

DESCRIPTION

Title of Invention

POSITIVE-TYPE PHOTSENSITIVE RESIN COMPOSITION,
THERMAL CROSSLINKING AGENT FOR POSITIVE-TYPE
5 PHOTSENSITIVE RESINS, PATTERNED CURED FILM AND
METHOD FOR PRODUCING SAME, SEMICONDUCTOR
ELEMENT, AND ELECTRONIC DEVICE

Technical Field

[0001] The present invention relates to a positive-type photosensitive
10 resin composition, a thermal crosslinking agent for a positive-type
photosensitive resin, a patterned cured film and a method for producing
the same, a semiconductor device, and an electronic device.

Background Art

[0002] Insulating layers such as interlayer insulating layers and surface
15 protective layers of semiconductor devices are required to have more
excellent heat resistance (coefficient of thermal expansion or the like),
mechanical characteristics (breaking strength, breaking elongation or
the like) and the like with the high integration and downsizing of
semiconductor devices in recent years. As materials for forming
20 insulating layers having such characteristics at the same time,
positive-type photosensitive resin compositions comprising
alkali-soluble resins have been developed (for example, refer to Patent
Literatures 1, 2 and 3). These positive-type photosensitive resin
compositions are applied to a substrate and dried to form resin films,
25 and the resin films are exposed and developed to obtain patterned resin
films (resin film on which a pattern is formed). Patterned cured films

(cured films on which patterns are formed) can be formed by thermally curing the above-mentioned patterned resin films, and the patterned cured films can be used as insulating layers. Moreover, there is an advantage in that these photosensitive resin compositions can be thermally cured at low temperature in a step of forming patterned cured films.

Citation List

Patent Literature

[0003] Patent Literature 1: JP 2008-309885

Patent Literature 2: JP 2007-057595

Patent Literature 3: WO 2010/073948

Summary of Invention

Technical Problem

[0004] Now then, as wafers are downsized and insulating layers are multilayered in semiconductor devices, the package warp resulting from the residual stress of patterned cured films used for insulating layers becomes a problem. Materials to be used are therefore required to reduce the residual stress of the formed patterned cured films.

[0005] It is considered that it is generally effective to reduce the crosslinking density of a cured film to reduce the residual stress of the cured film. However, when the crosslinking density is reduced, the film strength also tends to decrease simultaneously, and the chemical liquid resistance of the patterned cured film tends to decrease.

[0006] The present invention has been completed in view of such a situation, and the main object is to provide a positive-type photosensitive resin composition which can form a cured film the

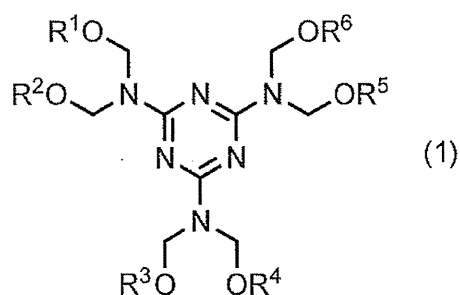
residual stress of which is low and which is excellent in chemical liquid resistance and adhesion to a substrate.

Solution to Problem

[0007] The present inventors have earnestly examined to achieve the above object and consequently found that a cured film the residual stress of which is low and which is excellent in chemical liquid resistance can be formed by combining specific compounds in a positive-type photosensitive resin composition. Moreover, the present inventors have been found that the obtained cured film is excellent in adhesion to a substrate, and have completed the present invention.

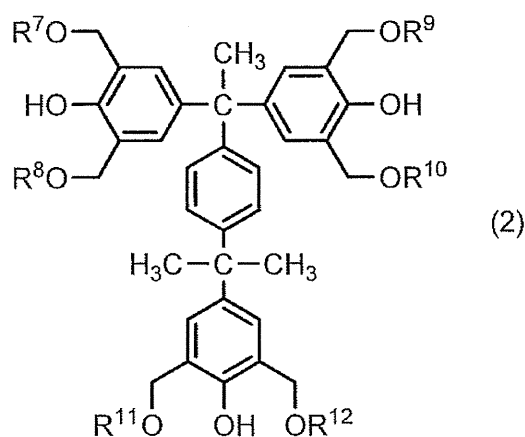
[0008] One aspect of the present invention provides a positive-type photosensitive resin composition, comprising an alkali-soluble resin (A), a compound represented by the following formula (1) or a compound represented by the following formula (2) (B), and a compound having two or more epoxy groups (C). According to such a positive-type photosensitive resin composition, a cured film the residual stress of which is low and which is excellent in chemical liquid resistance and adhesion to a substrate can be formed.

[0009]



In the formula (1), R^1 to R^6 each independently represent an alkyl group having 1 to 10 carbon atoms.

[0010]

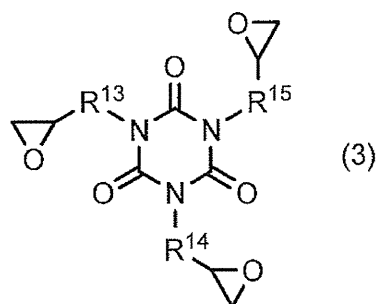


In the formula (2), R^7 to R^{12} each independently represent an alkyl group having 1 to 10 carbon atoms.

5 [0011] The molar ratio of the (C) component to the (B) component may be 1.0 or less. When the molar ratio is in such a range, chemical liquid resistance and breaking strength tend to be more excellent.

[0012] The (C) component may be a compound having an aromatic ring or a heterocycle. The (C) component may be a compound represented
10 by the following formula (3). When the (C) component is such a compound, the chemical liquid resistance of the formed patterned cured film tends to be more excellent.

[0013]

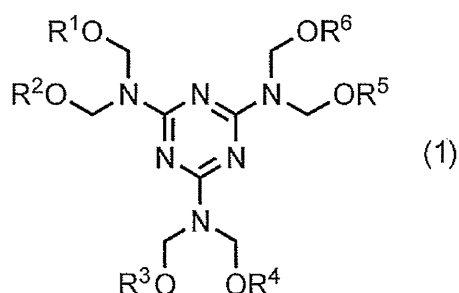


In the formula (3), R¹³ to R¹⁵ each independently represent an alkylene group having 1 to 10 carbon atoms.

[0014] The positive-type photosensitive resin composition may further comprise an elastomer (D). The positive-type photosensitive resin composition may further comprise a compound which generates an acid by light (E). The heat resistance (coefficient of thermal expansion) and the mechanical characteristics (breaking strength and breaking elongation) of the formed patterned cured film tend to be excellent by using these components.

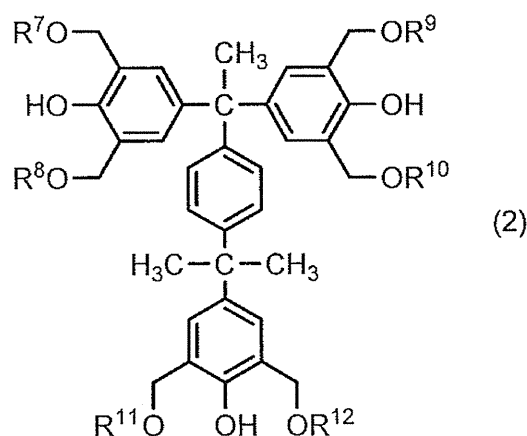
[0015] In another aspect, a thermal crosslinking agent for a positive-type photosensitive resin, consisting of a compound represented by the following formula (1) or a compound represented by the following formula (2) and a compound having two or more epoxy groups is provided. When such a thermal crosslinking agent for a positive-type photosensitive resin is used, a positive-type photosensitive resin composition which can form a patterned cured film the residual stress of which is low and which is excellent in chemical liquid resistance and adhesion to a substrate can be easily prepared.

[0016]



In the formula (1), R¹ to R⁶ each independently represent an alkyl group having 1 to 10 carbon atoms.

[0017]



In the formula (2), R⁷ to R¹² each independently represent an alkyl group having 1 to 10 carbon atoms.

5 [0018] In another aspect, a patterned cured film, the patterned cured film comprising a pattern, wherein the pattern comprises a cured product of a resin film consisting of the above-mentioned positive-type photosensitive resin composition is provided.

10 [0019] In another aspect, a method for producing a patterned cured film, the method comprising a step of applying the above-mentioned positive-type photosensitive resin composition to a part or whole of a substrate followed by drying to form a resin film, a step of exposing a part or whole of the resin film, a step of developing the resin film after exposure with an aqueous alkali solution to form a patterned resin film, and a step of heating a patterned resin film is provided.

[0020] In another aspect, a semiconductor device, comprising the above-mentioned patterned cured film as an interlayer insulating layer or a surface protective layer is provided.

[0021] In another aspect, an electronic device, comprising the

above-mentioned semiconductor device is provided.

Advantageous Effects of Invention

[0022] According to the present invention, a positive-type photosensitive resin composition which can form a patterned cured film the residual stress of which is low and which is excellent in chemical liquid resistance and adhesion to a substrate can be provided. A thermal crosslinking agent for a positive-type photosensitive resin with which such a positive-type photosensitive resin composition can be easily prepared can be provided. A patterned cured film using such a positive-type photosensitive resin composition, a method for producing the same, a semiconductor device, and an electronic device can be provided.

Brief Description of Drawings

[0023] Figure 1 is a schematic perspective view and a schematic end view describing one embodiment of a process for manufacturing a semiconductor device.

Figure 2 is a schematic perspective view and a schematic end view describing one embodiment of a process for manufacturing a semiconductor device.

Figure 3 is a schematic perspective view and a schematic end view describing one embodiment of a process for manufacturing a semiconductor device.

Figure 4 is a schematic perspective view and a schematic end view describing one embodiment of a process for manufacturing a semiconductor device.

Figure 5 is a schematic perspective view and a schematic end

view describing one embodiment of a process for manufacturing a semiconductor device.

Figure 6 is a schematic sectional view showing one embodiment of a semiconductor device.

5 Figure 7 is a schematic sectional view showing one embodiment of a semiconductor device.

Description of Embodiments

[0024] Embodiments of the present invention will be described in detail hereinafter. The present invention is not, however, limited to the
10 following embodiments.

[0025] The "(meth)acrylic acid" herein means "acrylic acid" or "methacrylic acid", and it is the same also in other similar expressions such as (meth)acrylate.

[0026] [Positive-type photosensitive resin composition]

15 A positive-type photosensitive resin composition of one embodiment comprises an alkali-soluble resin (A), a compound represented by the formula (1) or a compound represented by the formula (2) (B), and a compound having two or more epoxy groups (C).

[0027] <(A) component>

20 An (A) component is a resin soluble in an aqueous alkali solution (developer). The aqueous alkali solution is an alkaline solution such as an aqueous tetramethylammonium hydroxide (TMAH) solution, an aqueous metal hydroxide solution and an aqueous organic amine solution. An aqueous tetramethylammonium hydroxide
25 solution the concentration of which is 2.38% by mass is commonly used for development.

[0028] It can be confirmed that the (A) component is soluble in an alkali developer, for example, by performing the following.

[0029] A coated film having a film thickness of around 5 μm is formed by spin-coating a substrate such as a silicon wafer with varnish obtained by dissolving the (A) component in any solvent. This is immersed in any of an aqueous TMAH solution, an aqueous metal hydroxide solution or an aqueous organic amine solution at 20 to 25°C. When the coated film can be consequently dissolved homogeneously, it can be considered that the (A) component is soluble in an alkaline developer.

[0030] Examples of the (A) component include polyester resins, polyether resins, polyimide resins, polyamide resins, polyamide imide resins, polyetherimide resins, polyurethane resins, polyurethaneimide resins, polyurethaneamideimide resins, siloxane polyimide resins, polyesterimide resins, a polybenzoxazole resin, phenoxy resins, polysulfone resins, polyethersulfone resins, polyphenylene sulfide resins, polycarbonate resins, polyetherketone resins, (meth)acrylic copolymers, and resins having phenolic hydroxyl groups. These can be used alone or in combination of two or more. Glycol groups such as ethylene glycol and propylene glycol, carboxyl groups, or hydroxyl groups may be imparted to the main chains or side chains of these resins.

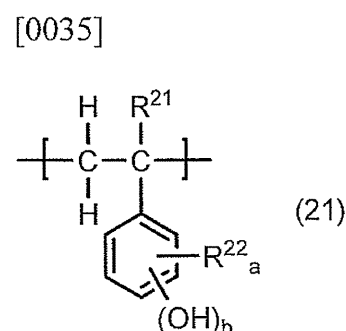
[0031] It is preferable that the (A) component be a resin having a phenolic hydroxyl group among these from the viewpoints of high-temperature adhesiveness, heat resistance and film-forming properties.

[0032] Examples of the resin having a phenolic hydroxyl group include

hydroxystyrene-based resins such as polyhydroxystyrene or copolymers containing hydroxystyrene as a monomer unit, a phenol resin, polybenzoxazole precursors such as poly(hydroxyamide), poly(hydroxyphenylene)ether, and polynaphthol. The (A) component may be constituted by only one of these resins, and may be constituted by incorporating two or more.

[0033] Since the (A1) hydroxystyrene-based resins are excellent in electrical properties (insulating properties), and the volume shrinkage at the time of curing is small, it is preferable among these. Since the (A2) phenol resin is at low prices, the contrast is high, and the volume shrinkage at the time of curing is small, it is preferable, and a novolac type phenol resin is more preferable.

[0034] The (A1) hydroxystyrene-based resins have a structure unit represented by the following formula (21).



[0036] In the formula (21), R^{21} represents a hydrogen atom or a methyl group, R^{22} represents an alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms, or an alkoxy group having 1 to 10 carbon atoms, a represents an integer of 0 to 3, and b represents an integer of 1 to 3. The total of a and b is 5 or less.

[0037] The (A1) hydroxystyrene-based resin can be obtained by

polymerizing a monomer or like which gives the structure unit represented by the formula (21).

[0038] In the formula (21), examples of the alkyl group having 1 to 10 carbon atoms and represented by R^{21} include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group and a decyl group. These groups may be linear or branched. Examples of the aryl group having 6 to 10 carbon atoms and represented by R^{22} include a phenyl group and a naphthyl group. Examples of the alkoxy group having 1 to 10 carbon atoms and represented by R^{21} include a methoxy group, an ethoxy group, a propoxy group, a butoxy group, a pentoxy group, a hexoxy group, a heptoxy group, an octoxy group, a nonoxy group and a decoxy group. These groups may be linear or branched.

[0039] Examples of the monomer which gives a structure unit represented by the formula (21) include p-hydroxystyrene, m-hydroxystyrene, o-hydroxystyrene, p-isopropenyl phenol, m-isopropenyl phenol and o-isopropenyl phenol. These monomers can be used alone or in combination of two or more.

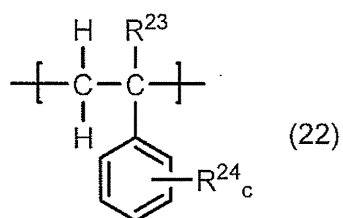
[0040] A method for producing the (A1) hydroxystyrene-based resin is not limited, and it can be obtained, for example, by protecting the hydroxyl groups of the monomers which give structure units represented by the formula (21) with t-butyl groups, acetyl groups or the like to form monomers in which hydroxyl groups are protected, polymerizing the monomers in which the hydroxyl groups are protected to obtain a polymer, and performing deprotection of the obtained polymer in a known method (performing deprotection in the presence of

an acid catalyst to convert into hydroxystyrene-based structure units, or the like).

[0041] The (A1) hydroxystyrene-based resin may be a polymer or a copolymer which consists of only the monomer which gives the structure unit represented by the formula (21), and may be a copolymer of the monomer which gives the structure unit represented by the formula (21) and another monomer. When the (A1) hydroxystyrene-based resin is a copolymer, it is preferable that the rate of the structure unit represented by the formula (21) in the copolymer be 10 to 100 mol%, it is more preferable that it be 20 to 97 mol%, it is further preferable that it be 30 to 95 mol%, and it is particularly preferable that it be 50 to 95 mol% based on the (A) component at a concentration of 100 mol% from the viewpoint of the solubility of exposed parts in an alkali developer.

[0042] It is preferable that the (A1) hydroxystyrene-based resin be an alkali-soluble resin further having a structure unit represented by the following formula (22) from the viewpoint that the inhibitory property of the solubility of unexposed parts in the alkali developer is improved.

[0043]



[0044] In the formula (22), R^{23} represents a hydrogen atom or a methyl group, R^{24} represents an alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms or an alkoxy group having 1 to

10 carbon atoms, and c represents an integer of 0 to 3.

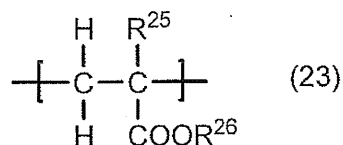
[0045] Examples of the alkyl group having 1 to 10 carbon atoms, the aryl group having 6 to 10 carbon atoms, or an alkoxy group having 1 to 10 carbon atoms which is represented by R^{24} include the same as R^{22} .

5 [0046] The alkali-soluble resin having a structure unit represented by the formula (22) is obtained by using a monomer which gives the structure unit represented by the formula (22). Examples of the monomer which gives the structure unit represented by the formula (22) include aromatic vinyl compounds, such as styrene, α -methylstyrene,
10 o-methylstyrene, m-methylstyrene, p-methylstyrene, o-methoxystyrene, m-methoxystyrene and p-methoxystyrene. These monomers can be used alone or in combination of two or more.

[0047] When the (A1) hydroxystyrene-based resin is an alkali-soluble resin having a structure unit represented by the formula (22), it is
15 preferable that the rate of the structure unit represented by the formula (22) be 1 to 90 mol%, it is more preferable that it be 3 to 80 mol%, it is further preferable that it be 5 to 70 mol%, and it is particularly preferable that it be 5 to 50 mol%, based on 100 mol% of the (A) component, from the viewpoints of the inhibitory property of the
20 solubility of unexposed parts in an alkali developer and the mechanical characteristics of a patterned cured film.

[0048] It is preferable that the (A1) hydroxystyrene-based resin be an alkali-soluble resin further having a structure unit represented by the following formula (23) from the viewpoint that the elastic modulus is
25 reduced.

[0049]



[0050] In the formula (23), R²⁵ represents a hydrogen atom or a methyl group, and R²⁶ represents an alkyl group having 1 to 10 carbon atoms or a hydroxyalkyl group having 1 to 10 carbon atoms.

5 [0051] The alkali-soluble resin having a structure unit represented by the formula (23) is obtained using a monomer which gives the structure unit represented by the formula (23). Examples of the monomer which gives the structure unit represented by the formula (23) include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, hydroxymethyl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxypentyl (meth)acrylate, hydroxyhexyl (meth)acrylate, hydroxyheptyl (meth)acrylate, hydroxyoctyl (meth)acrylate, hydroxynonyl (meth)acrylate and hydroxydecyl (meth)acrylate. These monomers can be used alone or in combination of two or more.

20 [0052] When the (A1) hydroxystyrene-based resin is an alkali-soluble resin having a structure unit represented by the formula (23), it is preferable that the rate of the structure unit represented by the formula (23) be 1 to 90 mol%, it is more preferable that it be 3 to 80 mol%, it is further preferable that it be 5 to 70 mol%, and it is particularly preferable that it be 5 to 50 mol%, based on 100 mol% of the (A)

component, from the viewpoints of the inhibitory property of the solubility of unexposed parts in the alkali developer and the mechanical characteristics of the patterned cured film.

[0053] The (A2) phenol resin is a polycondensation product of phenol or its derivative, and an aldehyde. Polycondensation is usually performed in the presence of a catalyst such as an acid or a base. Especially a phenol resin obtained when an acid catalyst is used is called a novolac type phenol resin. Examples of the novolac type phenol resin include a phenol/formaldehyde novolac resin, a cresol/formaldehyde novolac resin, a xylenol/formaldehyde novolac resin, a resorcinol/formaldehyde novolac resin and a phenol-naphthol/formaldehyde novolac resin.

[0054] Examples of the phenol derivative constituting the (A2) phenol resin include alkyl phenols such as o-cresol, m-cresol, p-cresol, o-ethylphenol, m-ethylphenol, p-ethylphenol, o-butylphenol, m-butylphenol, p-butylphenol, 2,3-xyleneol, 2,4-xyleneol, 2,5-xyleneol, 2,6-xyleneol, 3,4-xyleneol, 3,5-xyleneol, 2,3,5-trimethylphenol, 3,4,5-trimethylphenol; alkoxyphenols such as methoxyphenol and 2-methoxy-4-methylphenol; alkenylphenols such as vinylphenol and allylphenol; aralkylphenol such as benzylphenol; alkoxycarbonylphenols such as methoxycarbonylphenol; aryl carbonyl phenols such as benzoyloxy phenol; halogenated phenols such as chlorophenol; polyhydroxybenzenes such as catechol, resorcinol and pyrogallol; bisphenols such as bisphenol A and bisphenol F; naphthol derivatives such as α - or β -naphthol; hydroxyalkyl phenols such as p-hydroxyphenyl-2-ethanol, p-hydroxyphenyl-3-propanol,

p-hydroxyphenyl-4-butanol; hydroxyalkyl cresols such as hydroxyethyl cresol; alcoholic hydroxyl group-containing phenol derivatives such as a monoethylene oxide adduct of a bisphenol and a monopropylene oxide adduct of a bisphenol; and carboxyl group-containing phenol derivatives
5 such as p-hydroxyphenylacetic acid, p-hydroxyphenyl propionic acid, p-hydroxyphenyl butanoic acid, p-hydroxycinnamic acid, hydroxybenzoic acid, hydroxyphenyl benzoic acid, hydroxyphenoxy benzoic acid and diphenolic acid. These can be used alone or in combination of two or more.

10 [0055] Examples of the aldehyde constituting the (A2) phenol resin include formaldehyde, acetaldehyde, furfural, benzaldehyde, hydroxybenzaldehyde, methoxybenzaldehyde, hydroxyphenylacetaldehyde, methoxyphenylacetaldehyde, crotonic aldehyde, chloroacetaldehyde, chlorophenyl acetaldehyde,
15 glyceraldehyde, glyoxylic acid, methyl glyoxylate, phenyl glyoxylate, hydroxyphenyl glyoxylate, formylacetic acid, methyl formylacetate, 2-formylpropionic acid and methyl-2-formylpropionate. These can be used alone or in combination of two or more. A precursor of formaldehyde such as paraformaldehyde or trioxane, or a ketone such as
20 acetone, pyruvic acid, levulinic acid, 4-acetylbutyric acid, acetonedicarboxylic acid or 3,3',4,4'-benzophenonetetracarboxylic acid may be used for a reaction.

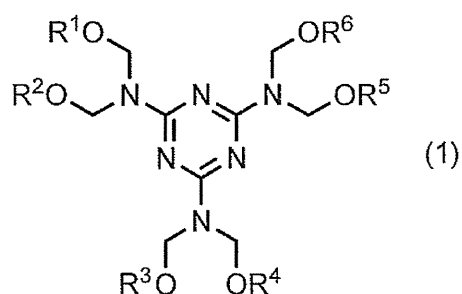
[0056] When the (A) component comprises the (A1)
hydroxystyrene-based resin or the (A2) phenol resin, it is preferable that
25 the weight average molecular weight of each of the (A1) component and the (A2) component be a weight average molecular weight of 1000 to

500000, it is more preferable that it be 2000 to 200000, and it is further preferable that it be 2000 to 100000 in view of the balance among the solubility in an aqueous alkali solution, the photosensitive characteristics and the mechanical characteristics of the patterned cured film. Here, the weight average molecular weight is a value obtained by measuring by gel permeation chromatography (GPC) and converting from a standard polystyrene calibration curve.

[0057] <(B) component>

A compound which is a (B) component is a compound having a structure which can react with an (A) component and form crosslinking structure when a photosensitive resin film after pattern formation is heated and cured. The (B) component is a compound represented by the following formula (1) or a compound represented by the following formula (2).

[0058]

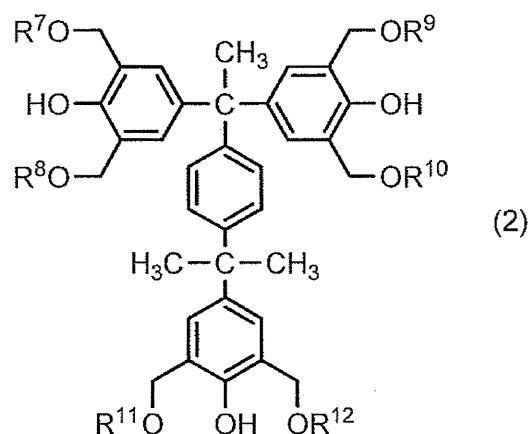


[0059] In the formula (1), R¹ to R⁶ each independently represent an alkyl group having 1 to 10 carbon atoms.

[0060] Examples of the alkyl groups having 1 to 10 carbon atoms and represented by R¹ to R⁶ include the same as R²². It is preferable that the carbon number of the alkyl groups be 1 to 5, it is more preferable that it be 1 to 3, it is further preferable that it be 1 or 2, and it is

particularly preferable that it be 1.

[0061]



[0062] In the formula (2), R^7 to R^{12} each independently represent an alkyl group having 1 to 10 carbon atoms.

[0063] Examples of the alkyl groups having 1 to 10 carbon atoms and represented by R^7 to R^{12} include the same as R^{22} . It is preferable that the carbon number of the alkyl groups be 1 to 5, it is more preferable that it be 1 to 3, it is further preferable that it be 1 or 2, and it is particularly preferable that it be 1.

[0064] <(C) component>

A compound which is a (C) component is a compound having 2 or more epoxy groups and a structure which can react with the (A) component together with a compound which is the above-mentioned (B) component and form a crosslinking structure when a photosensitive resin film after pattern formation is heated and cured.

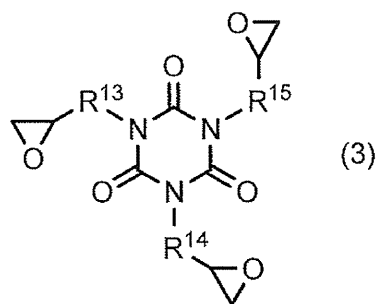
[0065] The (C) component can be used particularly without limitation as long as it has 2 or more epoxy groups. Examples of the (C) component include aliphatic epoxy compounds, aromatic epoxy

compounds, alicyclic epoxy compounds, heterocyclic epoxy compounds, bisphenol type epoxy compounds, novolac type epoxy compounds, glycidyl amine type epoxy compounds and halogenated epoxy compounds. These can be used alone or in combination of two or more.

[0066] It is preferable that the (C) component be an epoxy compound having an aromatic ring or heterocycle, it is more preferable that it be an epoxy compound having a heterocycle, and it is further preferable that it be an epoxy compound having a nitrogen-containing heterocycle among these from the viewpoint of superior chemical liquid resistance.

[0067] It is preferable that the (C) component be a compound represented by the following formula (3) from the viewpoint of superior chemical liquid resistance.

[0068]



[0069] In the formula (3), R^{13} to R^{15} each independently represent an alkylene group having 1 to 10 carbon atoms.

[0070] In the formula (3), examples of the alkylene groups having 1 to 10 carbon atoms and represented by R^{13} to R^{15} include a methylene group, an ethylene group, a propylene group, a butylene group, a pentylene group, a hexylene group, a heptylene group, a octylene group,

a nonylene group and a decylene group. These groups may be linear or branched. It is preferable that the carbon number of the alkylene group be 1 to 8, and it is more preferable that it be 1 to 6.

[0071] The molar ratio of the (C) component to the (B) component (molar number of the (C) component/molar number of the (B) component) is 1.0 or less, it is preferable that it be 0.9 or less, and it is more preferable that it be 0.8 or less from the viewpoint of superior chemical liquid resistance and breaking strength. The lower limit of the molar ratio of the (C) component to the (B) component is not particularly limited, and it may be 0.1 or more, 0.2 or more, or 0.3 or more.

[0072] It is preferable that the total amount of the (B) component and the (C) component be 2 to 35 parts by mass, it is more preferable that it be 4 to 30 parts by mass, and it is further preferable that it be 5 to 25 parts by mass, based on 100 parts by mass of the (A) component, from the viewpoint of superior residual stress and chemical liquid resistance.

[0073] The positive-type photosensitive resin composition of the present embodiment may further comprise an elastomer (D) or a compound which generates an acid by light (E) in addition to (A) to (C) components. A positive-type photosensitive resin composition which is excellent in breaking strength and thermal expansion property can be obtained by using these components.

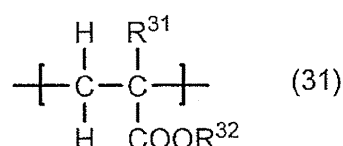
[0074] <(D) component>

Examples of the elastomer include styrene-based elastomers, olefin-based elastomers, urethane-based elastomers, polyester-based elastomers, polyamide-based elastomers, acrylic elastomers and

silicone-based elastomers. These can be used alone or in combination of two or more. Since the (D) component is excellent in the breaking strength, breaking elongation, and thermal expansion property of the obtained patterned cured film, it may be an acrylic elastomer among these.

[0075] It is preferable that the acrylic elastomer have a structure unit represented by the following formula (31).

[0076]



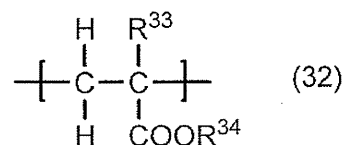
[0077] In the formula (31), R^{31} represents a hydrogen atom or a methyl group, and R^{32} represents a hydroxyalkyl group having 2 to 20 carbon atoms.

[0078] Examples of the hydroxyalkyl group having 2 to 20 carbon atoms and represented by R^{32} include a hydroxyethyl group, a hydroxypropyl group, a hydroxybutyl group, a hydroxypentyl group, a hydroxyhexyl group, a hydroxyheptyl group, a hydroxyoctyl group, a hydroxynonyl group, a hydroxydecyl group, a hydroxyundecyl group, a hydroxydodecyl group (occasionally called a hydroxylauryl group), a hydroxytridecyl group, a hydroxytetradecyl group, a hydroxypentadecyl group, a hydroxyhexadecyl group, a hydroxyheptadecyl group, a hydroxyoctadecyl group, a hydroxynonadecyl group and a hydroxyeicosyl group.

[0079] The acrylic elastomer may further have a structure unit represented by the following formula (32), a structure unit represented

by the following formula (33) or a structure unit represented by the following formula (34).

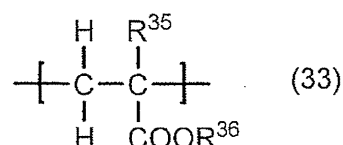
[0080]



5 [0081] In the formula (32), R^{33} represents a hydrogen atom or a methyl group, and R^{34} represents a monovalent organic group having a primary, secondary or tertiary amino group.

[0082] Examples of the primary, secondary or tertiary amino group represented by R^{34} include an aminoethyl group, an
10 N-methylaminoethyl group, an N,N-dimethylaminoethyl group, an N-ethylaminoethyl group, an N,N-diethylaminoethyl group, an aminopropyl group, an N-methylaminopropyl group, an N,N-dimethylaminopropyl group, an N-ethylaminopropyl group, an N,N-diethylaminopropyl group, a piperidin-4-yl group, a
15 1-methylpiperidin-4-yl group, a 2,2,6,6-tetramethylpiperidin-4-yl group, a 1,2,2,6,6-pentamethylpiperidin-4-yl group, a (piperidin-4-yl)methyl group and a 2-(piperidin-4-yl)ethyl group.

[0083]

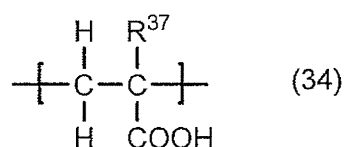


20 [0084] In the formula (33), R^{35} represents a hydrogen atom or a methyl group, and R^{36} represents an alkyl group having 4 to 20 carbon atoms.

[0085] Examples of the alkyl group having 4 to 20 carbon atoms and

represented by R³⁶ include a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group (occasionally called a lauryl group), a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl group and an eicosyl group. These groups may be linear or branched.

[0086]



[0087] In the formula (34), R³⁷ represents a hydrogen atom or a methyl group.

[0088] The acrylic elastomer can be obtained, for example, by blending a monomer which gives the structure unit represented by the above formula (31) and a monomer which is added if needed and gives the structure unit represented by the formula (32), (33) or (34), stirring the resulting blend in a solvents such as ethyl lactate, toluene and isopropanol, and heating the blend if needed.

[0089] It is preferable that the weight average molecular weight of the acrylic elastomer be 2000 to 100000, it is more preferable that it be 3000 to 60000, it is further preferable that it be 5000 to 50000, and it is particularly preferable that it be 10000 to 40000. Here, the weight average molecular weight is a value obtained by measuring by gel permeation chromatography (GPC) and converting from a standard polystyrene calibration curve.

[0090] It is preferable that the content of the (D) component be 1 to 35

parts by mass, it is more preferable that it be 3 to 30 parts by mass, and it is further preferable that it be 5 to 25 parts by mass, based on 100 parts by mass of the (A) component, from the viewpoint of superior breaking strength and breaking elongation.

5 [0091] <(E) component>

A compound which is an (E) component and generates an acid by light (by receiving light) functions as a sensitizer in a photosensitive resin composition. The (E) component has function to receive light irradiation, generate an acid and further increase the solubility of parts
10 which receive light irradiation in an aqueous alkali solution. As the (E) component, a compound generally called a photoacid generator can be used. Specific examples of the (E) component include an o-quinone diazide compound, an aryldiazonium salt, a diaryliodonium salt and a triarylsulfonium salt. The (E) component may consist of only one, and
15 may be constituted by containing two or more among these compounds. Since the sensitivity is high, the o-quinone diazide compound is preferable among these.

[0092] The o-quinone diazide compound or the like obtained, for example, by subjecting o-quinone diazide sulfonyl chloride and a
20 hydroxy compound or an amino compound to a condensation reaction in the presence of a dehydrochlorinating agent can be used.

[0093] It is preferable to use a condensate of 1,1-bis(4-hydroxyphenyl)-1-[4-{1-(4-hydroxyphenyl)-1-methylethyl}phenyl]ethane and 1-naphthoquinone-2-diazido-5-sulfonyl chloride and a
25 condensate of tris(4-hydroxyphenyl)methane or tris(4-hydroxyphenyl)ethane and

1-naphthoquinone-2-diazido-5-sulfonyl chloride as the o-quinone diazide compound.

[0094] It is preferable that the content of the (E) component be 5 to 25 parts by mass, it is more preferable that it be 6 to 20 parts by mass, and it is further preferable that it be 7 to 18 parts by mass, based on 100 parts by mass of the (A) component, from the viewpoint that the difference between dissolution rates in exposed parts and unexposed parts further increases, and the sensitivity becomes better.

[0095] <Other components>

The positive-type photosensitive resin composition of the present embodiment may comprise components such as a solvent, a compound which generates an acid by heating, a dissolution enhancer, a dissolution inhibitor, a coupling agent, a surfactant and a leveling agent in addition to the above (A) to (E) components.

[0096] (Solvent)

The coating of a substrate can be facilitated, and a coated film having a uniform thickness can be formed by using a solvent. Examples of the solvent include γ -butyrolactone, ethyl lactate, propylene glycol monomethyl ether acetate, benzyl acetate, n-butyl acetate, ethoxyethyl propionate, 3-methyl methoxy propionate, N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, hexamethylphosphorylamide, tetramethylene sulfone, diethyl ketone, diisobutyl ketone, methylamyl ketone, cyclohexanone, propylene glycol monomethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether and dipropylene glycol monomethyl ether.

These solvents can be used alone or in combination of two or more. It is preferable that it be ethyl lactate or propylene glycol monomethyl ether acetate among these from the viewpoints of the solubility and the uniformity of a coating film.

5 [0097] (Compound which generates acid by heating)

Since an acid can be generated when a patterned resin film is heated by using a compound which generates an acid by heating, the reaction of the (A) component, the (B) component, and the (C) component, namely a thermal crosslinking reaction, is promoted and the
10 heat resistance of a patterned cured film is improved. Since the compound which generates an acid by heating generates the acid also by light irradiation, the solubility of exposure parts in an aqueous alkali solution increases. Therefore, the difference between the solubility of unexposed parts and exposed parts in an aqueous alkali solution further
15 increases, and the resolution is further improved.

[0098] Examples of such a compound which generates an acid by heating include a compound which generates an acid by heating to 50 to 250°C. Specific examples of the compound which generates an acid by heating include salts such as onium salts formed by a strong acid and
20 a base, and imide sulfonate.

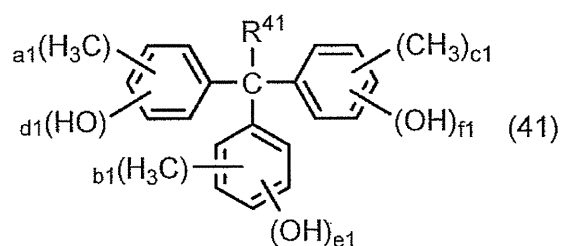
[0099] (Dissolution enhancer)

The dissolution rate of exposed parts at the time of developing with an aqueous alkali solution can be increased, and the sensitivity and the resolution properties can be improved by using a dissolution
25 enhancer. A conventionally known dissolution enhancer can be used. Specific examples thereof include a compound having a carboxyl group,

a sulfonic group or a sulfonamide group.

[0100] The dissolution enhancer may be a phenolic low-molecular compound represented by any of the following formulae (41) to (43).

[0101]

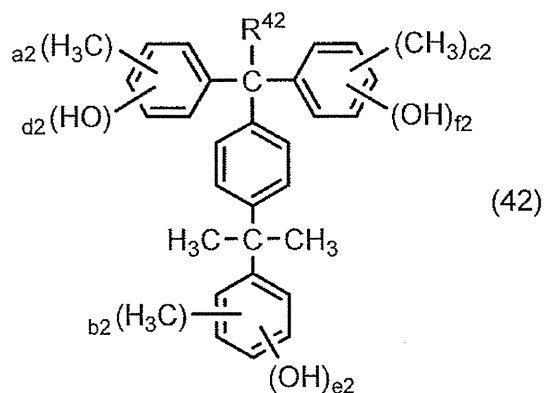


5

[0102] In the formula (41), R^{41} represents a hydrogen atom or a methyl group. a_1 to f_1 represent integers of 0 to 3, the total of d_1 to f_1 is 1 or more, the total of a_1 and d_1 is 5 or less, the total of b_1 and e_1 is 5 or less, and the total of c_1 and f_1 is 5 or less.

10

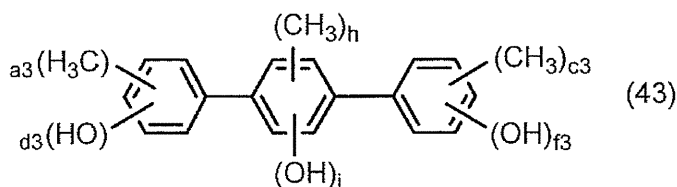
[0103]



[0104] In the formula (42), R^{42} represents a hydrogen atom or a methyl group. a_2 to c_2 represent integers of 0 to 3, d_2 to f_2 represent integers of 1 to 3, the total of a_2 and d_2 is 5 or less, the total of b_2 and e_2 is 5 or less, and the total of c_2 and f_2 is 5 or less.

15

[0105]



[0106] In the formula (43), a3, c3, h and i represent integers of 0 to 3, d3 and f3 represent integers of 1 to 3, the total of a3 and d3 is 5 or less, the total of c3 and f3 is 5 or less, and the total of h and i is 4 or less.

5 [0107] (Dissolution inhibitor)

A dissolution inhibitor is a compound which inhibits the dissolution of the (A) component in an aqueous alkali solution, and it is used to control the residual film thickness, the developing time and the contrast. Examples of the dissolution inhibitor include
 10 diphenyliodonium nitrate, bis(p-tert-butylphenyl)iodonium nitrate, diphenyliodonium bromide, diphenyliodonium chloride and diphenyliodonium iodide.

[0108] (Coupling agent)

The adhesiveness of a formed patterned cured film and a
 15 substrate can be further enhanced by using a coupling agent. Examples of the coupling agent include an organic silane compound and an aluminum chelate compound.

[0109] (Surfactant and leveling agent)

The coatability can be further improved by using a surfactant or
 20 a leveling agent. The striation (nonuniformity of film thickness) can be specifically further prevented, or the developability can be further improved, for example, by incorporating a surfactant or a leveling agent. Examples of the surfactant or the leveling agent include

polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether and polyoxyethylene octyl phenol ether.

[0110] The content in the case of using other components may be 0.01 to 20 parts by mass based on 100 parts by mass of the (A) component.

5 [0111] According to the positive-type photosensitive resin composition of the present embodiment, a patterned cured film the residual stress of which is low and which is excellent in chemical liquid resistance and adhesion to a substrate can be formed.

10 [0112] [Thermal crosslinking agent for positive-type photosensitive resin]

A thermal crosslinking agent for a positive-type photosensitive resin of one embodiment consists of the above-mentioned (B) component (the compound represented by the formula (1) or the compound represented by the formula (2)), and (C) component
15 (compound having 2 or more epoxy groups). According to such a thermal crosslinking agent for a positive-type photosensitive resin, a positive-type photosensitive resin composition which can form a patterned cured film the residual stress of which is low and which is excellent in chemical liquid resistance and adhesion to a substrate can
20 be easily prepared.

[0113] [Patterned cured film and method for producing the same]

A patterned cured film of one embodiment has a pattern, and the pattern comprises a cured product of a resin film consisting of the above-mentioned positive-type photosensitive resin composition. The
25 patterned cured film is obtained by heating the above-mentioned positive-type photosensitive resin composition. A method for

producing a patterned cured film will be described hereinafter.

[0114] The method for producing a patterned cured film of the present embodiment comprises a step of applying the above-mentioned positive-type photosensitive resin composition to a part or whole of a substrate followed by drying to form a resin film (applying and drying (film-forming) step), a step of exposing a part or whole of the resin film (exposing step), a step of developing the resin film after exposure with an aqueous alkali solution to form a patterned resin film (developing step), and a step of heating the patterned resin film (heat-treating step).

The steps will be described hereinafter.

[0115] <Applying and drying (film-forming) step>

First, a positive-type photosensitive resin composition of the present embodiment is applied to a substrate and dried to form a resin film. In this step, a substrate such as a glass substrate, a semiconductor, a metal oxide insulator (such as TiO_2 or SiO_2) or silicon nitride is spin-coated with a positive-type photosensitive resin composition of the present embodiment using a spinner or the like to form a coated film. The thickness of the coated film is not particularly limited, and it is preferable that it be 0.1 to 40 μm . This substrate on which the coated film is formed is dried using a hot plate, an oven or the like. The drying temperature and the drying time are not particularly limited, and it is preferable to perform drying at 80 to 140°C for 1 to 7 minutes. A resin film is formed on the supporting substrate thereby. The thickness of the resin film is not particularly limited, and it is preferable that it be 0.1 to 40 μm .

[0116] <Exposing step>

In the exposing step, the resin film formed on the substrate is next irradiated with active rays such as ultraviolet rays, visible light, and radiation through a mask. Since the (A) component has high transparency to i-lines in the positive-type photosensitive resin composition of the present embodiment, the irradiation of i-lines can be used suitably. Post-exposure baking (PEB) can also be performed after exposure from the viewpoint of improving the dissolution rate if needed. It is preferable that the temperature when post-exposure baking is performed be 70°C to 140°C, and the time of the post-exposure baking be 1 minute to 5 minutes.

[0117] <Developing step>

In the developing step, a resin film is patterned, and a patterned resin film is obtained by removing the exposed parts of the resin film after the exposure step with a developer. As the developer, aqueous alkali solutions such as sodium carbonate, sodium hydroxide, potassium hydroxide, sodium silicate, ammonia, ethyl amine, diethyl amine, triethyl amine, triethanol amine and tetramethylammonium hydroxide (TMAH) are used suitably. It is preferable that the base concentration of these aqueous solutions be 0.1 to 10% by mass. An alcohol or a surfactant can also be further added and used for the above-mentioned developer. These can be blended in the range of preferably 0.01 to 10 parts by mass, more preferably 0.1 to 5 parts by mass, based on 100 parts by mass of the developer, separately. When development is performed using the developer, the developer is disposed on a resin film by a method such as shower development, spray development, immersion development or paddle development, and it is left to stand

under a condition of 18 to 40°C for 30 to 360 seconds. A patterned resin film is washed by water-washing and spin-drying after leaving.

[0118] <Heat-treating step>

In the heat-treating step, a patterned cured film can be subsequently formed by heat-treating the patterned resin film. From the viewpoint of sufficiently preventing thermal damage to a semiconductor device, it is preferable that the heating temperature in the heat-treating step be 250°C or less, and it is more preferable that it be 230°C or less.

[0119] Heat treatment can be performed using an oven such as a quartz tube furnace, a hot plate, rapid thermal anneal, a vertical diffusion furnace, an infrared curing furnace, an electron beam curing furnace or a microwave curing furnace. Any of the air atmosphere or an inert atmosphere such as nitrogen can also be selected, and it is more desirable to perform heat treatment under nitrogen, because the oxidization of the pattern can be prevented. Since the above-mentioned preferable range of heating temperature is lower than the conventional heating temperature, damage to a supporting substrate and a semiconductor device can be reduced. An electronic device can be accordingly manufactured with a high yield by using the method for producing a resist pattern of the present embodiment. It leads to energy saving in the process. Since the volume shrinkage (cure shrinkage) seen in a photosensitive polyimide or the like in the heat-treating step is small according to the positive-type photosensitive resin composition of the present embodiment, the deterioration of the accuracy of dimension can be prevented.

[0120] Although the heat treatment time in the heat-treating step may be enough time for the positive-type photosensitive resin composition to cure, it is preferable that it be 5 hours or less in balance with working efficiency.

5 [0121] Heat treatment can also be performed using a microwave curing device or a frequency variable microwave curing device besides the above-mentioned oven. Only a photosensitive resin film can be heated effectively while the temperature of a substrate and a semiconductor device is maintained, for example, at 200°C or less by using these
10 devices (refer to J. Photopolym. Sci. Technol., 18, 327-332 (2005)).

[0122] According to the above-mentioned method for producing a patterned cured film of the present embodiment, a patterned cured film which has enough high sensitivity and resolution and is excellent also in adhesion and thermal shock resistance is obtained.

15 [0123] [Interlayer insulating layer and surface protective layer]

A patterned cured film of the present embodiment can be used as an interlayer insulating layer or a surface protective layer of a semiconductor device.

[0124] [Semiconductor device]

20 A semiconductor device of one embodiment comprises an interlayer insulating layer or a surface protective layer of the present embodiment. The semiconductor device of the present embodiment is not particularly limited, and it means a memory, a package or the like having multilayer wiring structure, rewiring structure or the like.

25 [0125] Here, an example of a process for manufacturing a semiconductor device will be described based on Figures. Figures 1 to

5 are schematic perspective views and schematic end views showing one embodiment of a process for manufacturing a semiconductor device having multilayer wiring structure. In Figures 1 to 5, (a) is schematic perspective views, and (b) is schematic end views showing the Ib-Ib to Vb-Vb end faces, respectively, in (a).

[0126] First, a structure 100 shown in Figure 1 is provided. The structure 100 comprises a semiconductor substrate 1 such as a Si substrate having a circuit element, a protective film 2 such as a silicon oxide film having a predetermined pattern in which the circuit element is exposed and covering a semiconductor substrate 1, a first conductor layer 3 formed on the exposed circuit element, and an interlayer insulating layer 4 film-formed on the protective film 2 and the first conductor layer 3 by spin coating or the like and consisting of a polyimide resin and the like.

[0127] Next, a structure 200 shown in Figure 2 is obtained by forming a photosensitive resin layer 5 having window parts 6A on the interlayer insulating layer 4. The photosensitive resin layer 5 is formed by applying a photosensitive resin, such as a chlorinated rubber-based resin, a phenol novolac-based resin, a polyhydroxystyrene-based resin or a polyacrylic ester-based resin, by spin coating. The window parts 6A are formed so that the interlayer insulating layer 4 in predetermined portions is exposed by a known photographic etching technique.

[0128] The interlayer insulating layer 4 is etched to form window parts 6B, and the photosensitive resin layer 5 is then removed to obtain a structure 300 shown in Figure 3. Dry etching means using gas such as oxygen or carbon tetrafluoride can be used for the etching of the

interlayer insulating layer 4. The interlayer insulating layer 4 in the portions corresponding to the window parts 6A is selectively removed by this etching to obtain the interlayer insulating layer 4 in which window parts 6B are provided so that the first conductor layer 3 is exposed. Subsequently, the photosensitive resin layer 5 is removed using an etching solution which corrodes only the photosensitive resin layer 5 without corroding the first conductor layer 3 exposed from the window parts 6B.

[0129] Moreover, a second conductor layer 7 is formed in portions corresponding to the window parts 6B to obtain a structure 400 shown in Figure 4. A known photographic etching technique can be used for forming the second conductor layer 7. The second conductor layer 7 and the first conductor layer 3 are electrically connected thereby.

[0130] Finally, a surface protective layer 8 is formed on the interlayer insulating layer 4 and the second conductor layer 7 to obtain a semiconductor device 500 shown in Figure 5. In the present embodiment, the surface protective layer 8 is formed as follows. First, the above-mentioned photosensitive resin composition is applied to the interlayer insulating layer 4 and the second conductor layer 7 by spin coating and dried to form a photosensitive resin film. Next, light is irradiated through a mask on which patterns corresponding to window parts 6C are drawn in predetermined portions, and the resin film after exposure is then developed with an aqueous alkali solution to form a patterned resin film. Then, the patterned resin film is cured by heating to form the patterned cured film used as the surface protective layer 8. This surface protective layer 8 protects the first conductor layer 3 and

the second conductor layer 7 from external stress, α -rays or the like, and a semiconductor device 500 using the surface protective layer 8 of the present embodiment is excellent in reliability.

[0131] A method for manufacturing a semiconductor device having a two-layer wiring structure is shown in the above-mentioned embodiment, and when a multilayer wiring structure having three or more layers is formed, the above-mentioned steps are however repeated, and layers can be formed. That is, a step of forming the interlayer insulating layer 4 and a step of forming the surface protective layer 8 are repeated, and a multilayer pattern can be formed. In the above-mentioned example, not only the surface protective layer 8 but also the interlayer insulating layer 4 can be formed using the photosensitive resin composition of the present embodiment.

An electronic device of the present embodiment is not limited to an electronic device having a surface protective layer, a cover coat layer or an interlayer insulating layer formed using an above-mentioned positive-type photosensitive resin composition, and can take various structures.

[0132] Figures 6 and 7 are schematic sectional views showing one embodiment of a semiconductor device having a rewiring structure. Since the photosensitive resin composition of the present embodiment is excellent in stress relaxation properties, adhesiveness and the like, it can be used in the semiconductor device having a rewiring structure as shown in Figures 6 and 7 and developed in recent years.

[0133] Figure 6 is a schematic sectional view showing a wiring structure as one embodiment of a semiconductor device. A

semiconductor device 600 shown in Figure 6 comprises a silicon substrate 23, an interlayer insulating layer 11 provided on one surface side of the silicon substrate 23, an Al wiring layer 12 formed on the interlayer insulating layer 11 and having a pattern including a pad part 15, an insulating layers 13 (for example, P-SiN layer or the like) and a surface protective layer 14 successively layered on the interlayer insulating layer 11 and the Al wiring layer 12 while forming an opening over the pad part 15, an island-shaped core 18 disposed near the opening over the surface protective layer 14, and a rewiring layer 16 extending on the surface protective layer 14 so as to be in contact with the pad part 15 in the openings of the insulating layer 13 and the surface protective layer 14 and in contact with the surface on the opposite side of the core 18 to the surface protective layer 14. Moreover, the semiconductor device 600 comprises a cover coat layer 19 formed by covering the surface protective layer 14, the core 18 and the rewiring layer 16 with an opening formed in the portion of the rewiring layer 16 over the core 18, a conductive ball 17 connected with the rewiring layer 16 with a barrier metal 20 therebetween in the opening of the cover coat layer 19, a collar 21 holding the conductive ball, and an underfill 22 provided on the cover coat layer 19 around the conductive ball 17. The conductive ball 17 is used as an external connection terminal, and is formed of solder, gold or the like. The underfill 22 is provided to relax stress when the semiconductor device 600 is mounted.

[0134] In the semiconductor device 700 of Figure 7, an Al wiring layer (not shown) and the pad part 15 of an Al wiring layer are formed on a silicon substrate 23, and an insulating layer 13 is formed thereover, and

the surface protective layer 14 of the element is further formed. A rewiring layer 16 is formed on the pad part 15, and this rewiring layer 16 extends to the upper portion of a connected part 24 with a conductive ball 17. Moreover, a cover coat layer 19 is formed on the surface protective layer 14. The rewiring layer 16 is connected with the conductive ball 17 through a barrier metal 20.

[0135] In the semiconductor devices of Figures 6 and 7, a photosensitive resin composition can be used as a material for forming not only the interlayer insulating layer 11 and the surface protective layer 14 but also the cover coat layer 19, the core 18, the collar 21, the underfill 22 and the like. Since the patterned cured film using the photosensitive resin composition of the present embodiment is excellent in adhesiveness with a metal layer such as the Al wiring layer 12 or the rewiring layer 16, a sealant, or the like, and the stress relaxation effect is also high, a semiconductor device using this patterned cured film for an interlayer insulating layer 11, a surface protective layer 14; a cover coat layer 19, a core 18, a collar 21 such as solder, an underfill 22 used in a flip chip or the like, and the like is extremely excellent in reliability.

[0136] It is suitable that the photosensitive resin composition of the present embodiment be used for the interlayer insulating layer 11, the surface protective layer 14, or the cover coat layer 19 of the semiconductor device having the rewiring layer 16 in Figures 6 and 7.

[0137] It is preferable that the film thicknesses of the interlayer insulating layer 11, the surface protective layer 14 and the above-mentioned cover coat layer 19 be 3 to 20 μm , and it is more preferable that it be 5 to 15 μm .

[0138] [Electronic device]

An electronic device of one embodiment has a semiconductor device of the present embodiment. An electronic device includes the above-mentioned semiconductor device, and examples include mobile phones, smart phones, tablet type terminals, personal computers and hard disk suspensions.

Examples

[0139] The present invention will be described specifically hereinafter based on Examples, but the present invention is not limited to these.

10 [0140] Materials used in Examples will be shown hereinafter.

[0141] [(A) component]

A1: Polymer of 4-hydroxystyrene (weight average molecular weight = 10000, manufactured by Maruzen Petrochemical Co., Ltd., trade name "MARUKA LYN CUR M")

15 A2: Copolymer of 4-hydroxystyrene/styrene = 85/15 (molar ratio) (weight average molecular weight = 10000, manufactured by Maruzen Petrochemical Co., Ltd., trade name "MARUKA LYN CUR CST")

A3: Copolymer of 4-hydroxystyrene/methyl methacrylate = 70/30 (molar ratio) (weight average molecular weight = 12000, manufactured by Maruzen Petrochemical Co., Ltd., trade name "MARUKA LYN CUR CMM")

20 A4: Cresol novolac resin (cresol/formaldehyde novolac resin, m-cresol/p-cresol (molar ratio) = 60/40, weight average molecular weight = 12000, manufactured by ASAHI YUKIZAI CORPORATION, trade name "EP4020G")

25

[0142] The weight average molecular weights were calculated by

standard polystyrene conversion using gel permeation chromatography (GPC) separately.

[0143] The weight average molecular weight was specifically measured with the following device under the following conditions.

5 Measuring device:

Detector: L4000UV manufactured by Hitachi, Ltd.

Pump: L6000 manufactured by Hitachi, Ltd.

Column: Gelpack GL-S300MDT-5 × 2 columns

Measurement conditions:

10 Eluate: THF

LiBr (0.03 mol/l), H₃PO₄ (0.06 mol/l)

Flow rate: 1.0 ml/minute, Detector: UV 270 nm

Measurement was performed using a solution in 1 ml of a solvent [THF/DMF = 1/1 (volume ratio)] per 0.5 mg of a sample.

15 [0144] [(B) component]

B1: Compound wherein all of R¹ to R⁶ in the formula (1) are methyl groups (hexakis(methoxymethyl)melamine, manufactured by SANWA CHEMICAL CO., LTD., trade name "NIKALAC MW-30HM", molecular weight: 390.4)

20 B2: Compound wherein all of R⁷ to R¹² in the formula (2) are methyl groups (manufactured by Honshu Chemical Industry Co., Ltd., trade name "HMOM-TPPA", molecular weight 688.9)

[0145] [(C) component]

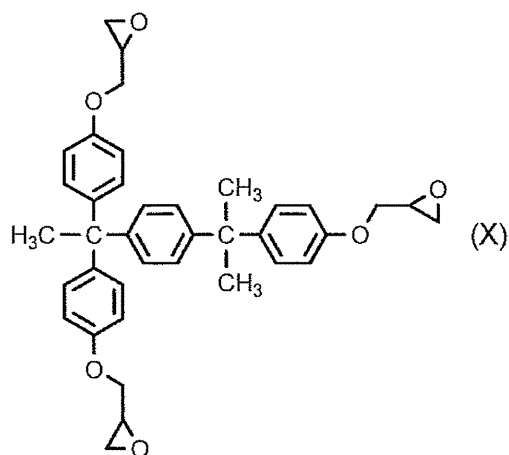
25 C1: Trifunctional epoxy compound (compound wherein all of R¹³ to R¹⁵ in the formula (3) are methylene groups, manufactured by Nissan Chemical Industries, Ltd., trade name "TEPIC-L", molecular weight:

297.3)

C2: Trifunctional epoxy compound (compound wherein all of R¹³ to R¹⁵ in the formula (3) are n-propylene groups, manufactured by Nissan Chemical Industries, Ltd., trade name "TEPIC-VL", molecular weight: 381.4)

C3: Trifunctional epoxy compound (compound wherein all of R¹³ to R¹⁵ in the formula (3) are n-hexylene groups, Nissan Chemical Industries, Ltd., trade name "TEPIC-FL", molecular weight: 507.7)

C4: Trifunctional epoxy compound (compound represented by the following formula (X), manufactured by Printec Corporation, trade name "TECHMORE VG3101L", molecular weight: 592.7)



C5: Difunctional epoxy compound (polyethylene glycol #400 diglycidyl ether, manufactured by Kyoeisha Chemical Co., Ltd., trade name "Epolte 400E", molecular weight: 526.6)

[0146] [(D) component]

D1: First, 55 g of ethyl lactate was weighed in a 100-ml three-necked flask comprising a stirrer, a nitrogen-introducing tube and a thermometer, and polymerizable monomers weighed separately (34.7 g

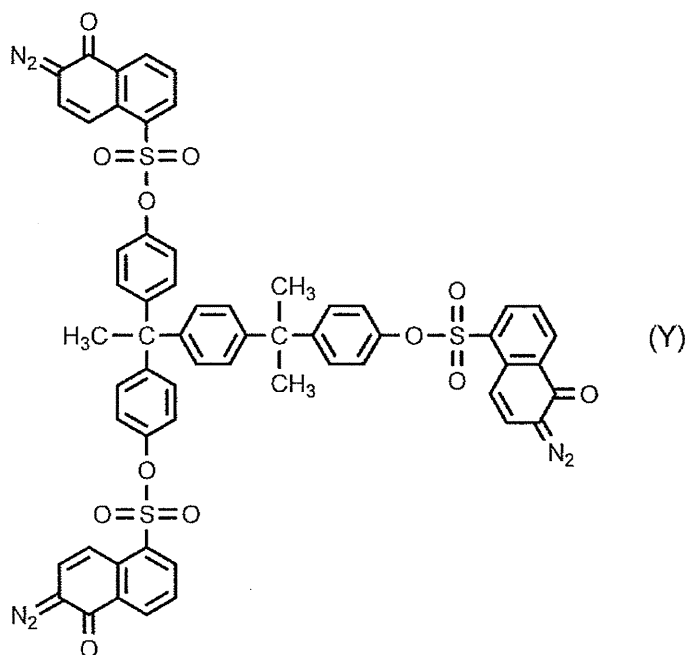
of n-butyl acrylate (BA), 2.2 g of lauryl acrylate (LA), 3.9 g of acrylic acid (AA), 2.6 g of hydroxybutyl acrylate (HBA), 1.7 g of 1,2,2,6,6-pentamethylpiperidin-4-yl methacrylate (trade name: FA-711MM, manufactured by Hitachi Chemical Company, Ltd.) and 0.29 g of azobisisobutyronitrile (AIBN)) were added. Nitrogen gas was made to flow at a flow rate of 400 ml/minute for 30 minutes with stirring at room temperature and a stirring rotational number of around 160 rpm to remove dissolved oxygen. Then, the inflow of nitrogen gas was stopped, the flask was shut tightly and heated to 65°C over around 25 minutes in a constant temperature water bath. The same temperature was maintained for 10 hours, and the polymerization reaction was performed to obtain an elastomer D1. The rate of polymerization in this time was 99%. The weight average molecular weight of this D1 was around 22000. The molar ratio of the polymerizable monomers in the elastomer D1 is as follows.

BA/LA/AA/HBA/FA-711MM = 70.5/2.5/20/5/2 (mol%)

[0147] The weight average molecular weight of the (D) component was determined by the same method as measurement of the weight average molecular weight of the (A) component.

[0148] [(E) component]

E1: Compound represented by the following formula (Y) (manufactured by Daito Chemix Corporation, trade name "PA-28")



[0149] (Examples 1 to 9 and Comparative Examples 1 to 3)

(A) to (C) components in blended amounts (part by mass) shown in Table 1 and 120 parts by mass of ethyl lactate as a solvent were blended, and the resulting blend was filtered under pressure using a Teflon (registered trademark) filter having 3- μ m pores to prepare the positive-type photosensitive resin compositions of Examples 1 to 9 and Comparative Examples 1 to 3.

[0150] <Evaluation of positive-type photosensitive resin composition>

(Production of a cured film)

First, a 6-inch silicon substrate was spin-coated with each of the positive-type photosensitive resin compositions of Examples 1 to 9 and Comparative Examples 1 to 3 and heated at 120°C for 3 minutes to form a resin film having a film thickness of around 12 to 14 μ m. Then, the resin film was heat-treated (cured) by the following method (i) to obtain a cured film having a film thickness of around 10 μ m.

(i) The resin film was heat-treated in nitrogen at a temperature of 230°C (temperature rise time 1.5 hours) for 2 hours using a vertical diffusion furnace (manufactured by Koyo Thermo Systems Co., Ltd., trade name "μ-TF").

5 [0151] (Chemical liquid swelling ratio)

Each of the cured films obtained by the above-mentioned (production of the cured film) was coated with flux (manufactured by SENJU METAL INDUSTRY CO., LTD., trade name "WF-6300LF") as a chemical liquid, heat-treated at 260°C for 3 minutes and water-washed
10 to remove the chemical liquid. The film thicknesses of the cured film before and after chemical liquid treatment were measured, and the chemical liquid swelling ratio was calculated from the following formula. The chemical liquid swelling ratio means that it becomes better as the numerical value becomes smaller (25% or less). The
15 result is shown in Table 1.

Chemical liquid swelling ratio (%) = [(film thickness of cured film after chemical liquid treatment)/(film thickness of cured film before chemical liquid treatment) - 1] × 100

[0152] (Residual stress)

20 The residual stress of each of the cured films obtained by the above-mentioned (Production of cured film) was measured using a stress measuring device (manufactured by KLA Corporation, FLX-2320 type). The residual stress means that it becomes better as the numerical value becomes smaller (20 MPa or less). The result is
25 shown in Table 1.

[0153] (Al adhesion strength)

A 6-inch aluminum substrate (substrate wherein Ti was formed on a silicon substrate by sputtering, and aluminum was then further formed on the Ti by sputtering) was spin-coated with each of the positive-type photosensitive resin compositions of Examples 1 to 9 and Comparative Examples 1 to 3 and heated at 120°C for 3 minutes to form a resin film having a film thickness of 11 to 13 μm . Then, it was heat-treated (cured) by the above-mentioned method (i) to obtain a cured film having a film thickness of around 10 μm . This cured film was cut into small pieces (1 cm $\times$ 1 cm) together with the substrate, and a stud made of aluminum and the cured film were bonded through an epoxy resin layer. Next, the stud was pulled, and the load at the time of exfoliation was measured. The adhesion strength means that it becomes better as the numerical value becomes larger (39.2 MPa (400 kgf/cm²) or more). The result is shown in Table 1.

[0154] Table 1

Component	Material	Example					
		1	2	3	4	5	6
(A)	A1	100	100	100	-	-	-
	A2	-	-	-	100	-	-
	A3	-	-	-	-	100	-
	A4	-	-	-	-	-	100
(B)	B1	10	10	10	10	10	10
	B2	-	-	-	-	-	-
(C)	C1	5	-	-	-	-	-
	C2	-	5	-	5	5	5
	C3	-	-	5	-	-	-
	C4	-	-	-	-	-	-
	C5	-	-	-	-	-	-
(C)/(B) (molar ratio)		0.66	0.51	0.38	0.51	0.51	0.51
Chemical liquid swelling ratio [%]		9	3	5	3	4	7
Residual stress [MPa]		17	16	16	16	15	18
Al adhesion strength [MPa]		46.1	54.9	62.7	51.9	52.9	49.0

Table 1 (continued)

Component	Material	Example			Comparative Example		
		7	8	9	1	2	3
(A)	A1	100	100	100	100	100	100
	A2	-	-	-	-	-	-
	A3	-	-	-	-	-	-
	A4	-	-	-	-	-	-
(B)	B1	-	10	10	10	15	-
	B2	10	-	-	-	-	-
(C)	C1	-	-	-	-	-	-
	C2	5	-	-	-	-	15
	C3	-	-	-	-	-	-
	C4	-	5	-	-	-	-
	C5	-	-	5	-	-	-
(C)/(B) (molar ratio)		0.90	0.33	0.37	-	-	-
Chemical liquid swelling ratio [%]		2	11	24	16	8	46
Residual stress [MPa]		17	19	15	19	24	10
Al adhesion strength [MPa]		49.0	41.2	41.2	38.2	25.5	51.9

[0155] As shown in Table 1, in the obtained cured film of a positive-type photosensitive resin composition comprising a (B) component and a (C) component, the residual stress was reduced, and it was excellent also in chemical liquid resistance and adhesion to a substrate as compared with a positive-type photosensitive resin composition not comprising a (B) component and a (C) component.

[0156] (Examples 10 and 11 and Comparative Examples 4 to 6)

(A) to (E) components in blended amounts (part by mass) shown

in Table 2 and 120 parts by mass of ethyl lactate as a solvent were blended, the resulting blend was filtered under pressure using a Teflon (registered trademark) filter having 3- μ m pores to prepare the positive-type photosensitive resin compositions of Examples 10 and 11 and Comparative Examples 4 to 6.

[0157] <Evaluation of positive-type photosensitive resin composition>
(Chemical liquid swelling ratio, residual stress and adhesion strength)

The evaluations were performed by the same techniques as the above-mentioned techniques. The result is shown in Table 2.

[0158] (Production of patterned cured film)

A 6-inch silicon substrate was spin-coated with each of the positive-type photosensitive resin compositions of Examples 10 and 11 and Comparative Examples 4 to 6 and heated at 120°C for 3 minutes to form a resin film having a film thickness of around 12 to 14 μ m. Then, this resin film was exposed at twice as much light exposure as the minimum light exposure at all wavelengths through a mask using a proximity exposure machine (manufactured by Canon Inc., trade name "PLA-600FA"). After exposure, development was performed using an aqueous 2.38% by mass TMAH (tetramethylammonium hydroxide) solution to obtain a patterned resin film having a width of 10 mm. Then, the patterned resin film was heat-treated (cured) by the following method (i) to obtain a patterned cured film having a film thickness of around 10 μ m.

(i) The patterned resin film was heat-treated in nitrogen at a temperature of 230°C (temperature rise time 1.5 hours) for 2 hours using a vertical diffusion furnace (manufactured by Koyo Thermo Systems Co., Ltd.,

trade name " μ -TF").

[0159] (Breaking strength after curing and breaking elongation after curing)

5 The breaking strength and breaking elongation of the obtained
patterned cured film were measured using an Autograph AGS-H100N
(manufactured by SHIMADZU CORPORATION). The width of a
sample was 10 mm, the film thickness was 9 to 11 μm , and the distance
between chucks was 20 mm. The pulling speed was 5 mm/minute, and
the measurement temperature was 20°C to 25°C. The averages of the
10 measured values of five or more specimens obtained from the patterned
cured film obtained under the same conditions were defined as
"breaking strength" and "breaking elongation". The breaking strength
means that it becomes better as the numerical value becomes larger (100
MPa or more). The breaking elongation means it becomes better as
15 the numerical value becomes larger (30% or more). The result is
shown in Table 2.

[0160] (CTE)

20 The average coefficient of thermal expansion (CTE) at 50 to
150°C of a cured film obtained by the same technique as the
above-mentioned (Production of patterned cured film) was measured
using TMA/SS600 (manufactured by Seiko Instruments Inc.). The
width of samples used for measurement was adjusted to 2 mm, the film
thickness was adjusted to around 10 μm , and the distance between
chucks was adjusted to 10 mm. The measurement conditions were
25 such that the load was 10 g, and the rate of temperature rise was
5°C/minute. The CTE means that it becomes better as the numerical

value becomes lower (70 ppm/K or less). The result is shown in Table 2.

[0161] Table 2

Component	Material	Example		Comparative Example		
		10	11	4	5	6
(A)	A1	-	-	100	100	100
	A2	100	100	-	-	-
(B)	B1	10	10	10	15	-
(C)	C2	5	-	-	-	15
	C3	-	5	-	-	-
(D)	D1	15	15	15	15	15
(E)	E1	10	10	10	10	10
(C)/(B) (molar ratio)		0.51	0.38	-	-	-
Chemical liquid swelling ratio [%]		4	6	18	9	51
Residual stress [MPa]		15	15	18	21	10
Al adhesion strength [MPa]		55.9	64.7	38.2	28.4	50.0
Breaking strength [MPa]		141	130	112	138	80
Breaking elongation [%]		45	50	41	36	19
CTE [ppm/K]		53	59	65	55	136

5 [0162] As shown in Table 2, in the obtained cured film of a positive-type photosensitive resin composition comprising a (B) component and a (C) component and further comprising the (D) component and the (E) component, the residual stress was reduced, and it was excellent also in chemical liquid resistance and adhesion to a
10 substrate, as compared with a positive-type photosensitive resin composition not comprising a (B) component and a (C) component. It was proved that the obtained patterned cured film was excellent also in

breaking strength, breaking elongation, and the coefficient of thermal expansion.

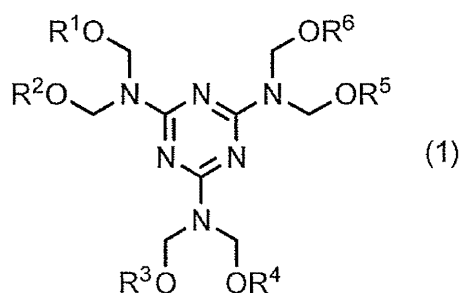
[0163] From the above, it was confirmed that a positive-type photosensitive resin composition of the present invention can form a cured film the residual stress of which is low and which is excellent in chemical liquid resistance and adhesion to a substrate.

Reference Signs List

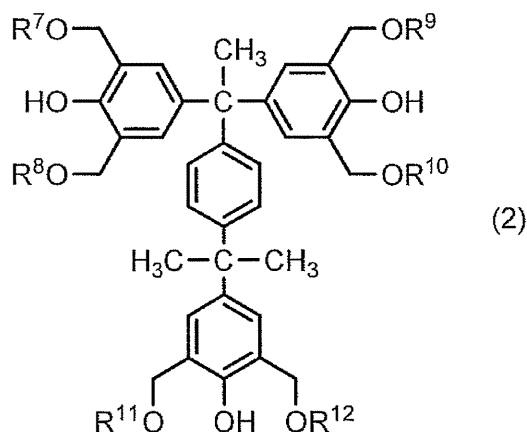
[0164] 1: semiconductor substrate, 2: protective film, 3: first conductor layer, 4: interlayer insulating layer, 5: photosensitive resin layer, 6A, 6B and 6C: window parts, 7: second conductor layer, 8: surface protective layer, 11: interlayer insulating layer, 12: Al wiring layer, 13: insulating layer, 14: surface protective layer, 15: pad part, 16: rewiring layer, 17: conductive ball, 18: core, 19: cover coat layer, 20: barrier metal, 21: collar, 22: underfill, 23: silicon substrate, 24: connected part, 100,200,300 and 400: structures, 500,600 and 700: semiconductor devices.

CLAIMS

1. A positive-type photosensitive resin composition, comprising:
 an alkali-soluble resin (A);
 a compound represented by the following formula (1) or a
 5 compound represented by the following formula (2) (B); and
 a compound having two or more epoxy groups (C),



wherein R¹ to R⁶ each independently represent an alkyl group
 having 1 to 10 carbon atoms,

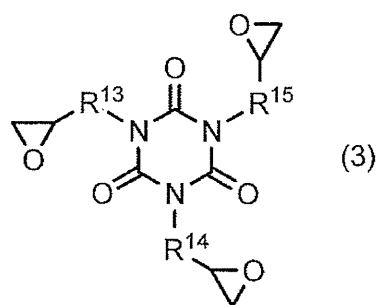


wherein R⁷ to R¹² each independently represent an alkyl group
 having 1 to 10 carbon atoms.

2. The positive-type photosensitive resin composition according to
 claim 1, wherein a molar ratio of the (C) component to the (B)
 15 component is 1.0 or less.

3. The positive-type photosensitive resin composition according to claim 1 or 2, wherein the (C) component is a compound having an aromatic ring or a heterocycle.

4. The positive-type photosensitive resin composition according to any one of claims 1 to 3, wherein the (C) component is a compound represented by the following formula (3):



wherein R^{13} to R^{15} each independently represent an alkylene group having 1 to 10 carbon atoms.

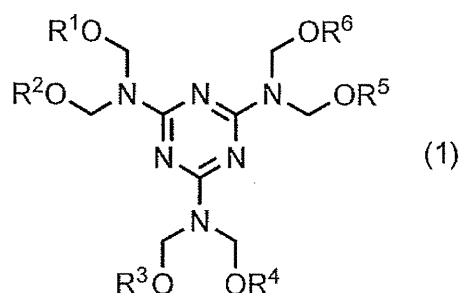
5. The positive-type photosensitive resin composition according to any one of claims 1 to 4, further comprising an elastomer (D).

6. The positive-type photosensitive resin composition according to any one of claims 1 to 5, further comprising a compound which generates an acid by light (E).

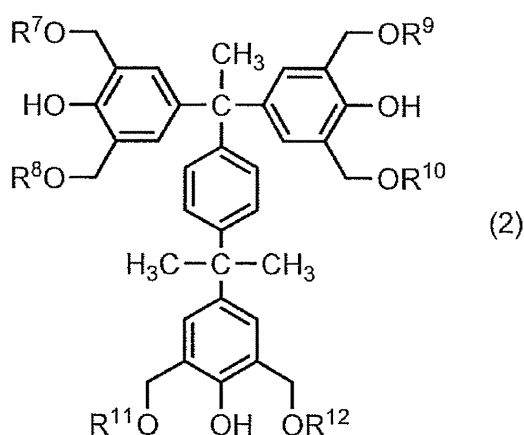
7. A thermal crosslinking agent for a positive-type photosensitive resin, consisting of:

a compound represented by the following formula (1) or a compound represented by the following formula (2); and

a compound having two or more epoxy groups,



wherein R¹ to R⁶ each independently represent an alkyl group having 1 to 10 carbon atoms,



5 wherein R⁷ to R¹² each independently represent an alkyl group having 1 to 10 carbon atoms.

8. A patterned cured film, the patterned cured film comprising a pattern,

10 wherein the pattern comprises a cured product of a resin film consisting of the positive-type photosensitive resin composition according to any one of claims 1 to 5.

9. A method for producing a patterned cured film, the method comprising:

15 applying the positive-type photosensitive resin composition according to any one of claims 1 to 6 to a part or whole of a substrate

followed by drying to form a resin film;

exposing a part or whole of the resin film;

developing the resin film after exposure with an aqueous alkali solution to form a patterned resin film; and

5 heating the patterned resin film.

10. A semiconductor device, comprising the patterned cured film according to claim 8 as an interlayer insulating layer or a surface protective layer.

11. An electronic device, comprising the semiconductor device
10 according to claim 10.