087]

The (C) heat-crosslinker content is preferably 1 part by mass or more, more preferably 5 parts by mass or more, with respect to the total amount of the (A1) resin

and the (A2) resin as 100 parts by mass, in order to enhance the density of cross-linking and chemical resistance of the resulting cured film and the adhesion of the film to a substrate. In addition, it is preferably 70 parts by mass or less, more preferably 50 parts by mass or less, in order to enhance mechanical properties.

5 [0088]

The weight-average molecular weight (Mw) of the (C) heat-crosslinker is preferably 100 or more, more preferably 300 or more, with a view to enhancing the mechanical properties of the cured film obtained after heat treatment. In addition, it is preferably 2,500 or less, more preferably 2,000 or less, with a view to enhancing the lamination suitability.

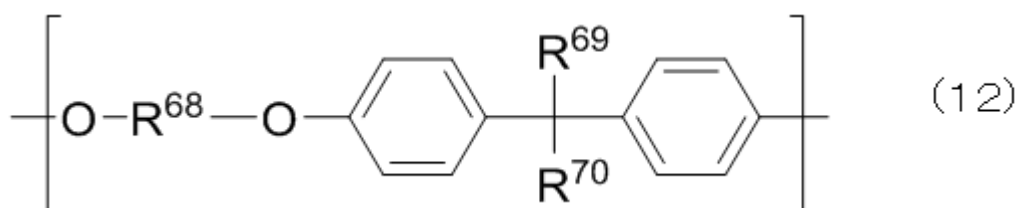
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[0089]

The photosensitive film according to the present invention preferably contains a heat-crosslinker containing a structural unit represented by the following general formula (12). Containing the crosslinker makes it possible to maintain heat resistance and lamination suitability and further to enhance the elongation.

15

[0090]



[0091]

(wherein in the general formula (12), R⁶⁹ and R⁷⁰ each independently represent a hydrogen atom or a methyl group; R⁶⁸ is a bivalent organic group having an alkylene group with two or more carbon atoms and may be linear, branched, or cyclic; and Examples of R⁶⁸ include an alkyl group, cycloalkyl group, alkoxy group, alkyl ether group, alkylsilyl group, alkoxysilyl group, aryl group, aryl ether group, carboxyl group, carbonyl group, allyl group, vinyl group, heterocyclic group,

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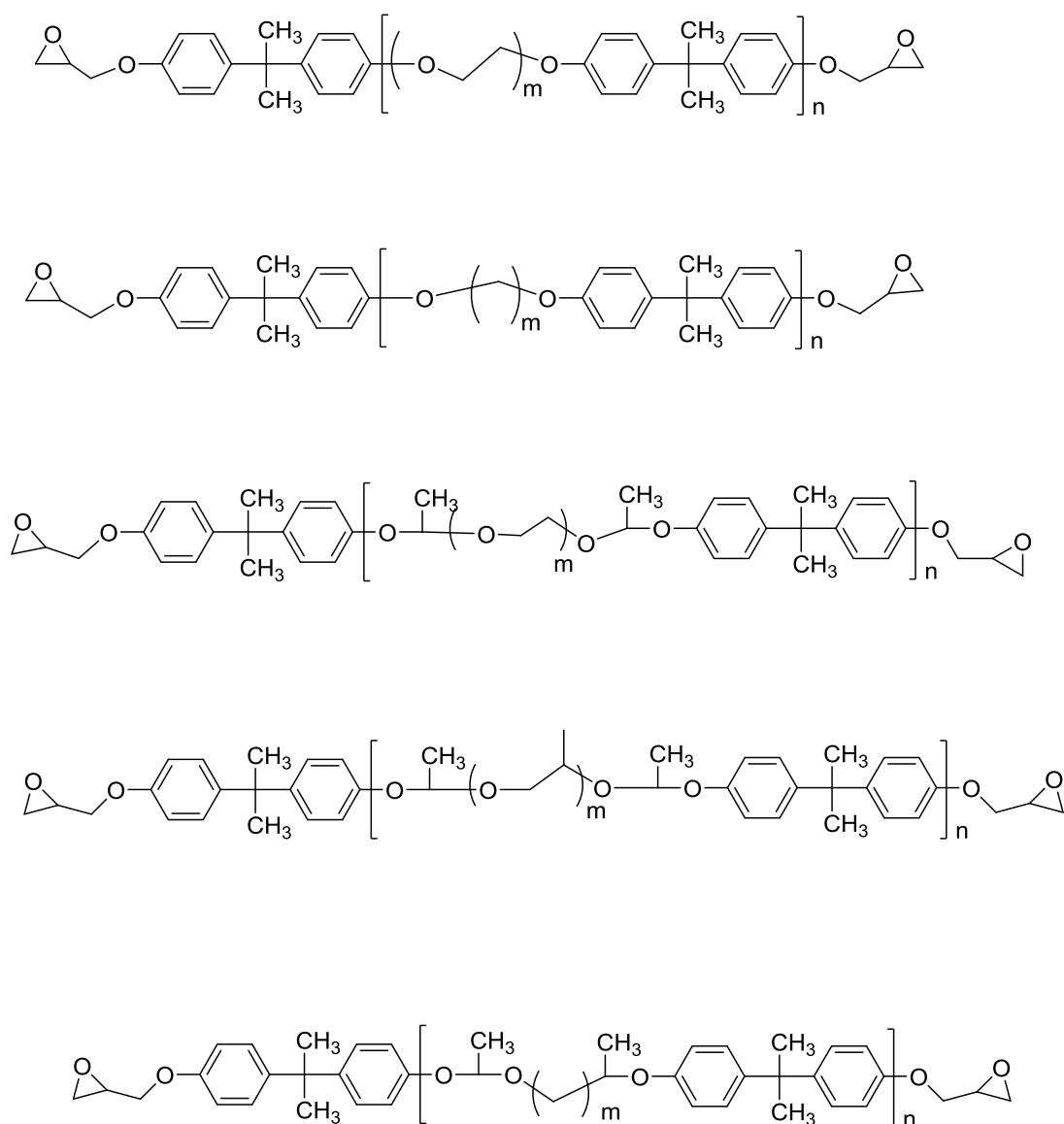
combinations thereof, and the like, and may further contain a substituent.)

The heat-crosslinker itself has a flexible alkylene group and a rigid aromatic group, hence affords heat resistance and lamination suitability, and, at the same time, enables the elongation to be enhanced. Examples of cross-linking groups include, but are not limited to, acrylic groups, methylol groups, alkoxymethyl groups, and epoxy groups. Among these, epoxy groups are preferable because epoxy groups react with a phenolic hydroxyl group of the (A1) resin or the (A2) resin and thus enhance the heat resistance of the cured film and that epoxy groups can react without dehydrating.

[0092]

Examples of compounds represented by the general formula (12) include, but are not limited to, the following structures:

[0093]



[0094]

(wherein n represents an integer from 1 to 5; and m is an integer from 1 to 20.)

In the above-mentioned structures, it is preferable that n is from 1 to 2 and m is from 3 to 7, with a view to enhancing both the heat resistance and elongation.

[0095]

The addition amount of the compound represented by the general formula (12) is preferably 2 to 35 parts by mass, more preferably 5 to 25 parts by mass, with respect to the total of the (A1) resin and the (A2) resin as 100 parts by mass.

Having the addition amount of 2 parts by mass or more affords a sufficient effect of

enhancing elongation, and 35 parts by mass or less makes it possible to suppress reduction in the photosensitivity of the photosensitive film obtained before curing.
[0096]

The photosensitive film according to the present invention may contain (D) an
5 acrylate compound, if necessary. As used herein, the (D) acrylate compound refers to a compound having an acryloyl group or a methacryloyl group. As (D) acrylate compounds, there are a monofunctional acrylate and a multifunctional acrylate. A monofunctional acrylate refers to a compound having at least any one of acryloyl groups or methacryloyl groups. Examples thereof include acrylic esters,
10 methacrylic esters, acrylamides, methacryl amides, and the like. A multifunctional acrylate compound refers to a compound having at least any two or more of acryloyl groups and methacryloyl groups.
[0097]

For the photosensitive film according to the present invention, heat treatment is
15 carried out after pattern processing. In the case of the photosensitive film used as a positive tone composition, acrylate compounds are thermally polymerized thereamong or react with an alkali soluble resin, and are crosslinked, thereby enhancing the elongation of the cured film. In the case of the photosensitive resin film used as a negative tone composition, acrylate compounds are photopolymerized
20 thereamong by exposure during pattern processing, thereby forming a network structure with an alkali soluble resin.
[0098]

With monofunctional acrylate compounds, film curing by crosslinking reaction does not progress sufficiently, resulting in a low effect of enhancing elongation, and
25 thus multifunctional acrylates are preferable.
[0099]

Preferable examples of (D) acrylate compounds include the NK Ester Series

made by Shin-Nakamura Chemical Co., Ltd.: 1G, 2G, 3G, 4G, 9G, 14G, 23G, BG, HD, NPG, 9PG, 701, BPE-100, BPE-200, BPE-500, BPE—1300, A-200, A-400, A-600, A-HD, A-NPG, APG-200, APG-400, APG-700, A-BPE-4, 701A, TMPT, A-TMPT, A-TMM-3, A-TMM-3L, A-TMMT, A-9300, ATM-4E, ATM-35E, ATM-4P, AD-TMP, AD-TMP-L, and A-DPH; and the like. Additional examples include the Light Ester Series made by Kyoeisha Chemical Co., Ltd.: P-1M, P-2M, EG, 2EG, 3EG, 4EG, 9EG, 14EG, 1.4BG, NP, 1.6HX, 1.9ND, 1.10DC, G-101P, G-201P, DCP-M, BP-2EM, BP-4EM, BP-6EM, and TMP; and the like. Additional examples include the “Light Acrylate” (registered trademark) Series made by Kyoeisha Chemical Co., Ltd.: 3EG-A, 4EG-A, 9EG-A, 14EG-A, TMGA-250, NP-A, MPD-A, 1.6HX-A, BEPG-A, 1.9ND-A, MOD-A, DCP-A, BP-4EA, BP-4PA, BA-134, BP-10EA, HPP-A, TMP-A, TMP-3EO-A, TMP-6EO-3A, PE-3A, PE-4A, and DPE-6A; and the like. Additional examples include the Epoxy Ester Series made by Kyoeisha Chemical Co., Ltd.: 40EM, 70PA, 200PA, 80MFA, 3002M, 3002A, 3000M, and 3000A; and the like. Additional examples include the “ARONIX” (registered trademark) Series made by Toagosei Co., Ltd.: M-203, M-208, M-210, M-211B, M-215, M-220, M-225, M-240, M-243, M-245, M-260, M-270, M-305, M-309, M-310, M-313, M-315, M-320, M-325, M-350, M-360, M-402, M-408, and M-450; and the like. Additional examples include the “KAYARAD” (registered trademark) Series made by Nippon Kayaku Co., Ltd.: R-526, NPGDA, PEG400DA, MANDA, R-167, HX-220, HX-620, R-551, R-712, R-604, R-684, GPO-303, TMPTA, THE-330, TPA-320, TPA-330, PET-30, T-1420(T), and RP-1040, and the like. Additional examples include the “BLEMMER” (registered trademark) Series made by NOF Corporation: GMR-H, GAM, PDE-50, PDE-100, PDE-150, PDE-200, PDE-400, PDE-600, PDE-1000, ADE-200, ADE-400, PDP-400, ADP-200, ADP-400, PDT-650, ADT-250, PDBE-200, PDBE-250, PDBE-450, PDBE-1300, ADBE-200, ADBE-250, and ADBE-450; and the like. Additional examples include

MBAA made by MRC Unitec Co., Ltd., and the like. The photosensitive film may contain two or more of these compounds.

[0100]

5 Among the above-mentioned (D) acrylate compounds, acrylate compounds having a molecular weight of 100 to 2,000 are preferable. Having a molecular weight of 100 or more affords a cured film having high elongation, and having a molecular weight of 2,000 or less affords a resin composition having suitable alkaline solubility and high compatibility with an alkali soluble resin.

[0101]

10 The photosensitive film according to the present invention may also contain another alkali soluble resin in addition to the (A2) resin, to the extent that the heat resistance of the cured film obtained by heating treatment is not impaired. Specific examples thereof include; acrylic polymer obtained by copolymerization of acrylic acids; siloxane resins; phenol resins such as novolac resin, resole resin, and
15 polyhydroxystyrene resin; resins in which crosslinking groups such as methylol groups, alkoxymethyl groups, or epoxy groups are introduced; copolymers of these resins; and the like. These resins are soluble in an alkaline aqueous solution containing an alkali such as tetramethylammonium hydroxide, choline, triethylamine, dimethylaminopyridine, monoethanolamine, diethylaminoethanol, sodium hydroxide,
20 potassium hydroxide, or sodium carbonate. The addition of any of these alkali soluble resins makes it possible to maintain the adhesion and high photosensitivity of the heat resistant resin film and, at the same time, provide the characteristics of this alkali soluble resin.

[0102]

25 As another alkali soluble resin, a phenol resin is preferable from a photosensitivity viewpoint. Phenol resins can be obtained by polycondensating a phenol and an aldehyde using a known method. A combination of two or more

resins containing a phenolic hydroxyl group may be contained.

[0103]

Preferable examples of the above-mentioned phenols include phenol, o-cresol, m-cresol, p-cresol, 2,3-xyleneol, 2,5-xyleneol, 3,4-xyleneol, 3,5-xyleneol, 2,3,5-trimethyl phenol, 3,4,5-trimethyl phenol, and the like. In particular, phenol, m-cresol, p-cresol, 2,3-xyleneol, 2,5-xyleneol, 3,4-xyleneol, 3,5-xyleneol, or 2,3,5-trimethyl phenol is preferable. These phenols may be used in combination of two or more kinds thereof. From the viewpoint of solubility in an alkaline developing solution, m-cresol is preferable, and a combination of m-cresol and p-cresol is also preferable.

In other words, as a resin having a phenolic hydroxyl group, a cresol novolac resin containing an m-cresol moiety or containing an m-cresol moiety and a p-cresol moiety is preferably contained. In this regard, a molar ratio of an m-cresol moiety to a p-cresol moiety in a cresol novolac resin (m-cresol moiety/p-cresol moiety, or m/p) is preferably 1.8 or more. This range enables suitable solubility in an alkaline developing solution to be exhibited and enables good photosensitivity to be obtained. More preferably, it is 4 or more.

[0104]

Preferable examples of the above-mentioned aldehydes include formalin, paraformaldehyde, acetaldehyde, benzaldehyde, hydroxybenzaldehyde, chloroacetaldehyde, salicylaldehyde, and the like. Among these, formalin is particularly preferable. These aldehydes may be used in combination of two or more kinds thereof. The amount of aldehyde used is preferably 0.6 mol or more, more preferably 0.7 mol or more, with respect to 1 mol of phenol. It is preferably 3 mol or less, more preferably 1.5 mol or less.

[0105]

For polycondensation reaction between a phenol and an aldehyde, an acidic catalyst is usually used. Examples of such acidic catalysts include hydrochloric

acid, nitric acid, sulfuric acid, formic acid, oxalic acid, acetic acid, p-toluene sulfonic acid, and the like. The amount of the acidic catalyst used is usually 1×10^{-5} to 5×10^{-1} mol with respect to 1 mol of phenol. In polycondensation reaction, water is usually used as a reaction medium, but in a case where the reaction system is carried out in the form of a heterogeneous system from the beginning, a hydrophilic solvent or lipophilic solvent is used as a reaction medium. Examples of hydrophilic solvents include: alcohols such as methanol, ethanol, propanol, butanol, and propylene glycol monomethyl ether; and cyclic ethers such as tetrahydrofuran and dioxane. Examples of lipophilic solvents include ketones such as methylethyl ketone, methylisobutyl ketone, and 2-heptanone. The amount of such a reaction medium used is usually 20 to 1,000 parts by mass with respect to 100 parts by mass of reaction raw materials.

[0106]

The reaction temperature for polycondensation can be adjusted as appropriate in accordance with the reactivity of the raw materials, and is usually 10 to 200°C. Examples of polycondensation reaction methods that can be adopted as appropriate include: a method in which phenols, aldehydes, acidic catalysts, and the like are fed in a lump and allowed to react; a method in which phenols, aldehydes, and the like are added in installments in the presence of an acidic catalyst as the reaction progresses; and the like. On completion of the polycondensation reaction, the reaction temperature is raised to generally 130 to 230°C in order to remove unreacted raw materials, acidic catalysts, reaction media, and the like present in the system, volatile components are removed under reduced pressure, and a resin having a phenolic hydroxyl group is recovered.

[0107]

In the present invention, the weight-average molecular weight of the phenol resin (hereinafter referred to as “Mw”) in terms of polystyrene is preferably 1,000 or

more, more preferably 2,000 or more. It is preferably 20,000 or less, more preferably 10,000 or less. These ranges afford excellent workability and photosensitivity for coating a base material with the positive tone photosensitive resin composition according to the present invention.

5 [0108]

The amount of the other alkali soluble resin is preferably 1 part by mass or more, more preferably 5 parts by mass or more, with respect to the total of the (A1) resin and the (A2) resin as 100 parts by mass, from a photosensitivity viewpoint. The amount is preferably 70 parts by mass or less, more preferably 50 parts by mass or less, from heat resistance and mechanical properties viewpoints.

[0109]

It is preferable that the resins containing structures represented by the general formulae (4) and (5) account for 30 mass% or more of the resin contained in the photosensitive film according to the present invention.

15 [0110]

Furthermore, for the purpose of improving the photosensitivity of the photosensitive film, (E) a compound having a phenolic hydroxyl group may be contained if necessary, provided that the shrinkage after curing is not reduced. Examples of (E) compounds 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, BisOI PP-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 made by 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 made by Asahi Organic Chemicals Industry Co., Ltd.).

[0111]

5 Examples of preferable (E) compounds having a phenolic hydroxyl group include 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, and the like.

[0112]

10 Particularly preferable (E) compounds having a phenolic hydroxyl group are Bis-Z, TekP-4HBPA, TrisP-HAP, TrisP-PA, BisRS-2P, BisRS-3P, BIR-PC, BIR-PTBP, and BIR-BIPC-F. Containing the (E) compound having a phenolic hydroxyl group affords a photosensitive film which is hardly soluble in an alkaline developing solution before exposure but easily soluble in the alkaline developing solution upon
15 exposure, and hence which allows the film reduction due to development to be low and can undergo development in a short time. The amount of the (E) compound having a phenolic hydroxyl group is preferably in a range of from 1 to 50 parts by mass, more preferably 3 to 40 parts by mass, with respect to the total of the (A1) resin and the (A2) resin as 100 parts by mass.

20 [0113]

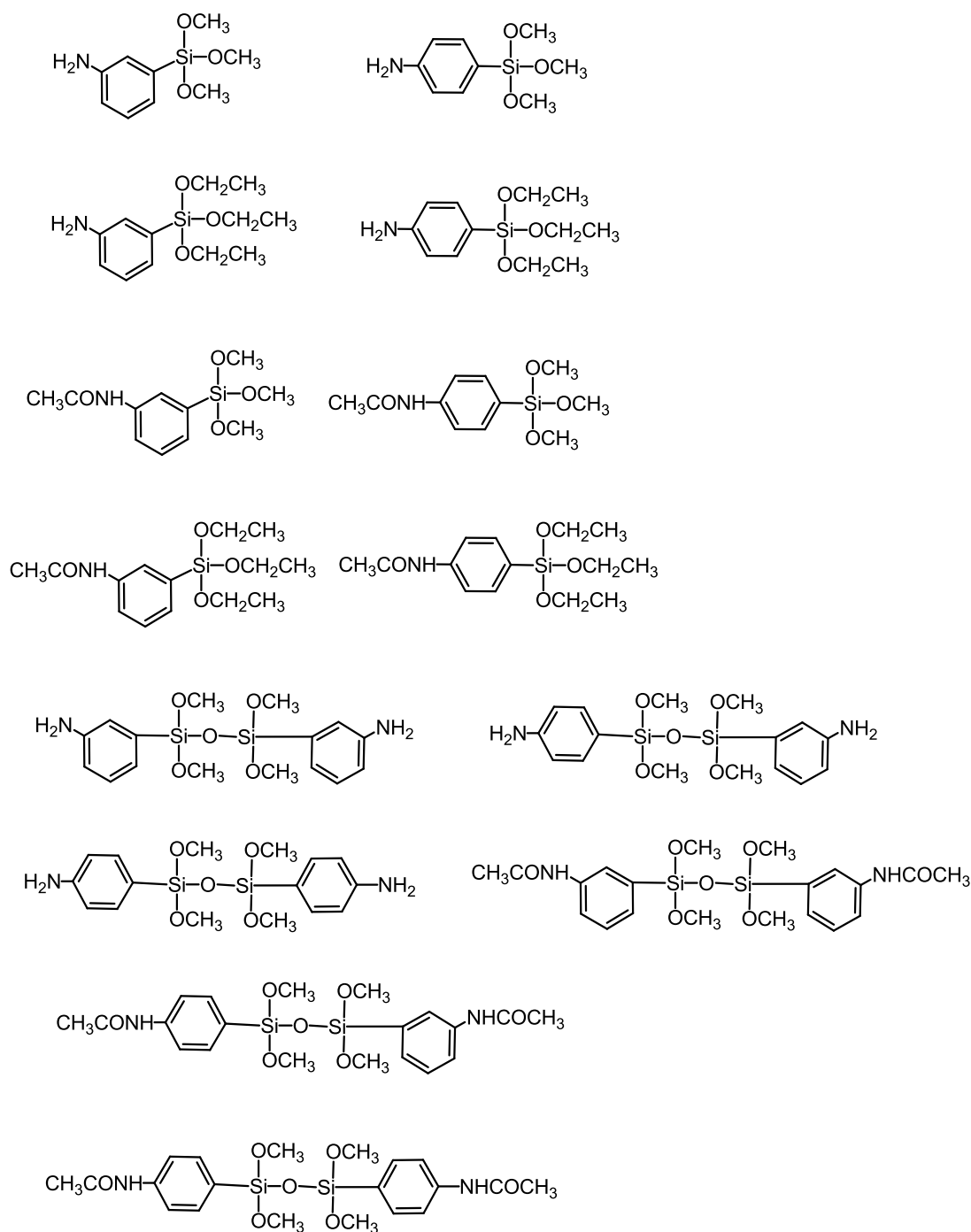
The photosensitive film according to the present invention may contain (F) a solvent. Examples of (F) solvents include: polar aprotic solvents such as γ -butyrolactone; ethers such as tetrahydrofuran, dioxane, and propylene glycol monomethyl ether; dialkylene glycol dialkyl ethers such as dipropylene glycol
25 dimethyl ether, diethylene glycol dimethyl ether, and diethylene glycol ethylmethyl ether; ketones such as acetone, methylethyl ketone, diisobutyl ketone, diacetone alcohol, N,N-dimethylformamide, and N,N-dimethylacetoamide; acetates such as 3-

methoxybutylacetate and ethylene glycol monoethyl ether acetate; esters such as ethyl acetate, propylene glycol monomethyl ether acetate, and ethyl lactate; and aromatic hydrocarbons such as toluene and xylene; and these can be used singly or in mixture. The (F) solvent content is preferably 0.0001 parts by mass or more, preferably 50 parts by mass or less, with respect to the total of the (A1) resin and the (A2) resin as 100 parts by mass.

[0114]

The photosensitive film according to the present invention can contain (G) a silane compound, which can be used as an adhesion promoter for enhancing adhesion to a base substrate. Specific examples of (G) silane compounds include, but are not limited to, 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, 3-methacryloxypropylmethyl diethoxysilane, and silane compounds having a structure described below. Two or more of these may be contained.

[0115]



[0116]

The (G) silane compound content is preferably 0.01 parts by mass to 15 parts by mass, with respect to the total of the (A1) resin and the (A2) resin as 100 parts by mass. This range enables the heat resistance of the positive tone photosensitive film to be maintained, and, at the same time, can achieve the sufficient effect of an adhesion promoter.

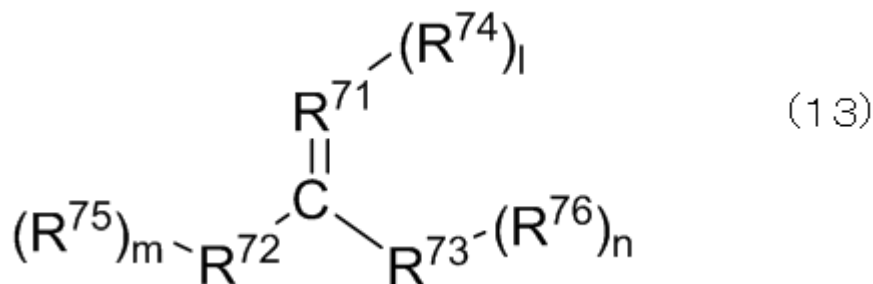
[0117]

In addition, for the purpose of enhancing wettability between the photosensitive film and a substrate, the photosensitive film may contain: an ester such as ethyl lactate or propylene glycol monomethyl ether acetate; an alcohol such as ethanol; a ketone such as cyclohexanone or methylisobutyl ketone; and an ether such as tetrahydrofuran or dioxane. Furthermore, the photosensitive film may contain: inorganic particles such as those of silicon dioxide or titanium dioxide; polyimide powder; or the like.

[0118]

The photosensitive film according to the present invention preferably contains (H) a compound represented by the following general formula (13) (hereinafter referred to as the (H) component). Containing the (H) component remarkably enhances the adhesion of the laminated film to a metal material, copper among others. This is because a S atom or N atom of the compound represented by the general formula (13) interacts with a metal surface and because the compound has a stereo structure that interacts more easily with a metal surface. These effects can impart photosensitivity to the resin composition, and afford a cured resin film having excellent adhesion to a metal material even when the composition contains additives. In the general formula (13), R^{71} to R^{73} represent any of an O atom, a S atom, or a N atom, and at least one of R^{71} to R^{73} represents a S atom. l represents 0 or 1, and R^{71} represents an oxygen atom or a sulfur atom when l is 0, and represents a nitrogen atom when l is 1. m and n represent 1 or 2. R^{74} to R^{76} each independently represent a hydrogen atom or a C_1 - C_{20} organic group. Examples of R^{74} to R^{76} include a hydrogen atom, an alkyl group, cycloalkyl group, alkoxy group, alkyl ether group, alkylsilyl group, alkoxysilyl group, aryl group, aryl ether group, carboxyl group, carbonyl group, allyl group, vinyl group, heterocyclic group, combinations thereof, and the like, and may further contain a substituent.

[0119]



[0120]

The addition amount of the (H) component is preferably 0.1 to 10 parts by mass with respect to the total of the (A1) resin and the (A2) resin as 100 parts by mass.

Using the addition amount of 0.1 parts by mass or more is preferable because it sufficiently affords the effect of enhancing the adhesion of the laminated film to a metal material, and 10 parts by mass or less is preferable because it can suppress the reduction in photosensitivity of the photosensitive film caused by the interaction of the (H) component to the photosensitizer, in a case where the photosensitive film used in the present invention is positive tone.

[0121]

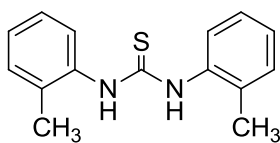
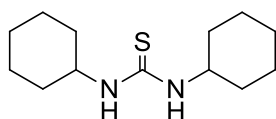
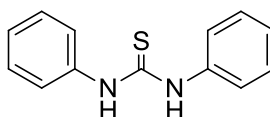
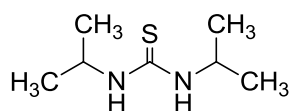
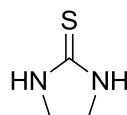
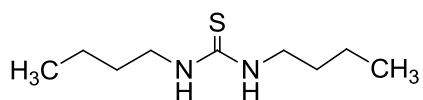
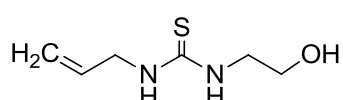
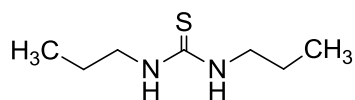
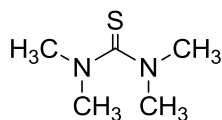
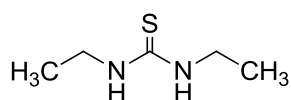
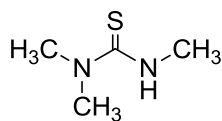
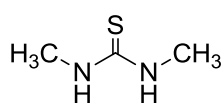
In the compound represented by the general formula (13) used in the present invention, R^{71} to R^{73} represent any of an O atom, a S atom, or a N atom, and at least one of R^{71} to R^{73} is preferably a S atom. In general, the composition to which a compound containing a N atom is added may have photosensitivity impaired through the interaction between a photosensitizer and a compound containing a N atom, but when the compound contains a S atom, the interaction is suitably controlled, and the effect of enhancing adhesion can be obtained without lowering the photosensitivity. In addition, having a trialkoxymethyl group is preferable from the viewpoint of the adhesion of the laminated film to a substrate of a non-metal such as silicon.

[0122]

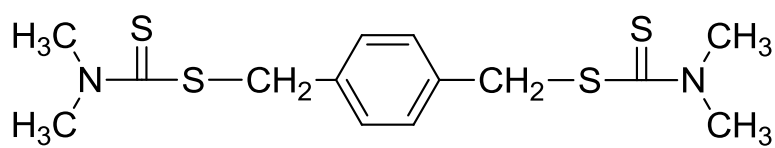
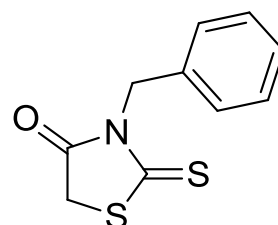
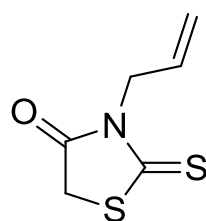
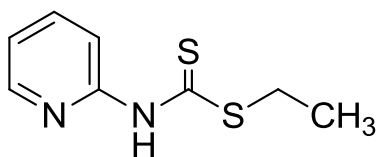
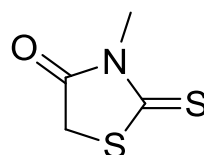
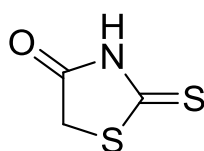
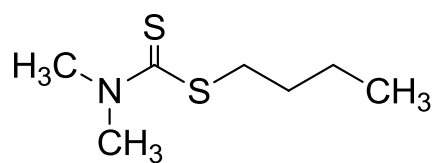
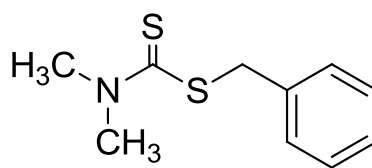
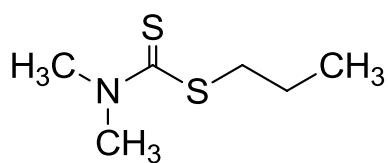
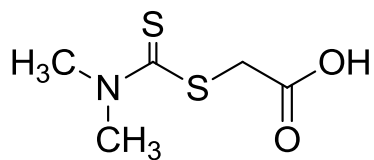
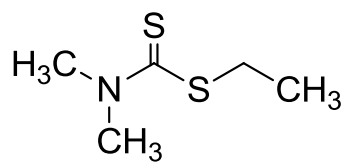
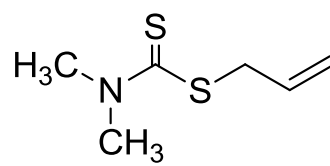
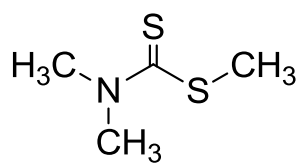
Examples of the compound represented by the general formula (13) include, but

are not limited to, the following structures:

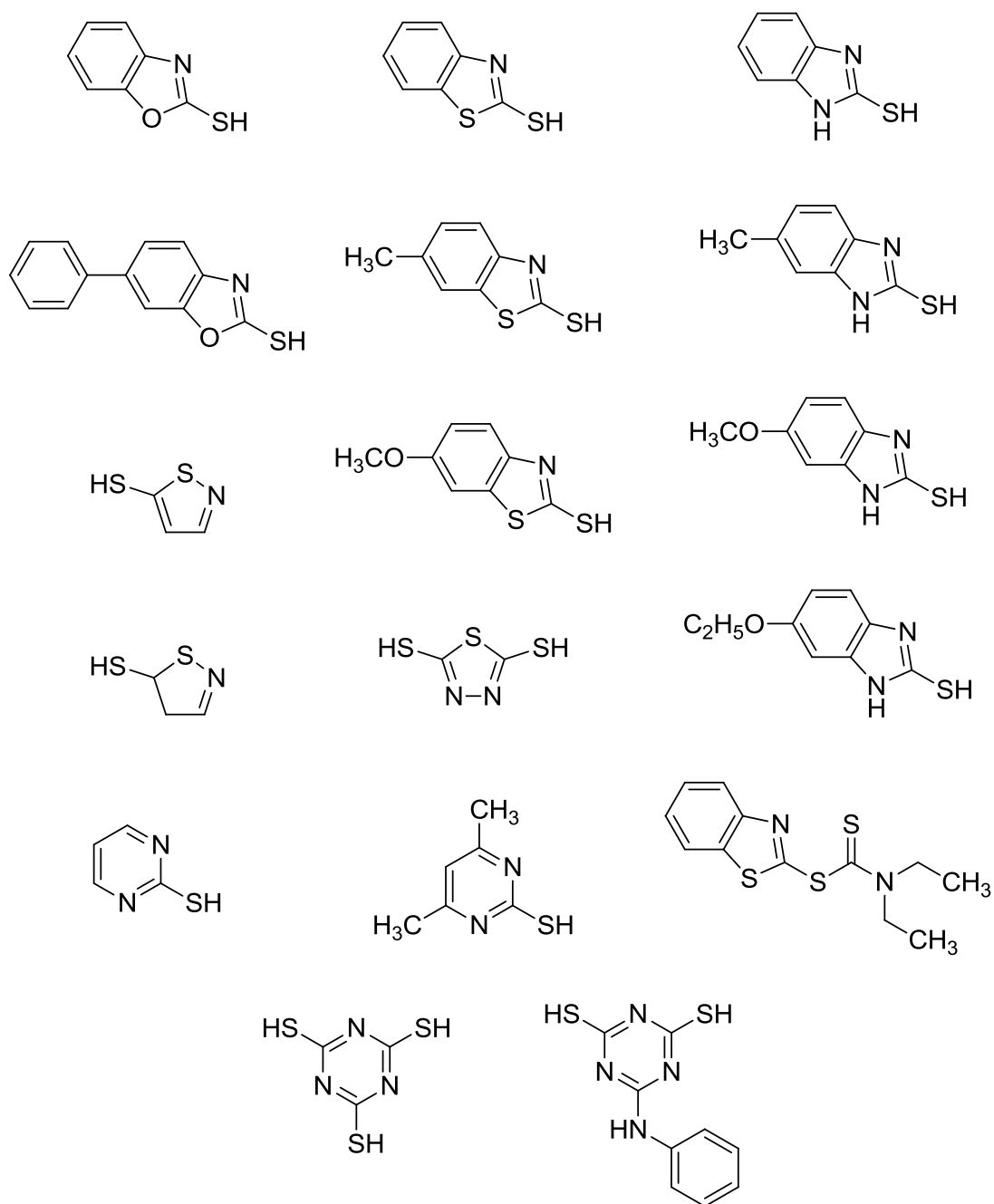
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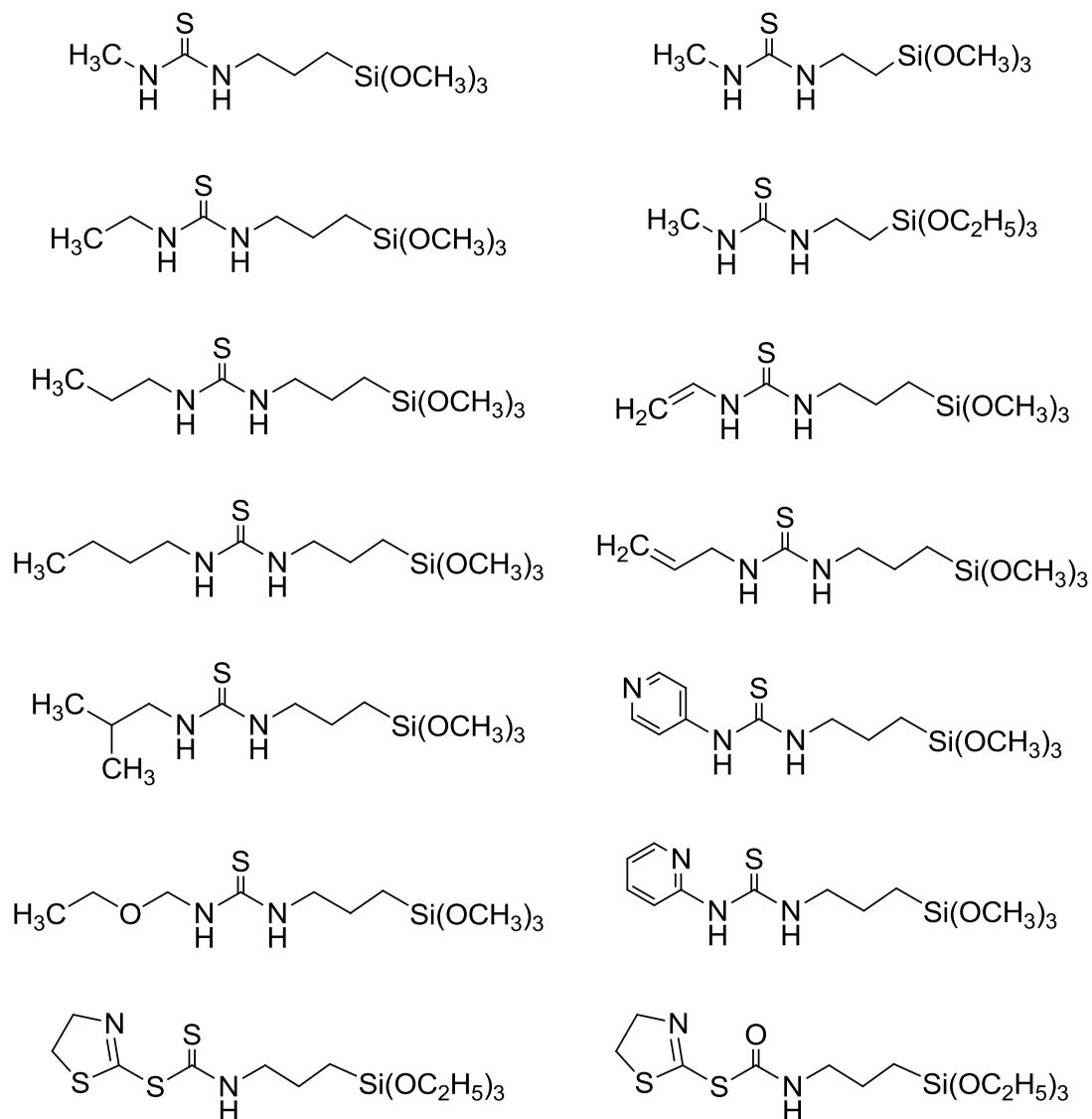
[0124]



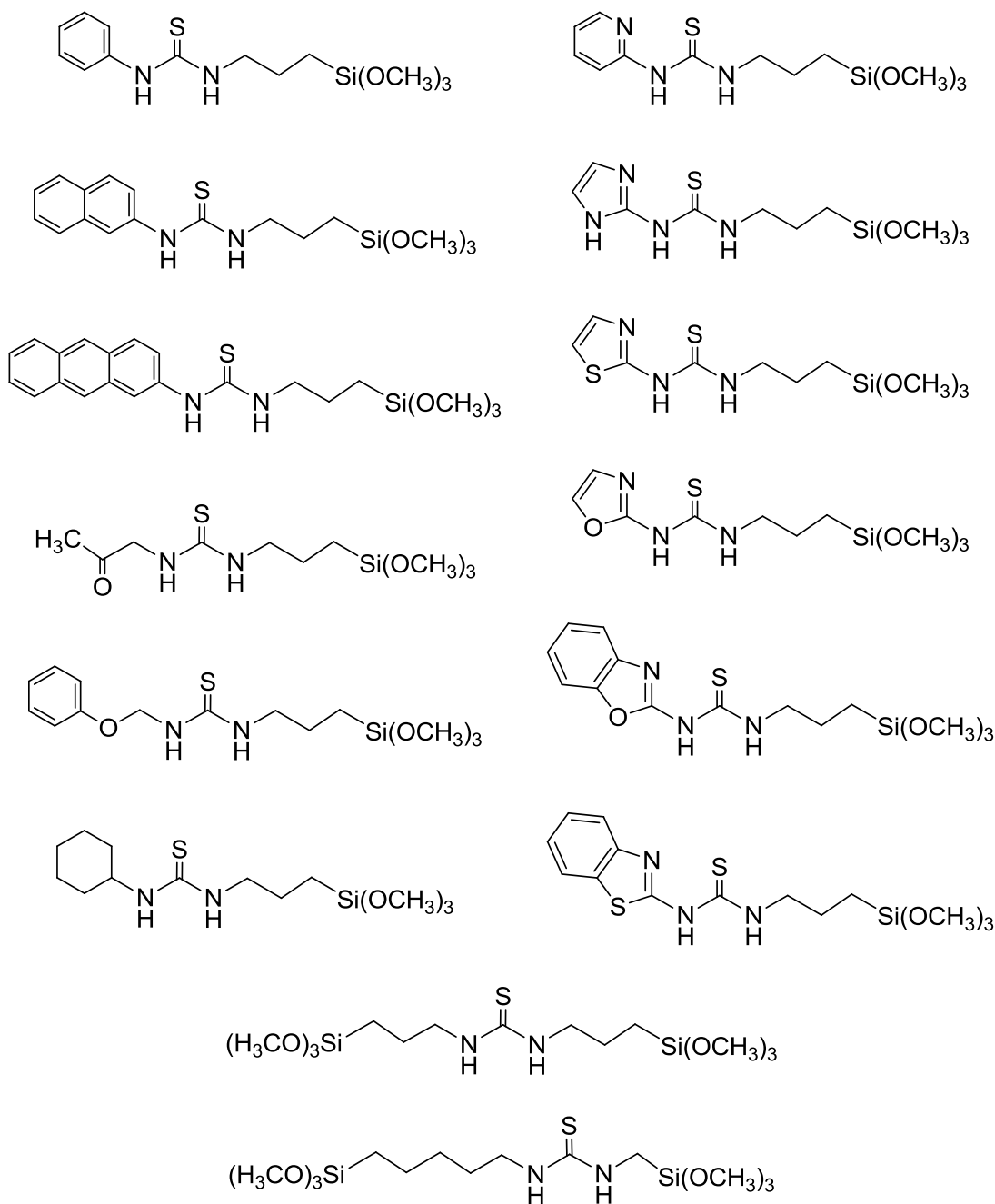
[0125]



[0126]



[0127]



[0128]

The following describes examples of methods of producing a photosensitive film according to the present invention. Examples of methods include: a method in which (A1) an alkali soluble resin containing a structural unit represented by the general formula (1); (A2) an alkali soluble resin containing one or more selected from polyimides, polybenzoxazoles, polyamideimides, precursors of these, and copolymers of these, which each contain a substituent that reacts with the (A1) alkali

soluble resin; (B) a photo acid generator; (C) a heat-crosslinker; (F) a solvent; and other components, if necessary, are added to a glass flask or a stainless steel container and dissolved with stirring with a mechanical stirrer or the like; a method in which they are dissolved by ultrasonication; a method in which they are dissolved with stirring with a planetary mixing deaerator; and the like. A composition containing the (A1) resin, the (A2) resin, the (B) photo acid generator, the (C) heat-crosslinker, the (F) solvent, and the like preferably has a viscosity of 200 to 10,000 mPa·s. Furthermore, the composition may be passed through a filter having a pore size of 0.1 μm to 5 μm for the purpose of removing impurities.

[0129]

The photosensitive film according to the present invention preferably contains a support film. A composition containing the (A1) resin, the (A2) resin, the (B) photo acid generator, the (C) heat-crosslinker, the (F) solvent, and the like is applied to a support film and then dried to afford a photosensitive film having a photosensitive layer on the support film.

[0130]

The support film is not limited to a particular one, but various films that are usually commercially available such as polyethylene terephthalate (PET) films, polyphenylene sulfide films, and polyimide films can be used. A surface treatment such as one with silicone, a silane coupling agent, an aluminum chelating agent, or polyurea may be provided in order to enhance the adhesion and releasability of a joined face between the support film and the photosensitive film. In addition, the thickness of the support film is not limited to a particular value, but is preferably in a range of from 10 to 100 μm from a workability viewpoint.

[0131]

In addition, the photosensitive film according to the present invention may have a protective film thereon in order to protect the surface thereof. Because of this, the

photosensitive film surface can be protected from pollutants such as dirt and dust in the atmosphere.

[0132]

5 Examples of protective films include polyolefin films, polyester films, and the like. Protective films are preferably ones which have a smaller adhesive force to a photosensitive film.

[0133]

10 Examples of methods of coating the support film with a composition containing the (A1) resin, the (A2) resin, the (B) photo acid generator, the (C) heat-crosslinker, the (F) solvent, and the like to thereby form a photosensitive layer include spray coating, roll coating, screen printing, blade coaters, die coaters, calender coaters, meniscus coaters, bar coaters, roll coaters, comma roll coaters, gravure coaters, screen coaters, slit die coaters, and the like. In addition, the coating film thickness depends on the coating technique, the solid content of the composition, the viscosity, and the like, but usually the photosensitive layer film thickness obtained after drying is preferably 0.5 μm to 100 μm . In addition, it is more preferably 3 μm to 40 μm .

[0134]

20 For drying, an oven, a hot plate, infrared light, and the like can be used. The drying temperature and the drying time have only to be in a range in which a solvent can be volatilized, and are preferably set, as appropriate, in a range such that a resin film material for semiconductors turns into the uncured or half-cured state. Specifically, it is preferably carried out in a range of from 40°C to 120°C for one to several tens of minutes. In addition, the temperatures in this range may be combined and applied one after another in a stepwise manner, and, for example, heat treatment may be carried out at 50°C, 60°C, and 70°C for one minute each.

[0135]

Next, a method of producing a semiconductor device using a photosensitive

film will be described. If the photosensitive film has a protective film, this protective film is released first. The photosensitive film is laminated on a substrate by placing them opposite to each other, attaching them to each other by thermal compression bonding, and then transferring the photosensitive film to the substrate.

5 Then, the support film is released to afford a photosensitive coating. Thermal compression bonding can be carried out by thermal pressing, thermal laminating, thermal vacuum laminating, and the like. The thermal compression bonding temperature for the lamination is preferably 40°C or more, more preferably 50°C or more, from the viewpoint of adhesion and embeddability to a substrate. In addition,
10 the thermal compression bonding temperature is preferably 150°C or less, more preferably 120°C or less, in order to prevent the photosensitive film from being cured during thermal compression bonding and thereby undergoing the deterioration of the resolution in pattern formation in the processes of light exposure and development. In addition, thermal compression bonding may be carried out under reduced pressure
15 for the purpose of removing foam.

[0136]

In addition, the support film is released from the photosensitive film in a temperature range of from 0°C to 100°C after the photosensitive film is laminated on a substrate.

20 [0137]

Examples of substrates used include, but are not limited to, silicon wafers, ceramics, gallium arsenide, organic circuit boards, inorganic circuit boards, and these substrates with components of a circuit disposed thereon.

[0138]

25 Examples of organic circuit boards include: glass-substrate copper-clad laminates such as glass fabric/epoxy copper-clad laminates; composite copper-clad laminates such as glass nonwoven fabric/epoxy copper-clad laminates; heat-

resistant/thermoplastic substrates such as polyether imide resin substrates, polyether ketone resin substrates, and polysulfone resin substrates; flexible substrates such as polyester copper-clad film substrates, and polyimide copper-clad film substrates; and the like. In addition, examples of inorganic circuit boards include: ceramic
5 substrates such as alumina substrates, aluminum nitride substrates, and silicon carbide substrates; and metallic substrates such as aluminum-based substrates and iron-based substrates. Examples of components of a circuit include: conductors containing metals such as gold, silver, and copper; resistance elements containing inorganic oxides and the like; low dielectric materials containing glass-based
10 materials, resins, and the like; high dielectric materials containing resins, high dielectric constant inorganic particles, and the like; insulating materials containing glass-based materials and the like; and the like.

[0139]

Next, the photosensitive coating formed by the above-mentioned method is
15 irradiated, for exposure, with actinic rays through a mask having a desired pattern. Examples of actinic rays used for exposure include ultraviolet rays, visible rays, electron beams, X-rays, and the like, and in the present invention, the i-line (365 nm), h-line (405 nm), and g-line (436 nm) of a mercury lamp are preferably used. In a case where a support film for the photosensitive film is a material transparent to
20 these rays, light exposure may be carried out after releasing the support film from the photosensitive film or without releasing the support film. In a case where light exposure is carried out without releasing the support film, the support film is released after light exposure and before development.

[0140]

25 To form a pattern, unexposed areas are removed using a developing solution after exposure. Examples of preferable developing solutions include: a tetramethylammonium aqueous solution; and aqueous solutions of compounds

exhibiting alkalinity such as diethanolamine, diethylaminoethanol, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, triethylamine, diethylamine, methylamine, dimethylamine, dimethylaminoethyl acetate, dimethylaminoethanol, dimethylaminoethyl methacrylate, cyclohexylamine, ethylene diamine, and hexamethylene diamine. In some cases, these alkaline aqueous solutions may contain one kind of or a combination of two or more kinds of: polar solvents such as N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethyl acetamide, dimethyl sulfoxide, γ -butyrolactone, and dimethyl acrylamide; 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.

[0141]

Development can be carried out by a method such as one in which the surface of the photosensitive coating side is sprayed with the aforementioned developing solution, dipped in the developing solution, ultrasonicated while being dipped, or sprayed with the developing solution while the substrate is being rotated.

Conditions for development such as a developing time and a developing solution temperature in a developing step have only to be ones under which unexposed areas are removed, and it is preferable that, after unexposed areas are removed, development is further carried out for micropatterning and for removing residues between patterns.

[0142]

After development, rinse treatment may be carried out with water. Here, the rinse treatment may be carried out with water to which alcohols such as ethanol and isopropyl alcohol, esters such as ethyl lactate and propylene glycol monomethyl ether acetate, or the like are added. A process of baking treatment may be introduced before development, if the process enhances a pattern resolution during

development, or if the process widens the permissible ranges of developing conditions. The temperatures for this is preferably in a range of from 50 to 180°C, more preferably in a range of from 60 to 120°C in particular. The time is preferably 5 seconds to several hours.

5 [0143]

After pattern formation, a temperature of from 120°C to 400°C is applied to afford a cured film. This heating treatment is carried out for 5 minutes to 5 hours while selected temperatures are applied one after another in a stepwise manner or while temperature is raised continuously in a selected temperature range. By way
10 of an example, heat treatment is carried out at 130°C and 200°C, each for 30 minutes. Alternatively, another example is a method in which temperature is raised linearly from room temperature to 250°C in 2 hours. In this case, the heating temperature is preferably 150°C to 300°C, more preferably 180°C to 250°C.

[0144]

15 The thickness of the cured film is preferably 0.5 μm or more, more preferably 2 μm or more, with a view to enhancing the insulation properties. In addition, it is preferably 100 μm, more preferably 40 μm or less, with a view to reducing the substrate warpage caused by the residual stress.

[0145]

20 The cured film formed by curing the photosensitive film according to the present invention is suitable for use in the applications of a passivation film of a semiconductor, a semiconductor protective film, an interlayer insulating film for multilayer wiring for high-density mounting, an insulating layer for an organic electroluminescent element, or the like. In addition, the cured film formed by
25 curing the photosensitive film according to the present invention can be used for semiconductor devices in which a relief pattern layer of the cured film is formed.

[0146]

In addition, it is also possible to make a semiconductor device by disposing a 2 to 40 μm thick layer of the cured film on a substrate as above-mentioned; disposing copper wiring thereon; and forming another 2 to 40 μm thick layer of the cured film as an insulating film between copper wiring layers.

5 [0147]

An example of a preferred structure of a semiconductor device in which the cured film formed by curing the photosensitive film according to the present invention is disposed will be described below with reference to Fig. 1. A passivation film 2 is formed on a semiconductor element 1. A photosensitive film according to the present invention is laminated on the passivation film 2 by thermal compression bonding, dried by heating using a hot plate or the like, and formed into a photosensitive coating pattern through exposure and development. After the photosensitive coating pattern is formed, the film is cured in a high temperature treatment process to form a cured film 3. On the cured film 3, metal wiring is formed using a technique such as sputtering, evaporation, electroless plating, or electrolytic plating. Further, to protect the metal wiring, a photosensitive film according to the present invention is laminated thereon by thermal compression bonding, dried by heating using a hot plate or the like, and formed into a pattern through exposure and development. After the photosensitive coating pattern is formed, the film is cured in a high temperature treatment process to form a cured film 5. Using the above-mentioned technique to form a cured film makes it possible to provide a highly flat semiconductor device having high adhesion between the cured films and high adhesion between the cured film and the metal wiring.

[0148]

25 The following describes an application example in which a cured film formed by curing the photosensitive film according to the present invention is disposed in a coil part of an inductor device, with reference to the drawings. Fig. 2 is a cross-

sectional view of a coil part having a cured film according to the present invention. As shown in Fig. 2, a substrate 6 is laid with an insulating film 7, on which a cured film 8 is formed in the form of a pattern. Ferrite or the like is used for the substrate 6. The photosensitive film according to the present invention may be used for either the cured film 7 or the cured film 8. In the aperture of this pattern, a metal film 9 (Cr, Ti, or the like) is formed, on which metal wiring 10 (Ag, Cu, or the like) is plated. The metal wiring 10 (Ag, Cu, or the like) is formed into a spiral shape. A multilayer formed by repeating the steps from 7 to 10 a plurality of times is allowed to have a function of a coil. In a final stage, the metal wiring 10 (Ag, Cu, or the like) is connected to an electrode 12 via metal wiring 11 (Ag, Cu, or the like), and sealed with a molding compound 13.

[0149]

The following describes an application example in which a cured film formed by curing the photosensitive film according to the present invention is disposed in an electronic component or a semiconductor device having a hollow portion, with reference to the drawings. Fig. 3 is an example of a cross-sectional view of the hollow portion of a surface acoustic wave device using a photosensitive film according to the present invention. As shown in Fig. 3, an IDT (Inter Digital Transducer) electrode 15, which is constituted by a pair of interlocking interdigital electrodes having a plurality of electrode fingers, and a bonding pad 16 for making electrical conduction are formed on a substrate 14. Here, examples of the substrate 14 include substrates of lithium niobate, potassium niobate, lithium tantalate, quartz, langasite, ZnO, PZT, lithium tetraborate, and the like. Examples of materials for the electrode 15 and the bonding pad include metals such as Al, Pt, Cu, Au, Ti, Ni, Cr, W, Pd, Co, Mn, and the like. Further, a relief pattern layer of the cured film of the photosensitive resin composition is formed as a support material 18 in order to ensure a hollow portion 17 on the piezo-electric substrate 14. Examples of

photosensitive resin compositions include polyimide-based resins, epoxy-based resins, acryl-based resins, phenol-based resins, and the like. A covering material 19 is provided on the substrate 15 via a support material 17 so as to cover the electrode 15. Here, the photosensitive film according to the present invention is used for the covering material 19, and may be used for the support material 17. The covering material 19 has a thickness of, for example, 20 μm . A protection member 20 is provided so as to cover the substrate 14, the support material 18, and the covering material 19. For example, the protection member 20 on the covering material 19 has a thickness of, for example, 30 μm . The protection member is made of an insulating material, and examples thereof include epoxy-based resins, benzocyclobutene resins, silicon-based resins, SOG (Spin On Glass), and the like. A via 21 may be provided inside the support material 17 and the covering material 19 in such a manner as to penetrate them in the thickness direction. A solder bump 22 is formed to be connected to the via 21.

[0150]

The following describes an application example in which the photosensitive film according to the present invention is applied to a semiconductor device including a substrate providing a level difference, with reference to the drawings. Fig. 4 is an enlarged cross-sectional view of a pad portion of a semiconductor device having a cured film according to the present invention, and shows a structure called fan-out wafer level package (fan-out WLP). A silicon wafer 23 with an Al pad 24 and a passivation film 25 formed thereon is diced and cut into chips, each of which is then sealed with a resin 26. The chip is heated when sealed, and the shrinkage of the resin 26 generates a level difference (T-1) between the chip 23 and the resin 26. Here, the level difference (T-1) between the (S-1) upper level at the chip 23 surface and the (S-2) lower level at the resin 26 surface is 2 to 40 μm . A cured film 27 in the form of a pattern of the photosensitive film according to the present invention is

formed on each of the (S-1) upper level and the (S-2) lower level, and the level difference (T-2) between the cured film disposed on the (S-1) upper level and the cured film disposed on the (S-2) lower level results in 5 μm or less.

[0151]

5 Further, a metal (Cr, Ti, or the like) film 28 and metal wiring 29 are formed. After this, a barrier metal 31 and a solder bump 32 are formed at the aperture that is in an insulating film 30 formed above the molding compound over the chip. A fan-out WLP is a semiconductor package in which a necessary number of terminals are ensured by providing the periphery of the semiconductor chip with a part extended

10 using a molding compound such as an epoxy resin, attaching a redistribution portion from the electrode to the extended part on the semiconductor chip, and mounting a solder ball also on the extended part. In the fan-out WLP, wiring is installed so as to be across the borderline formed by the principal surface of the semiconductor chip and the principal surface of the molding compound. In other words, the interlayer

15 insulating film is formed on a base material composed of two or more kinds of materials, i.e., a semiconductor chip and a molding compound with metal wiring disposed on them, and wiring is formed on the interlayer insulating film. Other than this, the type of semiconductor package that has a semiconductor chip embedded in a concave part which is formed in a glass epoxy resin substrate has

20 wiring installed so as to be across the borderline between the principal surface of the semiconductor chip and the principal surface of the printed board. Also in this aspect, an interlayer insulating film is formed on a base materials composed of two or more kinds of materials, and wiring is formed on the interlayer insulating film.

25 In a case where the cured film formed by curing the photosensitive film according to the present invention is disposed on a substrate composed of two or more kinds of materials, the cured film can reduce a level difference over the substrate and maintain the flatness of the cured film, and hence the cured film is preferably used as

an interlayer insulating film provided on a substrate composed of two or more kinds of materials.

EXAMPLES

5

[0152]

The present invention will be described below by way of Examples and Comparative Examples, but the present invention is not limited thereby. The esterification rate of the quinonediazide compound synthesized and the photosensitive film were evaluated by the following method.

10

[0153]

〈Method of Measuring Film Thickness〉

Prebaked films and developed films were measured using a Lambda Ace STM-602 made by Dainippon Screen Mfg. Co., Ltd. at a refractive index of 1.629 on the basis of polyimide.

15

[0154]

〈Measurement of Imidization Rate of Polyimide〉

In regard to the imidization rate of the (A2) alkali soluble resin, an N-methylpyrrolidone (hereinafter referred to as NMP) solution of a polyimide resin whose solid content is 50 mass% was applied on a 6 inch silicon wafer by a spin coating method, and then baked using a hot plate (SKW-636, made by Dainippon Screen Mfg. Co., Ltd.) at 120°C for 3 minutes to form a prebaked film having a thickness of $10\ \mu\text{m} \pm 1\ \mu\text{m}$. This film was divided into halves and one half was introduced in an inert oven (INH-21CD, made by Koyo Thermo Systems Co., Ltd.). The temperature was raised to the curing temperature of 350°C over 30 minutes and then a heating treatment was performed at 350°C for 60 minutes. After slowly cooling the oven until the temperature in the oven reaches 50°C or lower, a cured

20

25

film was obtained. With respect to the obtained cured film (A) and the film (B) before curing, an infrared absorption spectrum was measured using a Fourier transform infrared spectrophotometer FT-720 (made by Horiba, Ltd.). A peak intensity at about $1,377\text{ cm}^{-1}$ due to the C-N stretching vibration of an imide ring was determined, and a value obtained from “peak intensity of a film (B) before curing / peak intensity of a cured film (A)” was regarded as an imidization rate.

[0155]

〈Evaluation of Lamination Suitability〉

From the photosensitive film made in the below-mentioned Examples and Comparative Examples, a protective film was released. Then, the released side of the photosensitive film was laminated on a silicon wafer or a copper substrate. As a copper substrate, a substrate (copper-plated substrate) having, on its surface, a metal material layer formed by sputtering titanium and copper, 100 nm thick, onto a silicon wafer and then forming a 2 μm thick copper-plated film by electrolytic plating was used. The lamination was carried out using a laminating device (VTM-200M, made by Takatori Corporation) under the conditions including a stage temperature of 80°C, a roll temperature of 80°C, a degree of vacuum of 150 Pa, an attaching rate of 5 mm/second, and an attaching pressure of 0.2 MPa. After the lamination, a grid of cut lines were made in the center of the film on the substrate using a cutter guide such that 100 squares, 2 mm $\times$ 2 mm each, were made on the photosensitive coating. A piece of cellophane tape was adhered to the grid portion, pulled in the direction making an angle of 90° with the substrate, and released. After the release, the number of the photosensitive coating pieces released out of the 100 pieces was counted. A smaller number of pieces released means higher adhesion, and a larger number means lower adhesion. The number is preferably 50 or less, more preferably 20 or less, still more preferably 10 or less. The lamination suitability evaluation made to the silicon wafer was designated as the condition 1, and the

evaluation made to the copper substrate was designated as the condition 2.

[0156]

〈Evaluation of Patterning Property (High Resolution)〉

The protective film was released from the photosensitive film produced in Examples and Comparative Examples, and the released surface of the photosensitive film was laminated onto an 8 inch silicon wafer using a laminating device (VTM-200M, made by Takatori Corporation) under the conditions including a stage temperature of 80°C, a roll temperature of 120°C, a degree of vacuum of 150 Pa, an attaching rate of 5 mm/second, and an attaching pressure of 0.2 MPa. Then, the resulting laminate was baked using a hot plate (ACT-8) at 120°C for 3 minutes to produce a prebaked film having a thickness of 10 μm . This film was exposed to light using an i-line stepper (NIKON NSR i9) at a dose of from 0 to 1000 mJ/cm^2 at a step of 10 mJ/cm^2 . After the exposure, the film was developed with a 2.38 mass% tetramethylammonium (TMAH) aqueous solution (ELM-D, made by Mitsubishi Gas Chemical Co., Inc.) for 90 seconds, and then rinsed with pure water to obtain a developed film A having a 5 μm isolated aperture.

[0157]

In regard to the developed film A, the dose (referred to as the minimum dose, Eth) at which the exposed area of the 5 μm isolated aperture completely dissolved away after the exposure and development was regarded as a photosensitivity. When the Eth is 400 mJ/cm^2 or less, the photosensitivity can be determined as high. It is preferably 300 mJ/cm^2 or less, more preferably 250 mJ/cm^2 or less.

[0158]

〈Evaluation of High Elongation〉

The protective film was released from the photosensitive film produced in Examples and Comparative Examples, and the photosensitive film was laminated onto a silicon wafer using a laminating device (VTM-200M, made by Takatori

Corporation) under the conditions including a stage temperature of 80°C, a roll temperature of 120°C, a degree of vacuum of 150 Pa, an attaching rate of 5 mm/second, and an attaching pressure of 0.2 MPa, such that the film thickness T1 was 11 μ m. The laminated substrate was prebaked on a hot plate at 120°C for 3 minutes, and then heated to 220°C at 3.5°C/minute at an oxygen concentration of 20 ppm or less under a nitrogen flow using an inert oven CLH-21CD-S (made by Koyo Thermo Systems Co., Ltd.), and heated at 220°C for 1 hour. The heat-treated film was released using a 46 mass% hydrofluoric acid aqueous solution to afford a cured film (heat resistant resin film). The cured film obtained by this method was cut into 7 cm $\times$ 1 cm pieces using a single edged knife, which were tensioned at 50 mm/minute using a TENSILON Universal Material Testing Instrument (RTM-100, made by Orientec Corporation). The value of the amount of elongation obtained after this was divided by the sample length to determine a value of interest. This measurement was carried out to 10 samples, and the largest value of those obtained from them was regarded as an elongation. The elongation is preferably 10% or more, more preferably 20% or more, still more preferably 40% or more.

[0159]

〈5% Weight Loss Temperature Measurement (Evaluation of Heat Resistance)〉

The cured film obtained in the same manner as in the above-mentioned 〈Evaluation of High Elongation〉 was heated at a speed of 10°C/min under the conditions including a nitrogen flow of 80 mL/min using a thermo gravimetry analyzer (TGA50, made by Shimadzu Corporation), and measured. The 5% weight loss temperature is preferably 260°C or more, more preferably 300°C or more, still more preferably 340°C or more.

[0160]

The abbreviations and names of the compounds used in Examples and Comparative Examples are as follows:

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

TDA-100: 3,4-dicarboxy-1,2,3,4-tetrahydro-1-naphthalenesuccinic dianhydride

CBDA: cyclobutanetetracarboxylic dianhydride

6FDA: 4,4'-hexafluoroisopropylidenediphthalic dianhydride

5 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

DAE: 4,4'-diaminodiphenyl ether

NMP: N-methyl-2-pyrrolidone

10 ED-600: JEFFAMINE ED-600 (which is the name of a product made by
HUNTSMAN Corporation)

MAP: meta-aminophenol

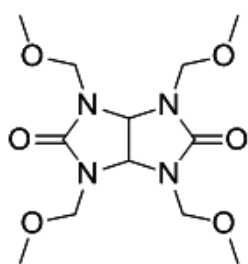
NA: 5-norbornene-2,3-dicarboxylic anhydride

KBM-403: 3-glycidoxypropyltrimethoxysilane (silane compound (a))

15 [0161]

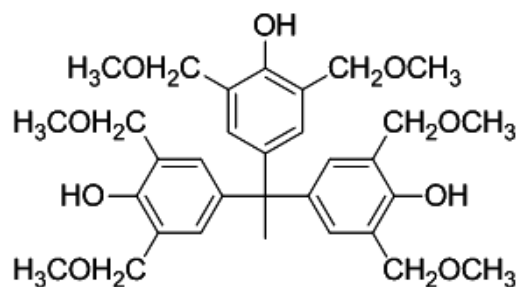
The following are the (C) heat-crosslinkers and the (H) compounds used in
Examples and Comparative Examples.

[0162]



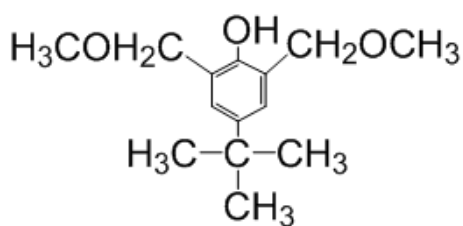
(C) Heat-Crosslinker (a)

MX-270

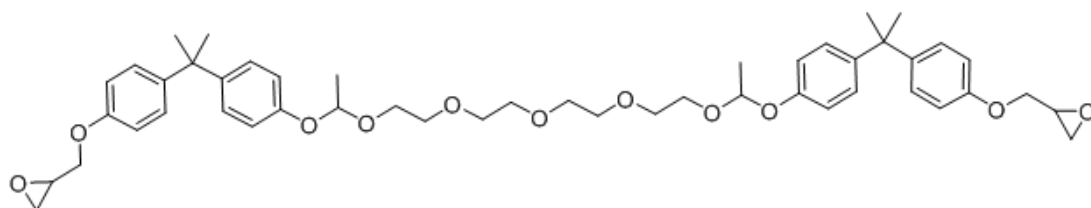


(C) Heat-Crosslinker (b)

HMOM-TPHAP

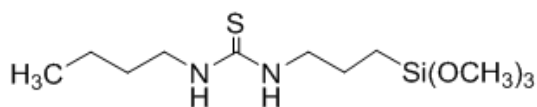


(C) Heat-Crosslinker (c)

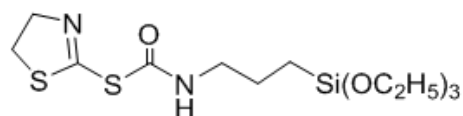


(C) Heat-Crosslinker (d)

[0163]



(H) Compound (h1)



(H) Compound (h2)

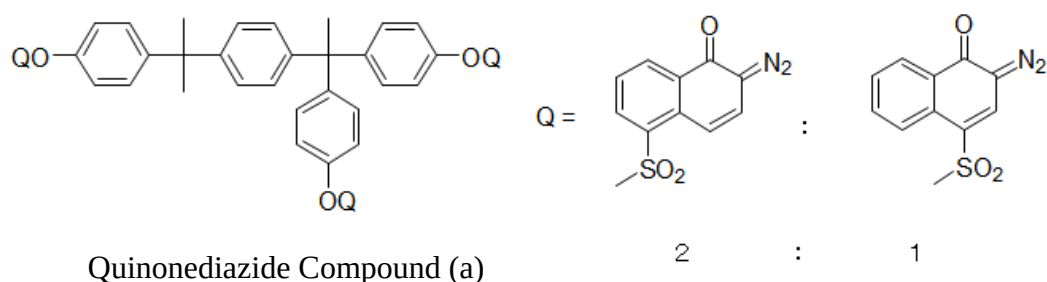
[0164]

5 Synthesis Example 1: Synthesis of Quinonediazide Compound (a)

In a dry nitrogen gas flow, 21.22 g (0.05 mol) of TrisP-PA (which is the name of a product made by 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 added dropwise while the temperature inside the system was kept at lower than 35°C. After the dropwise addition, 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 drying oven, to obtain a quinonediazide compound (a) represented by the following formula:

[0165]



[0166]

Synthesis Example 2: Synthesis of Polyhydroxystyrene Resin (a0-1)

A 20 g total amount of p-t-butoxystyrene and styrene 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 solution. 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, whereafter the mixture was then poured into water, the polymer was precipitated, p-t-butoxystyrene was deprotected to give hydroxystyrene, and the

resultant product was washed and dried, to obtain a purified copolymer of p-hydroxystyrene and styrene (hereinafter referred to as (a0-1)). The product was analyzed by GPC, and it was found that the product had a weight-average molecular weight (M_w) of 3500 (in terms of GPC polystyrene) and a polydispersity index (M_w/M_n) of 2.80.

[0167]

Synthesis Example 3: Synthesis of Polyhydroxystyrene Resin (a0-2)

The synthesis was carried out in the same manner as in Synthesis Example 2 except that m-t-butoxystyrene was used in place of p-t-butoxystyrene. The resulting copolymer (hereinafter referred to as (a0-2)) of m-hydroxystyrene and styrene was analyzed by GPC, and it was found that the copolymer had a weight-average molecular weight (M_w) of 5000 (in terms of GPC polystyrene) and a polydispersity index (M_w/M_n) of 3.20.

[0168]

Synthesis Example 4: Synthesis of Polyhydroxystyrene Resin (a0-3)

The synthesis was carried out in the same manner as in Synthesis Example 2 except that no styrene was added. The resulting p-hydroxystyrene resin (hereinafter referred to as (a0-3)) was analyzed by GPC, and it was found that the resin had a weight-average molecular weight (M_w) of 3000 (in terms of GPC polystyrene) and a polydispersity index (M_w/M_n) of 1.60.

[0169]

Synthesis Example 5: Synthesis of Alkali Soluble Resin (a1-1)

The polyhydroxystyrene resin (a0-1) was dissolved in a solution of 80 g of sodium hydroxide (2.0 moles) dissolved in 800 g of purified water. After the resin is completely dissolved, 686 g of a 36 to 38 mass% formalin aqueous solution was added dropwise to the above-mentioned solution at 20 to 25°C over 2 hours.

Subsequently, the resultant solution was stirred at 20 to 25°C for 17 hours. A 98 g

amount of sulfuric acid and 552 g of water were added to the solution to neutralize the solution, and the neutralized solution was allowed to stand for 2 days. A white solid material formed in the solution that had been allowed to stand was washed with 100 mL of water. The white solid material was dried in vacuo at 50°C for 48 hours.

5 [0170]

Subsequently, the white solid material thus produced was dissolved in 300 mL of methanol, then 2 g of sulfuric acid was added to the solution, and the resultant solution was stirred at room temperature for 24 hours. A 15 g amount of an anionic ion exchange polymer (AMBERLYST IRA96SB, made by Rohm and Haas

10 Company) was added to the solution, the resultant solution was stirred for 1 hour, and then the ion exchange polymer was removed by filtration. Subsequently, 500 mL of GBL was added to the solution, and methanol was removed from the solution using a rotary evaporator to produce a GBL solution. The solution was analyzed by ¹³C-NMR (GX-270, made by JOEL Ltd.), and it was confirmed that an alkali soluble resin (hereinafter referred to as (a1-1)) which was a partly alkoxyated polyhydroxystyrene resin was obtained. The product was analyzed by GPC, and it was found that the product had a weight-average molecular weight (Mw) of 8000 (in terms of GPC polystyrene) and contained an alkoxyated hydroxystyrene moiety at an introduction rate of 35 mol% per 1 mol of hydroxystyrene.

20 [0171]

Synthesis Example 6: Synthesis of Alkali Soluble Resin (a1-2)

The synthesis was carried out in the same manner as in Synthesis Example 5 except that (a0-2) was used in place of (a0-1). The resulting alkali soluble resin (hereinafter referred to as (a1-2)) which was an alkoxyated polyhydroxystyrene resin was analyzed by GPC, and it was found that the product had a weight-average molecular weight (Mw) of 7500 (in terms of GPC polystyrene) and contained an alkoxy group at an introduction rate of 55 mol% per 1 mol of hydroxystyrene.

25

[0172]

Synthesis Example 7: Synthesis of Alkali Soluble Resin (a1-3)

The synthesis was carried out in the same manner as in Synthesis Example 5 except that (a0-3) was used in place of (a0-1). The resulting alkali soluble resin (hereinafter referred to as (a1-3)) which was an alkoxyated polyhydroxystyrene resin was analyzed by GPC, and it was found that the product had a weight-average molecular weight (Mw) of 3500 (in terms of GPC polystyrene) and contained an alkoxy group at an introduction rate of 69 mol% per 1 mol of hydroxystyrene.

[0173]

10 Synthesis Example 8: Synthesis of Novolac Resin (e)

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 of a 37 mass% formaldehyde aqueous solution (0.93 mol of formaldehyde), 0.63 g (0.005 mol) of oxalic acid dihydrate, and 264 g of methylisobutyl ketone were fed, and then immersed in an oil bath, and the reaction solution 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 solution was cooled to room temperature, to obtain an alkali soluble novolac resin (e) in the form of a solid polymer. The product was analyzed by GPC, and it was confirmed that the product had a weight-average molecular weight (Mw) of 3,500. To the obtained novolac resin (e), γ -butyrolactone (GBL) was added to obtain a solution of the novolac resin (e) whose solid content is 43 mass%.

[0174]

Synthesis Example 9: Synthesis of Cyclized Polyimide Resin (A)

25 In a dry nitrogen gas flow, 4.48 g (0.020 mol) of PMDA-HH and 11.11 g (0.025 mol) of 6FDA were dissolved in 100 g of NMP. To this, 1.09 g (0.010 mol) of 3-aminophenol was added together with 20 g of NMP. Further to this solution, 11.90

g (0.033 mol) of BAHF, 1.00 g (0.005 mol) of DAE, and 6.00 g (0.010 mol) of ED-600, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP, were added, and allowed to react 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 drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (A) powder.

[0175]

Synthesis Example 10: Synthesis of Cyclized Polyimide Resin (B)

In a dry nitrogen gas flow, 1.12 g (0.005 mol) of PMDA-HH, 11.11 g (0.025 mol) of 6FDA, and 4.65 g (0.015 mol) of ODPa were dissolved in 100 g of NMP. To this, 1.09 g (0.010 mol) of 3-aminophenol was added together with 20 g of NMP. Further to this solution, 11.90 g (0.033 mol) of BAHF, 1.00 g (0.005 mol) of DAE, 6.00 g (0.010 mol) of ED600, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP, were added, and allowed to react 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 drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (B) powder.

[0176]

Synthesis Example 11: Synthesis of Cyclized Polyimide Resin (C)

In a dry nitrogen gas flow, 3.92 g (0.020 mol) of CBDA and 11.11 g (0.025 mol) of 6FDA were dissolved in 100 g of NMP. To this, 1.09 g (0.010 mol) of 3-aminophenol was added together with 20 g of NMP. Further to this solution, 11.90 g (0.033 mol) of BAHF, 1.00 g (0.005 mol) of DAE, 6.00 g (0.010 mol) of ED600, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP, were added, and allowed to react 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 drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (C) powder.

5 [0177]

Synthesis Example 12: Synthesis of Cyclized Polyimide Resin (D)

In a dry nitrogen gas flow, 0.98 g (0.005 mol) of CBDA, 11.11 g (0.025 mol) of 6FDA, and 4.65 g (0.015 mol) of ODPA were dissolved in 100 g of NMP. To this solution, 11.90 g (0.033 mol) of BAHF, 0.50 g (0.003 mol) of DAE, 7.50 g (0.013
10 mol) of ED600, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP, were added, and allowed to react at 60°C for 1 hour, and then stirred at 180°C for 4 hours, whereafter 1.64 g (0.010 mol) of 5-norbornene-2,3-dicarboxylic anhydride was added as an end-capping agent, together with 10 g of NMP, and allowed to react at 60°C for 1 hour. After the stirring was finished, the solution was poured into 2 L of
15 water to obtain white precipitate. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (D) powder.

[0178]

Synthesis Example 13: Synthesis of Cyclized Polyimide Resin (E)

In a dry nitrogen gas flow, 0.98 g (0.005 mol) of CBDA, 11.11 g (0.025 mol) of 6FDA, and 4.50 g (0.015 mol) of TDA-100 were dissolved in 100 g of NMP. To this solution, 11.90 g (0.033 mol) of BAHF, 0.50 g (0.003 mol) of DAE, 7.50 g (0.013 mol) of ED600, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP,
20 were added, and allowed to react at 60°C for 1 hour, and then stirred at 180°C for 4 hours, whereafter 1.64 g (0.010 mol) of 5-norbornene-2,3-dicarboxylic anhydride was added as an end-capping agent, together with 10 g of NMP, and allowed to react at 60°C for 1 hour. 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 drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (E) powder.

[0179]

5 Synthesis Example 14: Synthesis of Cyclized Polyimide Resin (F)

In a dry nitrogen gas flow, 10.09 g (0.045 mol) of PMDA-HH was dissolved in 100 g of NMP. To this, 1.09 g (0.010 mol) of 3-aminophenol was added together with 20 g of NMP. Further to this solution, 15.57 g (0.043 mol) of BAHF, 1.00 g (0.005 mol) of DAE, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP,
10 were added, allowed to react 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 drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (F) powder.

15 [0180]

Synthesis Example 15: Synthesis of Cyclized Polyimide Resin (G)

In a dry nitrogen gas flow, 8.82 g (0.045 mol) of CBDA was dissolved in 100 g of NMP. To this, 1.09 g (0.010 mol) of 3-aminophenol was added together with 20 g of NMP. Further to this solution, 15.57 g (0.043 mol) of BAHF, 1.00 g (0.005
20 mol) of DAE, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP, were added, allowed to react 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 drying oven at 50°C for 72 hours, to
25 obtain a cyclized polyimide resin (G) powder.

[0181]

Synthesis Example 16: Synthesis of Cyclized Polyimide Resin (H)

In a dry nitrogen gas flow, 13.96 g (0.045 mol) of ODPa was dissolved in 100 g of NMP. To this, 1.09 g (0.010 mol) of 3-aminophenol was added together with 20 g of NMP. Further to this solution, 11.90 g (0.033 mol) of BAHF, 1.00 g (0.005 mol) of DAE, 6.0 g (0.010 mol) of ED600, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP, were added, and allowed to react 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 drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (H) powder.

[0182]

Synthesis Example 17: Synthesis of Cyclized Polyimide Resin (I)

In a dry nitrogen gas flow, 6.01 g (0.020 mol) of TDA-100 and 11.11 g (0.025 mol) of 6FDA were dissolved in 100 g of NMP. To this, 1.09 g (0.010 mol) of 3-aminophenol was added together with 20 g of NMP. Further to this solution, 11.90 g (0.033 mol) of BAHF, 1.00 g (0.005 mol) of DAE, 6.0 g (0.010 mol) of ED600, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP, were added, and allowed to react 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 drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (I) powder.

[0183]

Synthesis Example 18: Synthesis of Cyclized Polyimide Resin (J)

In a dry nitrogen gas flow, 19.99 g (0.045 mol) of 6FDA was dissolved in 100 g of NMP. To this, 1.09 g (0.010 mol) of 3-aminophenol was added together with 20 g of NMP. Further to this solution, 11.90 g (0.033 mol) of BAHF, 1.00 g (0.005 mol) of DAE, 6.0 g (0.010 mol) of ED600, and 0.62 g (0.003 mol) of SiDA, together

with 20 g of NMP, were added, and allowed to react 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 drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (J) powder.

[0184]

Synthesis Example 19: Synthesis of Polybenzoxazole Precursor (K)

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, made by Nihon Nohyaku Co., Ltd.) in 25 g of GBL was dropped while the internal temperature was kept at lower than 0°C. After the dropwise addition finished, the solution continued to be stirred at -15°C for 6 hours. After the reaction finished, the solution was poured into 3 L of water containing 10 mass% of methanol, and white precipitate was deposited. The precipitate was collected by filtration, washed with water three times, and then dried with a vacuum drying oven at 50°C for 72 hours, to obtain an alkali soluble polybenzoxazole precursor (K).

[0185]

Synthesis Example 20: Synthesis of Polyimide Precursor Resin (L)

In a dry nitrogen gas flow, 7.51 g (0.038 mol) of 4,4'-diaminophenyl ether (hereinafter referred to as DAE), 1.86 g (0.007 mol) of SiDA, and 1.09 g (0.010 mol) of 3-aminophenol were dissolved in 100 g of NMP. To this solution, 13.96 g (0.045 mol) of ODP and 20 g of NMP were added and allowed to react at 20°C for 1 hour and then react at 50°C for 4 hours. After that, a solution obtained by diluting 9.25 g (0.08 mol) of N,N-dimethylformamide dimethyl acetal with 5 g of NMP was added dropwise over 10 minutes, and the resulting solution was allowed to react at 50°C for

3 hours. After the reaction finished, the solution was poured into 2 L of water, and a polymer solid precipitate was collected by filtration. Further, this precipitate was washed with 2 L of water 2 times, dried with a vacuum drying oven at 80°C for 20 hours to obtain a polyimide resin (K).

5 [0186]

Synthesis Example 21: Synthesis of Polyimide Resin (M)

In a dry nitrogen gas flow, 8.11 g (0.04 mol) of DAE and 1.09 g (0.010 mol) of 3-aminophenol were dissolved in 100 g of NMP. To this solution, 13.96 g (0.045 mol) of ODPA and 20 g of NMP were added and allowed to react at 20°C for 1 hour and then react at 50°C for 4 hours. Subsequently, the resultant solution was stirred at 180°C for 5 hours. After the stirring was finished, the solution was poured into 2 L of water to obtain white precipitate. This precipitate was collected by filtration, washed with water 3 times, dried with a vacuum drying oven at 80°C for 20 hours to obtain a polyimide resin (M).

15 [0187]

Synthesis Example 22: Synthesis of Cyclized Polyimide Resin (N)

In a dry nitrogen gas flow, 3.92 g (0.020 mol) of CBDA and 11.11 g (0.025 mol) of 6FDA were dissolved in 100 g of NMP. To this, 1.09 g (0.010 mol) of 3-aminophenol was added together with 20 g of NMP. Further to this solution, 10.07 g (0.028 mol) of BAHF, 1.00 g (0.005 mol) of DAE, 10.50 g (0.018 mol) of ED600, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP, were added, and allowed to react 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 drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (N) powder.

25 [0188]

Synthesis Example 23: Synthesis of Cyclized Polyimide Resin (O)

In a dry nitrogen gas flow, 3.92 g (0.020 mol) of CBDA and 11.11 g (0.025 mol) of 6FDA were dissolved in 100 g of NMP. To this, 1.09 g (0.010 mol) of 3-aminophenol was added together with 20 g of NMP. To this solution, 7.33 g (0.020 mol) of BAHF, 1.00 g (0.005 mol) of DAE, 15.00 g (0.025 mol) of ED600, and 0.62 g (0.003 mol) of SiDA, together with 20 g of NMP, were added, and allowed to react 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 drying oven at 50°C for 72 hours, to obtain a cyclized polyimide resin (O) powder.

[0189]

Synthesis Example 24: Synthesis of Novolac Resin (f)

Into a nitrogen-purged 1000 ml three-neck flask, 108.0 g of m-cresol, 108.0 g of methanol, and 40.0 g of sodium hydroxide were fed, heated at 67°C with stirring and then refluxed for 30 minutes. Then, the reaction solution was cooled to 40°C, fed with 65.2 g of 92 mass% paraformaldehyde, heated again to 67°C, and then refluxed for 5 hours. After the reaction finished, the reaction solution was cooled to 30°C or less, and to this, 140.0 g of 30 mass% sulfuric acid was added dropwise over 30 minutes with the reaction solution kept at less than 35°C. The resulting reaction solution had a pH of 4.9. In addition, 540.0 g of ion exchange water was added to the reaction solution, the resultant mixture was stirred for 20 minutes and allowed to stand for 20 minutes, and then the separated aqueous layer was removed. After the aqueous layer was removed, 108.0 g of dioxane was added to the resultant solution, and the residual water was removed from the resultant solution to less than 3 mass% at 40°C at a pressure of 0.08 MPa. To the reaction solution, 432.0 g of methanol and 2.0 g of 96 mass% sulfuric acid were added. The resulting reaction solution

had a pH of 0.8. The reaction solution was heated to 60°C, and allowed to undergo an alkoxylation reaction at 60°C for 3 hours. After the reaction finished, the reaction solution was cooled to 30°C or less, and to this, a 10 mass% sodium hydroxide aqueous solution was added dropwise over 30 minutes with the reaction solution temperature kept at less than 35°C until the reaction solution had a pH of 9.0. To the reaction solution, 216.0 g of methylisobutyl ketone (MIBK) that was a separating solvent for washing and 324.0 g of ion exchange water were added, the resulting mixture was stirred at 30°C for 20 minutes and allowed to stand for 20 minutes, and then the separated aqueous layer was removed. Further, 324.0 g of ion exchange water was added to the mixture, and washing operations were repeated with ion exchange water until the removed water had an electroconductivity of 100 μ scm or less. After the washing finished, 300 g of γ -butyrolactone was added to the mixture, and ion exchange water and MIBK were distilled off at 70°C at a pressure of 0.08 MPa to obtain a novolac resin solution (f) having a 50 mass% solid content.

[0190]

The resulting novolac resin solution (f) was analyzed by GPC, and it was found that the solution had a weight-average molecular weight (M_w) of 7000 (in terms of GPA polystyrene) and a polydispersity index of (M_w/M_n) of 7.5. A ^{13}C NMR measurement showed that the number of moles of alkoxyalkyl groups per 1 mol of phenol skeletons was 57 mol% and that the alkoxylation rate was 100 mol%.

[0191]

Example 1

A 10.5 g amount of the alkali soluble resin (a1-1), 10.5 g of the resin (A) obtained in Synthesis Example 9, 3.0 g of the quinonediazide compound (a) obtained in Synthesis Example 1, 7.2 g of a crosslinker MX-270, and 1.0 g of KBM-403 were added to 25 g of GBL to obtain a varnish A of a positive tone photosensitive resin

composition.

[0192]

The obtained varnish was applied to a 38 μm thick PET film using a comma roll coater and dried at 80°C for 8 minutes, whereafter a 10 μm thick PP film was
5 laminated as a protective film to obtain a photosensitive film. The photosensitive film was adjusted to have a film thickness of 10 μm .

[0193]

The photosensitive film obtained was evaluated for lamination suitability to a silicon substrate, high elongation, 5% weight loss temperature (heat resistance), and
10 patterning property.

[0194]

Examples 2 to 33 and Comparative Examples 1 to 8

A varnish was made in the same manner as in Example 1 except that the addition amounts of the (A1) alkali soluble resin, the (A2) alkali soluble resin, other
15 additives, the (B) photo acid generator, and the (C) crosslinker were changed to those in Table 1, Table 2-1, and Table 2-2. The photosensitive film obtained was evaluated for lamination suitability to a silicon substrate, high elongation, 5% weight loss temperature (heat resistance), and patterning property.

[0195]

20 The molar ratios of the components of the (A2) alkali soluble resin are shown in Table 1.

[0196]

[Table 1]

(A2) Alkali Soluble Resin	Molar Ratio										
	Acid Component (Molar Ratio)					Diamine Component (Molar Ratio)				End	
	PMDA-HH	CBDA	TDA-100	ODPA	6FDA	BAHF	ED-600	DAE	SiDA	MAP	NA
A	40				50	65	20	10	5	20	
B	10			30	50	65	20	10	5	20	
C		40			50	65	20	10	5	20	
D		10		30	50	65	25	5	5		20
E		10	30		50	65	25	5	5		20
F	90					85		10	5	20	
G		90				85		10	5	20	
H				90		65	20	10	5	20	
I			40		50	65	20	10	5	20	
J					90	65	20	10	5	20	
L					100			83	17	20	
M					110			100		20	
N		40			50	55	35	10	5	20	
O		40			50	40	50	10	5	20	

[0197]

[Table 2-1]

	(A1) Alkali Soluble Resin		(A2) Alkali Soluble Resin		Other Resins		(B) Photo Acid Generator		(C) Heat Crosslinker				(G) Silane Compound		(H) Compound	
		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)
Example 1	a1-1	10.5	A	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 2	a1-2	10.5	A	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 3	a1-3	10.5	A	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 4	a1-1	4.0	A	17.0	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 5	a1-1	17.0	A	4.0	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 6	a1-1	10.5	B	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 7	a1-1	10.5	C	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 8	a1-1	10.5	D	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 9	a1-1	10.5	E	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 10	a1-1	10.5	F	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 11	a1-1	10.5	G	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 12	a1-1	10.5	H	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 13	a1-1	10.5	I	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 14	a1-1	10.5	J	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 15	a1-1	10.5	K	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 16	a1-1	10.5	L	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 17	a1-1	10.5	M	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 18	a1-1	10.5	A	10.5	-	-	(a)	3.0	(a)	2.0	-	-	(a)	1.0	-	-
Example 19	a1-1	10.5	A	10.5	-	-	(a)	3.0	(a)	14	-	-	(a)	1.0	-	-
Example 20	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	-	-	(a)	1.0	-	-
Example 21	a1-1	10.5	A	10.5	-	-	(a)	3.0	(c)	8.5	-	-	(a)	1.0	-	-

[0198]

[Table 2-2]

	(A1) Alkali Soluble Resin		(A2) Alkali Soluble Resin		Other Resins		(B) Photo Acid Generator		(C) Heat Crosslinker				(G) Silane Compound		(H) Compound	
		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)		Addition Amount (g)
Example 22	a1-1	10.5	N	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 23	a1-1	10.5	O	10.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Example 24	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	(d)	1.2	(a)	1.0	-	-
Example 25	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	(d)	4.0	(a)	1.0	-	-
Example 26	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	(d)	21.0	(a)	1.0	-	-
Example 27	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	(d)	24.0	(a)	1.0	-	-
Example 28	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	-	-	(a)	1.0	h1	0.06
Example 29	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	-	-	(a)	1.0	h1	0.20
Example 30	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	-	-	(a)	1.0	h1	6.00
Example 31	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	-	-	(a)	1.0	h1	6.50
Example 32	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	-	-	(a)	1.0	h2	0.20
Example 33	a1-1	10.5	A	10.5	-	-	(a)	3.0	(b)	7.2	(d)	4.0	(a)	1.0	h1	0.20
Comparative Example 1	a0-1	8.5	A	12.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Comparative Example 2	a0-2	8.5	A	12.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Comparative Example 3	a0-3	8.5	A	12.5	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Comparative Example 4	a1-1	21.0	-	-	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Comparative Example 5	-	-	A	21.0	-	-	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
Comparative Example 6	a1-1	10.5	A	10.5	-	-	(a)	3.0	-	-	-	-	(a)	1.0	-	-
Comparative Example 7	-	-	A	10.5	(e)	10.5	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-

Comparative Example 8	-	-	A	10.5	(f)	21.0	(a)	3.0	(a)	7.2	-	-	(a)	1.0	-	-
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[0199]

The evaluation results are shown in Tables 3-1 and 3-2.

[0200]

[Table 3-1]

	Lamination Suitability (Number of Pieces Released) (Condition 1)	Lamination Suitability (Number of Pieces Released) (Condition 2)	Evaluation of Elongation (%)	5% Weight Loss Temperature (°C)	Evaluation of Photosensitivity (mJ/cm ²)
Example 1	0	8	40	342	240
Example 2	0	7	45	344	280
Example 3	0	8	45	345	290
Example 4	10	17	50	350	170
Example 5	10	18	10	280	290
Example 6	20	28	20	323	240
Example 7	0	8	40	347	210
Example 8	15	24	20	320	250
Example 9	15	25	20	315	210
Example 10	40	46	40	274	170
Example 11	35	43	40	278	180
Example 12	35	43	10	340	220
Example 13	40	46	10	346	210
Example 14	35	44	10	343	260
Example 15	50	50	25	304	310
Example 16	45	48	10	263	250
Example 17	45	49	15	347	350
Example 18	10	20	35	300	250
Example 19	0	8	35	310	210
Example 20	0	9	50	340	230
Example 21	0	8	5	253	235

[0201]

[Table 3-2]

	Lamination Suitability (Number of Pieces Released) (Condition 1)	Lamination Suitability (Number of Pieces Released) (Condition 2)	Evaluation of Elongation (%)	5% Weight Loss Temperature (°C)	Evaluation of Photosensitivity (mJ/cm ²)
Example 22	0	11	35	323	200
Example 23	15	27	25	310	190
Example 24	0	5	52	342	230
Example 25	0	5	57	351	230
Example 26	0	5	54	349	250
Example 27	0	7	53	347	300
Example 28	0	0	57	342	230
Example 29	0	0	57	342	230
Example 30	0	0	56	340	240
Example 31	0	0	54	335	270
Example 32	0	2	57	342	230
Example 33	0	0	57	351	230
Comparative Example 1	0	12	5	255	350
Comparative Example 2	0	11	5	261	370
Comparative Example 3	0	10	5	267	360
Comparative Example 4	100	100	15	249	360
Comparative Example 5	10	24	40	318	Pattern Eluted
Comparative Example 6	60	71	30	281	270
Comparative Example 7	80	87	20	296	280
Comparative Example 8	85	91	20	305	275

Reference Signs List

[0202]

1: semiconductor element

2: passivation film

5 3: cured film

4: metal wiring

5: cured film

6: substrate

7: cured film

10 8: cured film

9: metal film

10: metal wiring

11: metal wiring

12: electrode

15 13: molding compound

14: substrate

15: IDT electrode

16: bonding pad

17: hollow portion

20 18: support material

19: covering material

20: protection member

21: via

22: solder bump

25 23: silicon wafer

24: Al pad

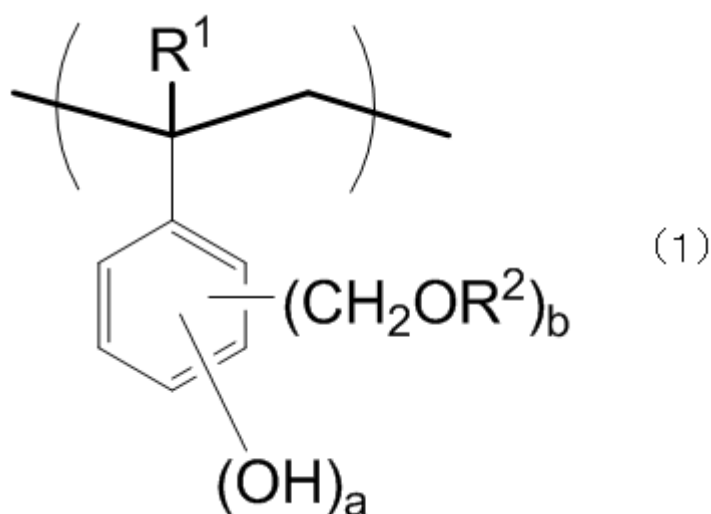
25: passivation film

- 26: resin
- 27: cured film
- 28: metal film
- 29: metal wiring
- 5 30: insulating film
- 31: barrier metal
- 32: solder bump

CLAIMS

1. A photosensitive film comprising:

(A1) an alkali soluble resin containing a structural unit represented by the
5 general formula (1):



(wherein in the general formula (1), R¹ represents a hydrogen atom or a C₁-C₅ alkyl group;

10 a is an integer in a range of from 0 to 4;

b is an integer in a range of from 1 to 3; and

R² is a hydrogen atom, methyl group, ethyl group, or propyl group);

(A2) an alkali soluble resin containing one or more selected from polyimides, polybenzoxazoles, polyamideimides, precursors of these, and copolymers of these;

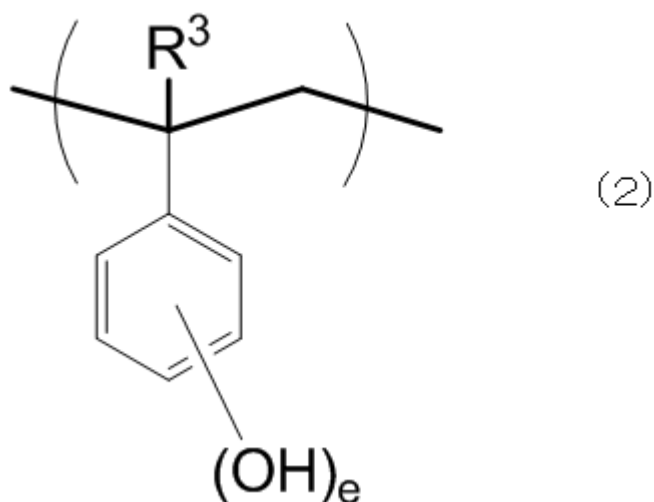
15 (B) a photo acid generator; and

(C) a heat-crosslinker.

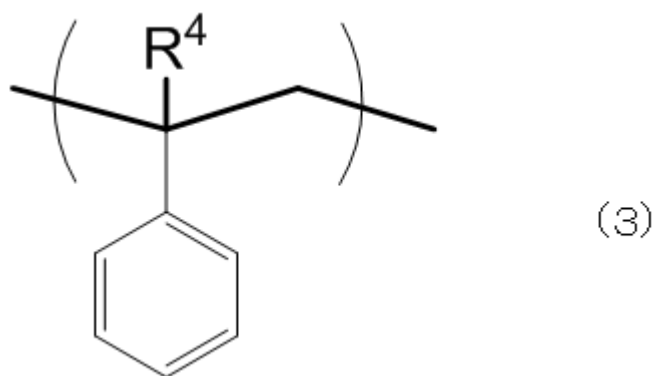
2. The photosensitive film according to claim 1, wherein said (A1) alkali soluble resin has a weight-average molecular weight (M_w) in a range of from 3,000 to 60,000.

20 3. The photosensitive film according to claim 1 or 2, wherein said (A1) alkali

soluble resin further comprises at least any one of structural units represented by the general formula (2) and the general formula (3):



- 5 (wherein in the general formula (2), R^3 represents a hydrogen atom or a C_1 - C_5 alkyl group; and
e represents an integer in a range of from 1 to 5);



- 10 (wherein in the general formula (3), R^4 represents a hydrogen atom or a C_1 - C_5 alkyl group).

4. The photosensitive film according to any one of claims 1 to 3, wherein said (C) heat-crosslinker has a weight-average molecular weight (M_w) of 100 to 2,500.

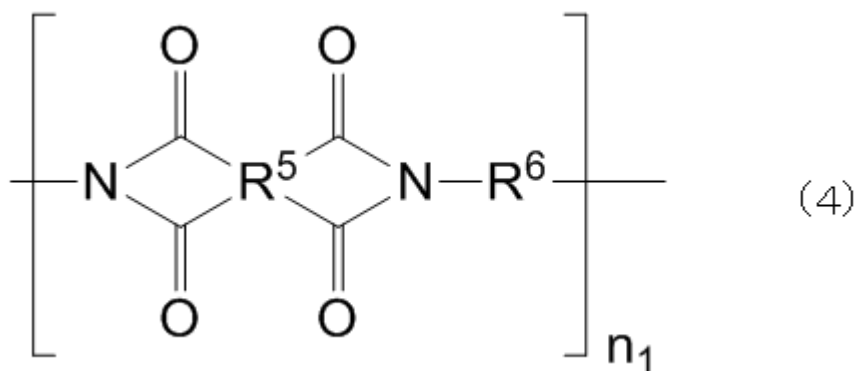
5. The photosensitive film according to any one of claims 1 to 4, wherein said

- 15 (A2) alkali soluble resin comprises one or more substituents selected from carboxyl

group, phenolic hydroxyl group, sulfonic group, and thiol group.

6. The photosensitive film according to any one of claims 1 to 5, wherein said (A2) alkali soluble resin comprises at least any one of structural units represented by the general formula (4) and the general formula (5):

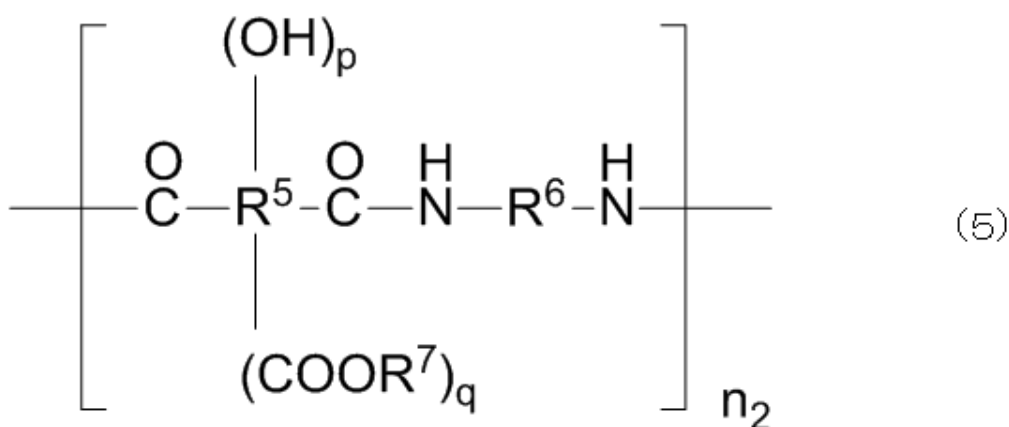
5



(wherein in the general formula (4), R^5 represents a C_4 - C_{40} bivalent to tetravalent organic group;

R^6 represents a C_{20} - C_{100} bivalent organic group; and

10 n_1 represents an integer in a range of from 10 to 100,000);



(wherein in the general formula (5), R^5 represents a C_4 - C_{40} bivalent to tetravalent organic group;

15 R^6 represents a C_{20} - C_{100} bivalent organic group;

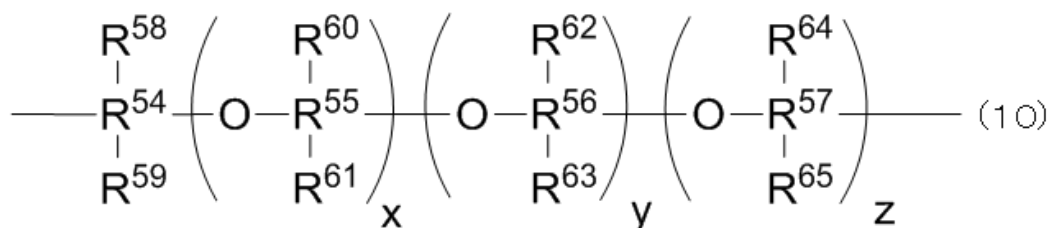
R^7 represents hydrogen or a C_1 - C_{20} organic group;

n_2 represents an integer in a range of from 10 to 100,000; and

p and q each represent an integer satisfying $0 \leq p + q \leq 2$).

7. The photosensitive film according to claim 6, wherein R^6 in the general formulae (4) and (5) contains 10 to 80 mol% of a C_{20} - C_{100} organic group having a polyether structure with respect to 100 mol% of the total amount of repeating units in the general formulae (4) and (5).

8. The photosensitive film according to claim 7, wherein said C_{20} - C_{100} organic group having a polyether structure is an organic group represented by the general formula (10):



(wherein R^{54} to R^{57} independently represent a C_1 - C_6 alkylene group;

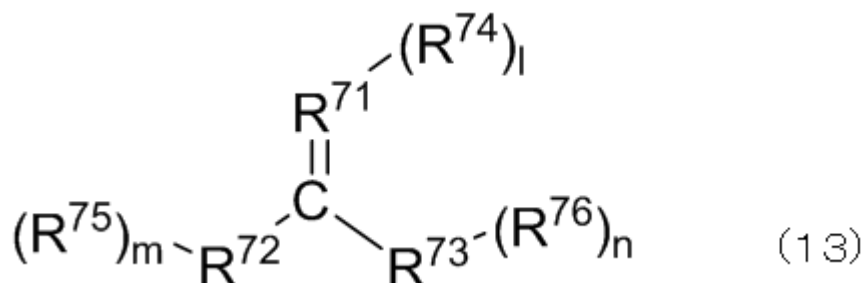
R^{58} to R^{65} independently represent hydrogen, fluorine, or a C_1 - C_6 alkyl group;

with the proviso that the structure represented in the parentheses of the repeating unit x is different from the structure represented in the parentheses of the repeating unit y , and with the proviso that the structure represented in the parentheses of the repeating unit z is different from the structure represented in the parentheses of the repeating unit y ; and

x , y , and z independently represent an integer from 0 to 35).

9. The photosensitive film according to any one of claims 6 to 8, wherein R^5 in the general formulae (4) and (5) contains 10 to 80 mol% of a C_4 - C_{40} organic group having an alicyclic structure with respect to 100 mol% of the total amount of repeating units in the general formulae (4) and (5).

10. The photosensitive film according to any of claims 1 to 9, further comprising
(H) a compound represented by the general formula (13):



5 (wherein in the general formula (13), R^{71} to R^{73} represent any one of an O atom, a S atom, or a N atom;

at least one of R^{71} to R^{73} represents a S atom;

l represents 0 or 1;

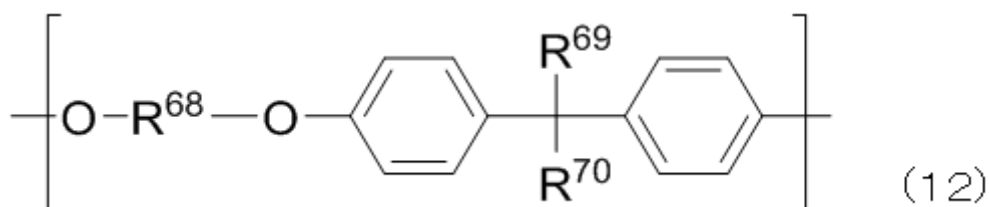
R^{71} represents an oxygen atom or a sulfur atom when l is 0, and represents a nitrogen
10 atom when l is 1;

m and n represent 1 or 2; and

R^{74} to R^{76} independently represent a hydrogen atom or a $\text{C}_1\text{-C}_{20}$ organic group).

11. The photosensitive film according to any one of claims 1 to 10, wherein said (C)
heat-crosslinker further comprises a heat-crosslinker having a structural unit

15 represented by the general formula (12):



(wherein in the general formula (12), R^{69} and R^{70} each independently represent a
hydrogen atom or a methyl group; and

20 R^{68} is a bivalent organic group having an alkylene group with two or more carbon

atoms and may be linear, branched, or cyclic).

12. The photosensitive film according to any one of claims 1 to 11, comprising a photosensitive layer having a film thickness of 3 to 45 μm .

13. The photosensitive film according to claim 12, comprising a protective film on
5 said photosensitive layer and a support film under said photosensitive layer.

14. A cured film obtained by curing said photosensitive film according to any one of claims 1 to 13.

15. An interlayer insulating film or a semiconductor protective film comprising said cured film according to claim 14.

10 16. An electronic component or a semiconductor device comprising a relief pattern layer of said cured film according to claim 14.

17. An electronic component or a semiconductor device, comprising:

a substrate;

15 a first layer of said cured film according to claim 14 with a film thickness of 2 to 40 μm on said substrate;

a plurality of copper wiring layers on said first layer; and

a second layer of said cured film according to claim 14 with a film thickness of 2 to 40 μm as an insulating film between said copper wiring layers.

18. An electronic component or a semiconductor device, comprising:

20 a substrate;

a relief pattern layer of a cured film of a photosensitive resin composition as a support material on said substrate, an aperture(s) being formed in said relief pattern layer; and

25 said cured film according to claim 14 as a covering material on said support material;

wherein said covering material is disposed on said aperture(s) to provide a hollow portion(s) formed among said support material, said covering material, and

said substrate.

19. An electronic component or a semiconductor device, comprising said cured film according to claim 14 and a substrate;

wherein said substrate has an (S-1) upper level and an (S-2) lower level;

5 wherein said cured film according to claim 14 is disposed on both of said (S-1) upper level and said (S-2) lower level;

wherein a (T-1) level difference between said (S-1) upper level and said (S-2) lower level is 2 to 40 μm ; and

10 wherein a (T-2) level difference between said cured film according to claim 14 disposed on said (S-1) upper level and said cured film according to claim 14 disposed on said (S-2) lower level is 5 μm or less.

20. A method of producing an electronic component or a semiconductor device using said photosensitive film according to any one of claims 1 to 13, comprising the steps of:

15 forming a photosensitive coating by thermal compression bonding of said photosensitive film onto a substrate at a temperature of 40 to 150°C;

exposing said photosensitive coating to light through an exposure mask; and

carrying out development by removing an exposed area from said photosensitive coating with an alkaline developing solution.

20