

DESCRIPTION

PHOTOSENSITIVE COMPOSITION, CURED FILM FORMED FROM THE SAME, AND ELEMENT HAVING CURED FILM

TECHNICAL FIELD

5 [0001] The present invention relates to a photosensitive composition which is used to form a planarization film for thin-film transistor (TFT) substrate of a liquid crystal display device, an organic EL display device or the like, a protective film or an insulation film for a touch panel, an interlayer insulation film of a semiconductor device, a planarization film or a microlens array pattern for a solid-state image
10 sensing device, or a core or clad material of an optical waveguide. The present invention also relates to a cured film formed from the photosensitive composition and an element comprising the cured film.

BACKGROUND ART

[0002] In recent years, in the fields of liquid crystal displays, organic EL displays
15 and the like, there is an increasing demand for higher definition and higher resolution.

[0003] Furthermore, in recent years, touch panels have been more actively used in liquid crystal displays and the like and, in particular, touch panels utilizing a capacitance system have drawn attention. In order to improve the transparency and functionalities of a touch panel, a transparent electrode member, ITO, is required to
20 have high transparency and a highly conductive protective film and insulation film are also required to have heat resistance for a high-temperature treatment.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0004] For example, as a method for realizing higher definition and higher resolution
25 in a liquid crystal display, an organic EL display or the like, Patent Document 1 discloses a method of increasing the aperture ratio of a display device. This method enables to overlap a dataline with a pixel electrode by arranging a transparent

planarization film on top of a TFT substrate as a protective film and attains an increased aperture ratio as compared to prior art.

[0005] The material of such planarization film for a TFT substrate is required to have properties such as high heat resistance and high transparency and be capable of forming a hole-pattern of about several micrometers to 50 μm in order to connect a TFT substrate electrode with an ITO electrode. As such a material, a positive photosensitive material is generally employed.

[0006] In Patent Documents 2, 3 and 4, as representative positive photosensitive materials, materials obtained by combining an acrylic resin with a quinone diazide compound are disclosed.

[0007] Meanwhile, polysiloxanes are known as materials having properties such as high heat resistance and high transparency. In Patent Documents 5 and 6, materials in which a polysiloxane is combined with a quinone diazide compound used to provide positive photosensitivity are disclosed. These materials have high heat resistance and thus even a high-temperature treatment does not cause a defect such as cracking, so that a cured film having high transparency can be obtained.

[0008] In Patent Document 7, as a method of improving the wet-heat resistance, a method in which a metal chelating agent is added to a polysiloxane is disclosed. This method is thought to present a mechanism by which a titanium or zirconium chelating agent promotes crosslinking of siloxane to improve the wet-heat resistance.

[0009] Further, in Patent Document 8, a negative photosensitive material containing an organic metal chelate compound is reported.

[0010] In addition, in Patent Document 9, a positive photosensitive material in which metal particles are added to siloxane is reported.

[0011] Moreover, in Patent Document 10, a method for improving the coating variation of a siloxane composition containing a specific solvent is reported. In Patent Document 10, as examples of a method for providing positive photosensitivity,

addition of a naphthoquinonediazide and addition of a chelate compound are separately described.

Patent Document 1: JP H9-152625A (claim 1)

Patent Document 2: JP 2001-281853A (claim 1)

5 Patent Document 3: JP H5-165214A (claim 1)

Patent Document 4: JP 2002-341521A (claim 1)

Patent Document 5: JP 2006-178436A (claim 1)

Patent Document 6: JP 2009-211033A (claim 1)

Patent Document 7: JP H07-331173A (claim 1)

10 Patent Document 8: JP 2007-308688A (claim 1)

Patent Document 9: JP 2007-246877A (claims 1 to 6)

Patent Document 10: WO2007-049440 (paragraphs [0040], [0041] and [0054])

SUMMARY OF THE INVENTION

15 PROBLEMS TO BE SOLVED BY THE INVENTION

[0012] However, since the transparent planarization film of Patent Document 1 is produced by using an acrylic resin as a material, the film does not have sufficient heat resistance.

[0013] Further, those acrylic resins described in Patent Documents 2, 3 and 4 do not
20 have sufficient heat resistance and chemical resistance; therefore, there are problems in that the resulting cured film becomes colored and the transparency of the film is impaired by a high-temperature treatment of substrate, high-temperature film formation on a transparent electrode or treatment with various etching solutions; and that the conductivity of the resulting electrode is deteriorated by degassing during
25 high-temperature film formation. In addition, since these acrylic materials generally have low sensitivity, their film productivity is low, so that a material having higher sensitivity is desired. Moreover, with advancements of displays, the

aperture sizes of hole-patterns and the like have been made smaller year after year and there are now cases where a fine pattern of 3 μm or smaller is required to be formed; however, the above-described acrylic materials do not have sufficient resolution therefor.

5 [0014] The polysiloxane materials described in Patent Documents 5 and 6 have high heat resistance and high transparency; however, in these materials as well, the adhesion between a patterned film and a substrate at the time of development (hereinafter, referred to as "adhesion in development") cannot be considered sufficient and, in particular, the resulting fine pattern is detached along with a
10 developer and a rinse solution. Therefore, a positive photosensitive material having better adhesion in development is strongly demanded.

[0015] In general, in order to attain good adhesion in development, the temperature of prebaking performed after application is increased. However, since a
15 photosensitizer is deactivated by increasing the prebaking temperature, the sensitivity of the resulting film is impaired. On the other hand, when the prebaking temperature is set to be low, the amount of residual solvent in the film is increased and the adhesion in development is consequently deteriorated. This trade-off relationship makes it very difficult to satisfy both of the properties.

[0016] Furthermore, also for the wet-heat resistance, these materials cannot be
20 considered satisfactory; therefore, a positive photosensitive material having superior wet-heat resistance is strongly demanded.

[0017] Patent Document 7 offers no description with regard to the amount of the chelating agent to be added to the photosensitive composition.

[0018] In Patent Document 8, calcination is performed to form a conductive film and
25 there is no residual insulating organic film.

[0019] Patent Document 9 offers no description with regard to wet-heat resistance.

[0020] In Patent Document 10, there is absolutely no description with regard to the

use of a naphthoquinonediazide and a chelate compound at the same time.

Furthermore, Patent Document 10 offers absolutely no description from which it can be easily inferred that, by using a naphthoquinonediazide and a chelate compound at the same time, a material which has positive photosensitivity and satisfies both wet-heat resistance and adhesion in development is attained.

[0021] As described in the above, despite there is a demand for a positive photosensitive material having high transparency, high wet-heat resistance and good adhesion in development, a technology therefor has not been established until now.

[0022] The present invention was made in view of the above-described

circumstances and an object of the present invention is to provide a photosensitive composition which has high heat resistance and high transparency as well as excellent adhesion in development and wet-heat resistance. Another object of the present invention is to provide a cured film which is formed from the above-described photosensitive composition and used as a planarization film for a TFT substrate, an interlayer insulation film, a protective film or insulation film for a touch panel, a core or clad material or a lens material. Yet another object of the present invention is to provide an element comprising the cured film, such as a display element, a semiconductor element, a solid-state image sensing device or an optical waveguide.

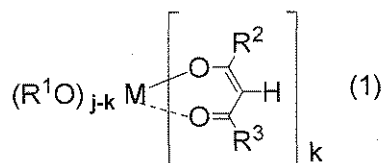
MEANS FOR SOLVING THE PROBLEMS

[0023] In order to solve the above-described problems, the positive photosensitive composition according to the present invention has the following constitution. That is, the positive photosensitive composition according to the present invention comprises (A) an alkali-soluble polysiloxane and/or an alkali-soluble acrylic resin, (B) a naphthoquinone diazide compound, (C) a solvent and (D) a metal chelate compound, and the (D) metal chelate compound has a structure represented by the following Formula (1) and the content of the (D) metal chelate compound is 0.1 to 5

parts by weight compared to 100 parts by weight of the (A) alkali-soluble polysiloxane and/or alkali-soluble acrylic resin (hereinafter, may be referred to as "alkali-soluble resin").

[0024]

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[0025] (wherein, M is a metal atom; R¹s, the same or different, each represent hydrogen, an alkyl group, an aryl group, an alkenyl group, or a substitution product thereof; R² and R³, the same or different, each represent hydrogen, an alkyl group, an aryl group, an alkenyl group, an alkoxy group, or a substitution product thereof; j represents the valency of the metal atom M; and k represents an integer of 0 to j).

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Further, the cured film according to the present invention has either of the following constitutions (1) and (2). That is, the cured film according to the present invention is:

(1) a cured film which is formed from the above-described positive photosensitive composition, wherein the light transmittance per film thickness of 3 μm at a wavelength of 400 nm is not less than 85%; or

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(2) a cured film which is formed from the above-described positive photosensitive composition, wherein the content ratio of at least one metal selected from the group consisting of titanium, zirconium, aluminum, zinc, cobalt, molybdenum, lanthanum, barium, strontium, magnesium and calcium is 0.005 to 1 part by weight compared to 100 parts by weight of the alkali-soluble polysiloxane and/or the alkali-soluble acrylic resin composition.

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[0026] The element according to the present invention has the following constitution. That is, the element according to the present invention comprises the above-described cured film.

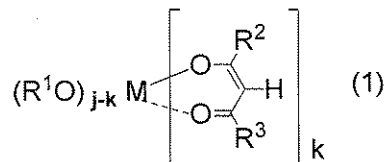
EFFECTS OF THE INVENTION

[0027] The positive photosensitive composition according to the present invention has high heat resistance and high transparency, as well as excellent adhesion in development and wet-heat resistance. Further, a cured film obtained therefrom can be suitably used as a planarization film for a TFT substrate, an interlayer insulation film, a protective film or an insulation film for a touch panel, or a core or clad material of an optical waveguide.

MODE FOR CARRYING OUT THE INVENTION

[0028] The positive photosensitive composition according to the present invention comprises (A) an alkali-soluble resin, (B) a naphthoquinone diazide compound, (C) a solvent and (D) a metal chelate compound and, in the positive photosensitive composition, the (D) metal chelate compound has a structure represented by the following Formula (1) and the content of the (D) metal chelate compound is 0.1 to 5 parts by weight compared to 100 parts by weight of the (A) alkali-soluble resin.

[0029]



[0030] (wherein, M is a metal atom; R^1 's, the same or different, each represent hydrogen, an alkyl group, an aryl group, an alkenyl group, or a substitution product thereof; R^2 and R^3 , the same or different, each represent hydrogen, an alkyl group, an aryl group, an alkenyl group, an alkoxy group, or a substitution product thereof; j represents the valency of the metal atom M; and k represents an integer of 0 to j).

The (A) alkali-soluble resin used in the present invention is a polysiloxane and/or an acrylic resin which dissolve in an aqueous alkaline solution having a pH of not lower than 8. In order to express alkali-solubility, the resin has at least one acidic functional group such as a silanol group, a carboxylic acid group and/or a

phenol group. Examples of preferred resin include acrylic resins and polysiloxanes which have the above-described acidic functional group(s). From the standpoint of heat resistance, it is preferred that the (A) alkali-soluble resin be a polysiloxane.

[0031] The alkali-soluble acrylic resin used in the present invention may also contain, as a copolymerization component, a polymerization unit of an unsaturated carboxylic acid (a-1) and, as required, a polymerization unit of other radical polymerizable compound (a-2) capable of copolymerizing with the above-described unsaturated carboxylic acid (a-1) (hereinafter, referred to as "other radical polymerizable compound").

[0032] Preferred examples of the above-described unsaturated carboxylic acid (a-1) used in the present invention include unsaturated carboxylic acids having an ethylenically unsaturated double bond.

[0033] Specific examples of such unsaturated carboxylic acid (a-1) include monocarboxylic acids such as methacrylic acid, acrylic acid, crotonic acid, o-vinylbenzoic acid, m-vinylbenzoic acid and p-vinylbenzoic acid; and dicarboxylic acids such as maleic acid, fumaric acid, citraconic acid, mesaconic acid, itaconic acid, 1,4-cyclohexene dicarboxylic acid, 3-vinylphthalic acid, 4-vinylphthalic acid, methyl-5-norbornene-2,3-dicarboxylic acid, 3,4,5,6-tetrahydrophthalic acid, 1,2,3,6-tetrahydrophthalic acid and dimethyltetrahydrophthalic acid. Thereamong, for example, methacrylic acid, acrylic acid or itaconic acid is preferably employed.

[0034] Alternatively, in the present invention, as the unsaturated carboxylic acid (a-1), a partial esterification product or a partial amidation product of the above-described unsaturated carboxylic acids in which a carboxylic acid group partially remains in the free state, such as a half-ester or a half-amide of an unsaturated dicarboxylic acid, may also be employed. As such a half-ester or half-amide of an unsaturated carboxylic acid, for example, monomethyl itaconate or monobutyl itaconate is preferably employed. These unsaturated carboxylic acids may be used

individually, or two or more thereof may be used in combination.

[0035] Specific examples of other radical polymerizable compound (a-2) used in the present invention include epoxy group-containing radical polymerizable compounds such as glycidyl (meth)acrylate, α -ethylglycidyl (meth)acrylate, α -n-propylglycidyl (meth)acrylate, α -n-butylglycidyl (meth)acrylate, 3,4-epoxybutyl (meth)acrylate, 3,4-epoxyheptyl (meth)acrylate, α -ethyl-6,7-epoxyheptyl (meth)acrylate, allyl glycidyl ether, vinyl glycidyl ether, o-vinylbenzyl glycidyl ether, m-vinylbenzyl glycidyl ether, p-vinylbenzyl glycidyl ether and 3-vinylcyclohexene oxide; (meth)acryloyl group-containing radical polymerizable compounds such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, iso-propyl (meth)acrylate, n-butyl (meth)acrylate, sec-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, dodecyl (meth)acrylate, dicyclopentanylmethyl (meth)acrylate, iso-bornyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-methylcyclohexyl (meth)acrylate, dicyclohexyl (meth)acrylate, adamantyl (meth)acrylate, allyl (meth)acrylate, propargyl (meth)acrylate, phenyl (meth)acrylate, naphthyl (meth)acrylate, anthracenyl (meth)acrylate, cyclopentyl (meth)acrylate, furyl (meth)acrylate, tetrahydrofuryl (meth)acrylate, pyranyl (meth)acrylate, benzyl (meth)acrylate, phenethyl (meth)acrylate, cresyl (meth)acrylate, 1,1,1-trifluoroethyl (meth)acrylate, perfluoroethyl (meth)acrylate, perfluoro-n-propyl (meth)acrylate, perfluoroiso-propyl (meth)acrylate, triphenylmethyl (meth)acrylate, cumyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, amide (meth)acrylate, N,N-dimethylamide (meth)acrylate, N,N-dipropylamide (meth)acrylate, anilide (meth)acrylate, (meth)acrylonitrile and tricyclo[5.2.1.0^{2,6}]decane-8-yl methacrylate; vinyl group-containing radical polymerizable compounds such as acrolein, vinyl chloride, vinylidene chloride, N-vinylpyrrolidone, vinyl acetate, styrene, α -methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-methoxystyrene, p-methoxymethylstyrene, p-t-

butoxystyrene, chloromethylstyrene, butadiene, 2,3-dimethylbutadiene, isoprene, o-vinylbenzyl methyl ether, m-vinylbenzyl methyl ether, p-vinylbenzyl methyl ether, o-vinylbenzyl ethyl ether, m-vinylbenzyl ethyl ether and p-vinylbenzyl ethyl ether; and unsaturated dicarboxylic acid diesters such as diethyl maleate, diethyl fumarate and diethyl itaconate.

[0036] Thereamong, for example, glycidyl (meth)acrylate, styrene, α -methylstyrene, p-t-butoxystyrene, dicyclopentanyl methacrylate, methyl methacrylate, 2-hydroxyethyl methacrylate, benzyl methacrylate, butadiene, isoprene, o-vinylbenzyl methyl ether, m-vinylbenzyl methyl ether, p-vinylbenzyl methyl ether, o-vinylbenzyl ethyl ether, m-vinylbenzyl ethyl ether and p-vinylbenzyl ethyl ether are preferably used. By using these compounds as a copolymerization component, the alkali-solubility, glass transition temperature, dielectric constant and the like of the resulting polymer can be controlled and consequently, an improvement may be attained in those performances that are required for a resist, such as resolution and normalized remaining film thickness, and those properties that are required for a permanent film, such as transparency and heat resistance. As a copolymerization component, these compounds may be used individually, or two or more thereof may be used in the combination.

[0037] The alkali-soluble acrylic resin used in the present invention can be obtained by copolymerizing the above-described compounds. The alkali-soluble acrylic resin contains a polymerization unit of the unsaturated carboxylic acid (a-1) in an amount of preferably 5 to 50% by weight, particularly preferably 10 to 40% by weight. Further, the alkali-soluble acrylic resin contains a polymerization unit of other radical polymerizable compound (a-2) in an amount of preferably not more than 90% by weight, particularly preferably 20 to 60% by weight.

[0038] When the content of the polymerization unit of the unsaturated carboxylic acid (a-1) in the alkali-soluble acrylic resin is in the above-described preferred range,

the resulting coating film is highly soluble to a developer composed of an aqueous alkaline solution and has excellent developing properties and sensitivity.

Meanwhile, the resulting coating film does not have excessively high solubility in an aqueous alkaline solution; therefore, the normalized remaining film thickness of the resulting resist pattern is not deteriorated. When the content of the polymerization unit of other radical polymerizable compound (a-2) in the alkali-soluble acrylic resin is in the above-described preferred range, the resulting polymer has good balance of solubility in a developer composed of an aqueous alkaline solution, so that the patterning thereof is easily performed.

[0039] The alkali-soluble acrylic resin used in the present invention has a polystyrene-based weight-average molecular weight (hereinafter, referred to as "Mw") of preferably 2×10^3 to 1×10^5 , more preferably 5×10^3 to 5×10^4 . When the Mw is in the above-described preferred range, the developing properties, normalized remaining film thickness and the like of the resulting coating film are not deteriorated and the coating film has excellent pattern shape, heat resistance and the like. Meanwhile, the sensitivity is not impaired and the pattern shape is not deteriorated. Further, the acrylic resin used in the present invention is alkali-soluble. The acrylic resin has an acid value of preferably 50 to 150 mg KOH/g, more preferably 70 to 130 mg KOH/g. When the acid value of the acrylic resin is in the above-described preferred range, it is not likely to be left undissolved at the time of development. Meanwhile, the film loss of the non-exposed area is not increased at the time of development.

[0040] The above-described acrylic resin used in the present invention can be obtained by copolymerizing the unsaturated carboxylic acid (a-1) and other radical polymerizable compound (a-2) in accordance with a variety of polymerization methods and a method in which the copolymerization is performed in a solvent in the presence of a catalyst (polymerization initiator) is preferred.

[0041] Specific examples of the solvent used in the copolymerization include alcohols such as methanol, ethanol, propanol and butanol; cyclic ethers such as tetrahydrofuran and dioxane; cellosolve esters such as methyl cellosolve acetate and ethyl cellosolve acetate; glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol dimethyl ether, diethylene glycol ethylmethyl ether and propylene glycol monomethyl ether; propylene glycol alkyl ether acetates such as propylene glycol methyl ether acetate, propylene glycol ethyl ether acetate and propylene glycol propyl ether acetate; aromatic hydrocarbons such as benzene, toluene and xylene; ketones such as methyl ethyl ketone, cyclohexanone, 2-heptanone and 4-hydroxy-4-methyl-2-pentanone; esters such as ethyl-2-hydroxypropionate, ethyl-2-hydroxy-2-methylpropionate, ethyl-2-hydroxy-2-methylpropionate, ethyl ethoxyacetate, ethyl hydroxyacetate, methyl-2-hydroxy-3-methylbutyrate, methyl-3-methoxypropionate, ethyl-3-methoxypropionate, ethyl-3-ethoxypropionate, methyl-3-ethoxypropionate, ethyl acetate and butyl acetate; and aprotic polar solvents such as dimethylformamide and N-methyl-2-pyrrolidone. These solvents are normally used in an amount of 20 to 1,000 parts by weight compared to a total of 100 parts by weight of the polymerizable compounds [(a-1) and (a-2)].

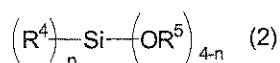
[0042] Further, as the catalyst, those catalysts that are generally known as radical polymerization initiators may be widely employed. For example, azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile) and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile); organic peroxides such as benzoyl peroxide, lauroyl peroxide, t-butyl peroxyvalerate and 1,1'-bis(t-butylperoxy)cyclohexane; and hydrogen peroxide can be used. In cases where a peroxide is used as a radical polymerization initiator, the peroxide may also be used in combination with a reducing agent as a redox-type polymerization initiator.

Further, in the above-described copolymerization, a molecular weight modifier such as an α -methylstyrene dimer may also be added.

[0043] The above-described acrylic resin has an appropriate solubility in aqueous alkaline solutions and provides a radiation-sensitive resin composition having high sensitivity, high normalized remaining film thickness and excellent developing properties and the like. Further, a resin pattern obtained by using this acrylic resin is excellent in a variety of properties such as heat resistance, adhesion with a substrate, transparency in the visible wavelength range and chemical resistance.

[0044] The alkali-soluble polysiloxane used in the present invention contains (a-3) at least one organosilane represented by the following Formula (2) and/or (a-4) a polysiloxane synthesized by hydrolysis and condensation of at least one organosilane represented by the following Formula (3).

[0045]



[0046] In the organosilane represented by the Formula (2), R^4 represents hydrogen, an alkyl group having 1 to 10 carbon atoms, an alkenyl group having 2 to 10 carbon atoms or an aryl group having 6 to 15 carbon atoms and plural R^4 's are optionally the same or different. Further, these alkyl, alkenyl and aryl groups are all optionally unsubstituted or substituted and can be selected in accordance with the properties of the composition. Specific examples of the alkyl group and a substitution product thereof include methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, t-butyl group, n-hexyl group, n-decyl group, trifluoromethyl group, 3,3,3-trifluoropropyl group, 3-glycidoxypropyl group, 2-(3,4-epoxycyclohexyl)ethyl group, [(3-ethyl-3-oxetanyl)methoxy]propyl group, 1-carboxy-2-carboxypentyl group, 3-aminopropyl group, 3-mercaptopropyl group and 3-isocyanatepropyl group. Specific examples of the alkenyl group and a substitution product thereof include

vinyl group, 3-acryloxypropyl group and 3-methacryloxypropyl group. Specific examples of the aryl group and a substitution product thereof include phenyl group, tolyl group, p-hydroxyphenyl group, 1-(p-hydroxyphenyl)ethyl group, 2-(p-hydroxyphenyl)ethyl group, 4-hydroxy-5-(p-hydroxyphenylcarbonyloxy)pentyl group and naphthyl group.

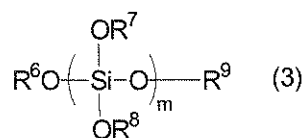
[0047] In the Formula (2), R^5 represents hydrogen, an alkyl group having 1 to 6 carbon atoms, an acyl group having 2 to 6 carbon atoms or an aryl group having 6 to 15 carbon atoms and plural R^5 s are optionally the same or different. Further, these alkyl, acyl and aryl groups are all optionally unsubstituted or substituted and can be selected in accordance with the properties of the composition. Specific examples of the alkyl group include methyl group, ethyl group, n-propyl group, iso-propyl group and n-butyl group. Specific examples of the acyl group include acetyl group. Specific examples of the aryl group include phenyl group.

[0048] In the Formula (2), n represents an integer of 1 to 3. When n is 1, the organosilane represented by the Formula (2) is a trifunctional silane; when n is 2, the organosilane is a bifunctional silane; and when n is 3, the organosilane is a monofunctional silane.

[0049] Specific examples of the organosilane represented by the Formula (2) include trifunctional silanes such as methytrimethoxysilane, methyltriethoxysilane, methyltriiso-propoxysilane, methyl-tri-n-butoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, ethyltriiso-propoxysilane, ethyl-tri-n-butoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, n-butyltrimethoxysilane, n-butyltriethoxysilane, n-hexyltrimethoxysilane, n-hexyltriethoxysilane, decyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltrimethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, p-hydroxyphenyltrimethoxysilane, 1-(p-hydroxyphenyl)ethyltrimethoxysilane, 2-(p-

hydroxyphenyl)ethyltrimethoxysilane, 4-hydroxy-5-(p-hydroxyphenylcarbonyloxy)pentyltrimethoxysilane, trifluoromethyltrimethoxysilane, trifluoromethyltriethoxysilane, 3,3,3-trifluoropropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, [(3-ethyl-3-oxetanyl)methoxy]propyltrimethoxysilane, [(3-ethyl-3-oxetanyl)methoxy]propyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-trimethoxysilylpropylsuccinic acid, 3-mercaptopropyltrimethoxysilane and 3-trimethoxysilylpropylsuccinic anhydride; bifunctional silanes such as dimethyldimethoxysilane, dimethyldiethoxysilane, dimethyldiacetoxysilane, di-n-butyl dimethoxysilane, diphenyldimethoxysilane, (3-glycidoxypropyl)methyldimethoxysilane and (3-glycidoxypropyl)methyldiethoxysilane; and monofunctional silanes such as trimethylmethoxysilane, tri-n-butylethoxysilane, (3-glycidoxypropyl)dimethylmethoxysilane and (3-glycidoxypropyl)dimethylethoxysilane. These organosilanes may be used individually, or two or more thereof may be used in combination. Among these organosilanes, from the standpoints of crack resistance and hardness of the resulting cured film, a trifunctional silane is preferably used.

[0050]



[0051] In the organosilane represented by the Formula (3), R⁶ to R⁹ each independently represent hydrogen, an alkyl group having 1 to 6 carbon atoms, an acyl group having 2 to 6 carbon atoms or an aryl group having 6 to 15 carbon atoms.

These alkyl, acyl and aryl groups are all optionally unsubstituted or substituted and can be selected in accordance with the properties of the composition. Specific examples of the alkyl group include methyl group, ethyl group, n-propyl group, isopropyl group and n-butyl group. Specific examples of the acyl group include acetyl group. Specific examples of the aryl group include phenyl group. In the Formula (3), m is an integer of 1 to 8.

[0052] By using the organosilane represented by the Formula (3), a positive photosensitive composition which has excellent sensitivity and resolution while maintaining high heat resistance and transparency can be obtained.

[0053] In the polysiloxane used in the present invention, the content ratio of the organosilane represented by the Formula (3) is preferably not higher than 50% in terms of molar ratio of Si atom compared to the number of moles of Si atoms in the polysiloxane as a whole. When the content ratio of the organosilane represented by the Formula (3) in the polysiloxane is in the above-described preferred range in terms of molar ratio of Si atom compared to the number of moles of Si atoms in the polysiloxane as a whole, good compatibility is attained between the polysiloxane and the naphthoquinone diazide compound, so that the resulting cured film has excellent transparency. The content ratio of the organosilane represented by the Formula (3) can be determined by a combination of, for example, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^{29}\text{Si-NMR}$, IR, TOF-MS, elementary analysis and ash measurement.

[0054] Specific examples of the organosilane represented by the Formula (3) include tetramethoxysilane; tetraethoxysilane; tetra-n-propoxysilane; tetraiso-propoxysilane; tetra-n-butoxysilane; tetraacetoxysilane; METHYL SILICATE 51 (manufactured by FUSO Chemical Co., Ltd.); M SILICATE 51, SILICATE 40 and SILICATE 45 (which are manufactured by Tama Chemicals Co., Ltd.); and METHYL SILICATE 51, METHYL SILICATE 53A, ETHYL SILICATE 40 and ETHYL SILICATE 48 (which are manufactured by Colcoat Co., Ltd.).

[0055] As a mode of the polysiloxane used in the present invention, a polysiloxane which is synthesized by a reaction of at least one organosilane represented by the above-described Formula (2) and/or at least one organosilane represented by the Formula (3) with silica particles may also be used. By allowing the organosilanes
5 to react with silica particles, the pattern resolution is improved. This is believed to be because incorporation of silica particles into the polysiloxane increases the glass transition temperature of the resulting film to inhibit the reflow of the pattern during heat curing.

[0056] The silica particles have a number average particle size of preferably 2 nm to
10 200 nm, more preferably 5 nm to 70 nm. When the silica particles have a number average particle size in the above-described preferred range, the pattern resolution-improving effect can be sufficiently attained, while the resulting cured film is not likely to cause scattering of light and has excellent transparency. Here, the number average particle size of the silica particles is determined as follows when a specific
15 surface area method is employed: after drying and calcinating the silica particles, the specific surface areas of the resulting particles are measured and the particle sizes are then derived from the thus measured specific surface areas with an assumption that the particles are spherical, thereby determining the average particle size as a number average value of the derived particle sizes. The equipment used for this
20 measurement is not particularly restricted and, for example, "ASAP" 2020 (trade name, manufactured by Micrometrics Instrument Corp.) can be employed.

[0057] Specific examples of the silica particles include: IPA-ST which contains isopropanol as a dispersion medium and has a particle size of 12 nm, MIBK-ST which contains methyl iso-butyl ketone as a dispersion medium and has a particle size of 12
25 nm, IPA-ST-L which contains isopropanol as a dispersion medium and has a particle diameter of 45 nm, IPA-ST-ZL which contains isopropanol as a dispersion medium and has a particle diameter of 100 nm and PGM-ST which contains

propylene glycol monomethyl ether as a dispersion medium and has a particle diameter of 15 nm (all of which are trade names and manufactured by Nissan Chemical Industries, Ltd.); "OSCAL" 101 which contains γ -butyrolactone as a dispersion medium and has a particle diameter of 12 nm, "OSCAL" 105 which
5 contains γ -butyrolactone as a dispersion medium and has a particle diameter of 60 nm, "OSCAL" 106 which contains diacetone alcohol as a dispersion medium and has a particle diameter of 120 nm and "CATALOID"-S which contains water as a dispersion medium and has a particle size of 5 to 80 nm (all of which are trade names and manufactured by JGC Catalysts and Chemicals Ltd.); "QUARTON" PL-2L-
10 PGME which contains propylene glycol monomethyl ether as a dispersion medium and has a particle diameter of 16 nm, "QUARTON" PL-2L-BL which contains γ -butyrolactone as a dispersion medium and has a particle diameter of 17 nm, "QUARTON" PL-2L-DAA which contains diacetone alcohol as a dispersion medium and has a particle diameter of 17 nm, and "QUARTON" PL-2L and GP-2L
15 which contain water as a dispersion medium and have a particle diameter of 18 to 20 nm (all of which are trade names and manufactured by FUSO Chemical Co., Ltd.); SILICA (SiO_2) SG-SO100 having a particle size of 100 nm (trade name, manufactured by KCM Corporation); and "REOLOSIL" having a particle size of 5 to 50 nm (trade name, manufactured by Tokuyama Corporation). Further, these silica
20 particles may be used individually, or two or more thereof may be used in combination.

[0058] In cases where a silica particle is used, the mixing ratio thereof is not particularly restricted; however, it is preferably not higher than 70% in terms of molar ratio of Si atom compared to the number of moles of Si atoms in the
25 polysiloxane as a whole. When the mixing ratio is in the above-described preferred range in terms of molar ratio of Si atom compared to the number of moles of Si atoms in the polysiloxane as a whole, good compatibility is attained between the

polysiloxane and the naphthoquinone diazide compound, so that the resulting cured film has excellent transparency.

[0059] Further, in the polysiloxane used in the present invention, in order to ensure sufficient compatibility with the later-described naphthoquinone diazide compound and the like and to form a uniform cured film without phase separation, the content ratio of phenyl group in the polysiloxane is preferably not less than 5 mol%, more preferably not less than 20 mol%, still more preferably not less than 30 mol%, particularly preferably not less than 40 mol%, with respect to Si atom. When the content ratio of phenyl group is in the above-described preferred range, the polysiloxane and the naphthoquinone diazide compound are not likely to undergo phase separation during coating, drying, heat curing and the like, so that the resulting film does not become clouded and the cured film attains excellent transmittance. Further, the content ratio of phenyl group is preferably not higher than 70 mol%, more preferably not higher than 60 mol%, still more preferably not higher than 50 mol%. When the content ratio of phenyl group is in the above-described preferred range, crosslinking occurs sufficiently during heat curing, so that the resulting cured film attains excellent chemical resistance. The content ratio of phenyl group can be determined by, for example, measuring ²⁹Si-NMR of the polysiloxane and calculating the ratio between the peak area of Si bound with a phenyl group and that of Si not bound with a phenyl group.

[0060] Further, in the polysiloxane used in the present invention, the content ratio of epoxy group and/or vinyl group is preferably not less than 1 mol%, more preferably not less than 3 mol%, still more preferably not less than 5 mol%, particularly preferably not less than 10 mol%, with respect to Si atom. When the content ratio of epoxy group and/or vinyl group is in the above-described preferred range, the photosensitive composition has excellent solvent resistance. Further, the content ratio of epoxy group and/or vinyl group is preferably not higher than 70 mol%, more

preferably not higher than 50%. When the content ratio of epoxy group and/or vinyl group is in the above-described preferred range, the polysiloxane and the naphthoquinone diazide compound are not likely to undergo phase separation during coating, drying, heat curing and the like, so that the resulting film does not become clouded and the cured film attains excellent transmittance. The content ratio of epoxy group and/or vinyl group can be determined by, for example, measuring ^{29}Si -NMR of the polysiloxane and calculating the ratio between the peak area of Si bound with an epoxy group and/or a vinyl group and that of Si not bound with an epoxy group and/or a vinyl group. Alternatively, the content ratio of epoxy group and/or vinyl group can be determined by measuring ^1H -NMR and ^{13}C -NMR as well as the content ratio of epoxy group and/or vinyl group and combining the results thereof with the measurement of ^{29}Si -NMR.

[0061] Further, the weight-average molecular weight (Mw) of the polysiloxane used in the present invention is not particularly restricted; however, based on polystyrene measured by GPC (gel permeation chromatography), it is preferably 500 to 100,000, more preferably 1,000 to 50,000. When the Mw of the polysiloxane is in the above-described preferred range, good coatability is attained while the solubility in a developer at the time of pattern formation is also good.

[0062] The polysiloxane used in the present invention is synthesized by hydrolysis and partial condensation of monomers such as the organosilanes represented by the Formula (2) and/or (3). For the hydrolysis and partial condensation, a commonly-used method can be employed. For example, a solvent, water and, as required, a catalyst are added to a mixture and the resultant is heated with stirring at 50 to 150°C, preferably 90 to 130°C, for about 0.5 to 100 hours. Here, while stirring, as required, the hydrolysis by-product (alcohol such as methanol) and condensation by-product (water) may be distilled off as well.

[0063] The above-described reaction solvent is not particularly restricted; however,

usually, a solvent comparable to the later-described (C) solvent is employed. It is preferred that the solvent be added in an amount of 10 to 1,000 parts by weight compared to 100 parts by weight of monomers such as the organosilanes. Further, it is preferred that the water used for the hydrolysis reaction be added in an amount of 0.5 to 2 moles compared to 1 mole of hydrolyzable group.

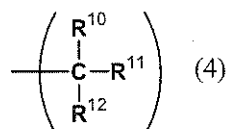
[0064] The catalyst added as required is not particularly restricted; however, an acid catalyst or a basic catalyst is preferably employed. Specific examples of the acid catalyst include hydrochloric acid, nitric acid, sulfuric acid, hydrofluoric acid, phosphoric acid, acetic acid, trifluoroacetic acid, formic acid, polycarboxylic acids and anhydrides thereof, and ion-exchange resins. Specific examples of the basic catalyst include triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, triheptylamine, trioctylamine, diethylamine, triethanolamine, diethanolamine, sodium hydroxide, potassium hydroxide, amino group-containing alkoxysilanes and ion-exchange resins. It is preferred that the catalyst be added in an amount of 0.01 to 10 parts by weight compared to 100 parts by weight of monomers such as the organosilanes.

[0065] Further, from the standpoint of storage stability of the composition, it is preferred that the polysiloxane solution after the hydrolysis and partial condensation do not contain the above-described catalyst, and the catalyst can be removed as required. The method of removing the catalyst is not particularly restricted; however, from the standpoints of operational simplicity and removability, the catalyst is preferably removed by washing with water and/or a treatment with an ion-exchange resin. The "washing with water" refers to a method in which, after diluting the polysiloxane solution with an appropriate hydrophobic solvent and washing the resultant with water several times, the resulting organic layer is concentrated using an evaporator or the like. The "treatment with an ion-exchange resin" refers to a method in which the polysiloxane solution is brought into contact

with an appropriate ion-exchange resin.

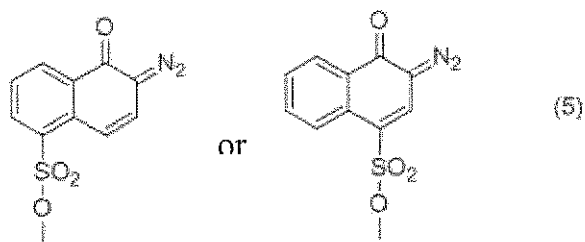
[0066] The positive photosensitive composition according to the present invention contains (B) a naphthoquinone diazide compound. The positive photosensitive composition containing the naphthoquinone diazide compound forms a positive-type film in which an exposed area is removed by a developer. The naphthoquinone diazide compound to be used is not particularly restricted; however, it is preferably a compound in which naphthoquinone diazide sulfonate is bound to a compound having a phenolic hydroxyl group through an ester bond, in which compound the ortho and para positions of the phenolic hydroxyl group are each independently hydrogen, a hydroxyl group or a substituent represented by the Formula (4) or (5).

[0067]



[0068] In the Formula (4), R^{10} , R^{11} and R^{12} each independently represent an alkyl group having 1 to 10 carbon atoms, a carboxyl group, a phenyl group or a substituted phenyl group. Further, R^{10} , R^{11} and R^{12} also optionally form a ring. The alkyl group is optionally either unsubstituted or substituted and can be selected in accordance with the properties of the composition. Specific examples of the alkyl group include methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, iso-butyl group, t-butyl group, n-hexyl group, cyclohexyl group, n-heptyl group, n-octyl group, trifluoromethyl group and 2-carboxyethyl group. Further, examples of a substituent on the phenyl group include hydroxyl group and methoxy group. Specific examples of the ring which is optionally formed by R^{10} , R^{11} and R^{12} include cyclopentane ring, cyclohexane ring, adamantane ring and fluorene ring.

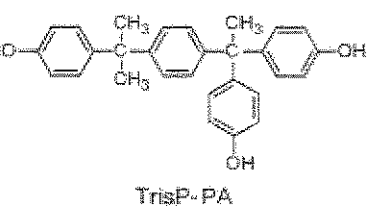
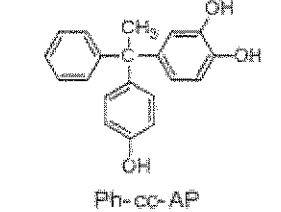
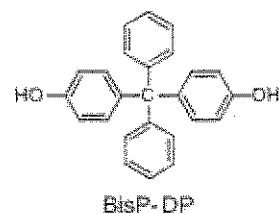
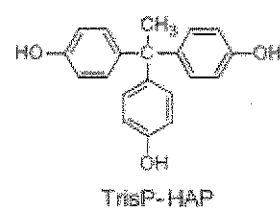
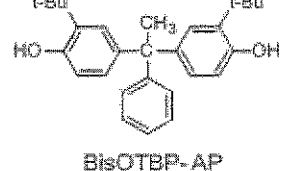
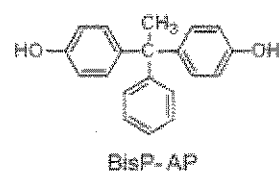
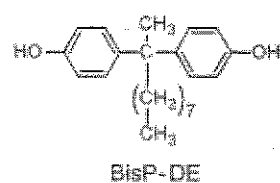
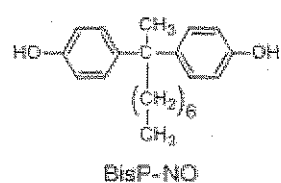
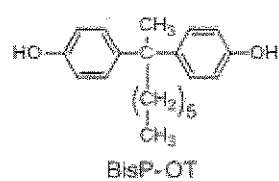
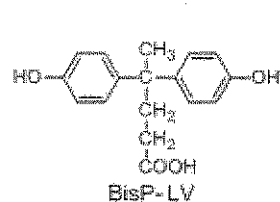
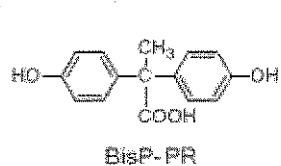
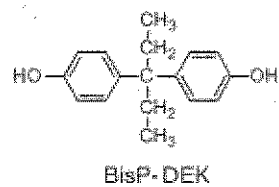
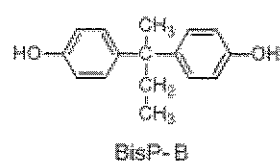
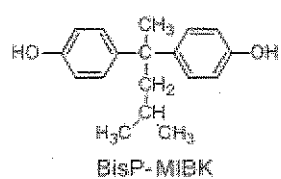
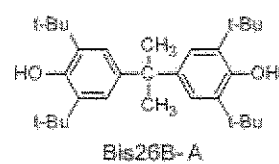
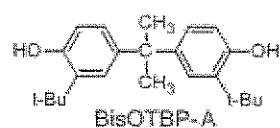
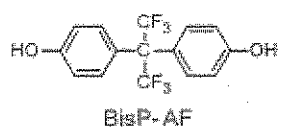
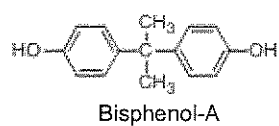
[0069]



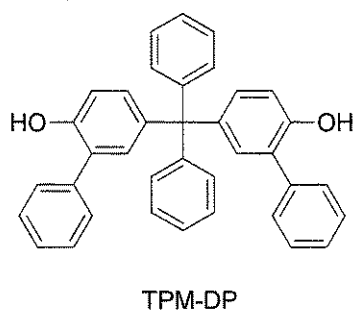
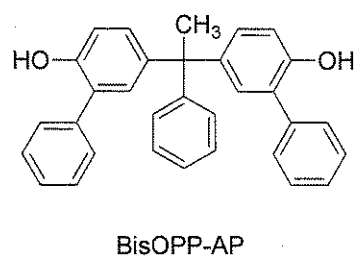
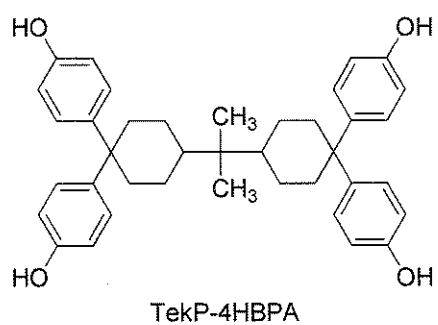
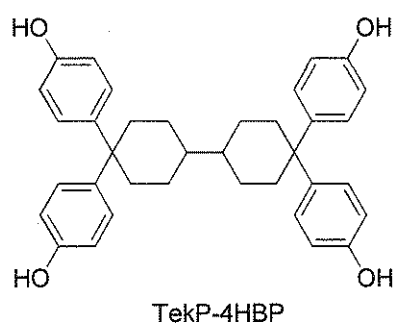
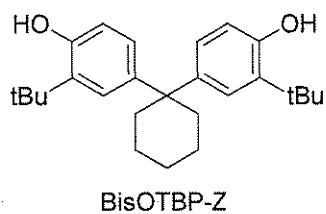
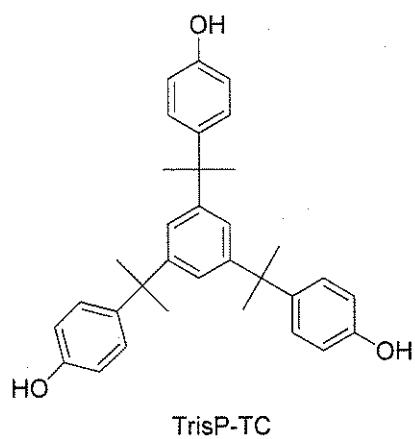
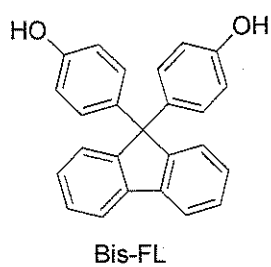
[0070] When the ortho and para positions of the phenolic hydroxyl group are each the above-described preferred substituent, since heat curing is not likely to cause oxidative decomposition and a conjugated compound characterized by a quinoid structure is not likely to be formed, the resulting cured film is not easily colored and maintains colorless and transparent properties. Here, these naphthoquinone diazide compounds can be synthesized by a known esterification reaction between the compound having a phenolic hydroxyl group and naphthoquinonediazidesulfonic acid chloride.

[0071] Specific examples of the compound having a phenolic hydroxyl group include the following compounds (all of which are manufactured by Honshu Chemical Industry Co., Ltd.).

[0072]



[0073]



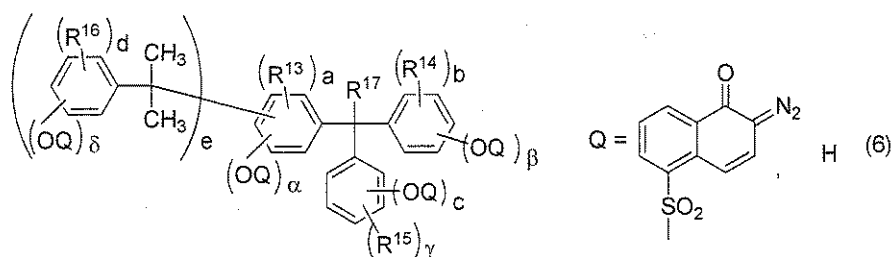
[0074] As the naphthoquinonediazidesulfonic acid chloride used as a starting material, 4-naphthoquinonediazidesulfonic acid chloride or 5-naphthoquinonediazidesulfonic acid chloride can be employed. A 4-

naphthoquinonediazidesulfonic ester compound is suitable for i-line exposure since it shows absorption in the i-line (wavelength: 365 nm) region. Further, a 5-naphthoquinonediazidesulfonic acid ester compound is suitable for exposure in a wide wavelength range since it shows absorption over a wide range of wavelengths.

It is preferred to select a 4-naphthoquinonediazidesulfonic ester compound or a 5-naphthoquinonediazidesulfonic ester compound in accordance with the wavelength used for exposure. A 4-naphthoquinonediazidesulfonic acid ester compound and a 5-naphthoquinonediazidesulfonic acid ester compound may also be used in combination.

[0075] Examples of the naphthoquinone diazide compound preferably used in the present invention include those compounds represented by the following Formula (6).

[0076]



[0077] In the Formula (6), R¹³, R¹⁴, R¹⁵ and R¹⁶ each represent hydrogen, an alkyl group, an alkoxy group, a carbonyl group or an ester group, in which groups the number of carbon atoms is selected from 1 to 8. R¹³, R¹⁴, R¹⁵ and R¹⁶ are optionally the same or different. R¹⁷ represents hydrogen, an alkyl group or an aryl group, in which groups the number of carbon atoms is selected from 1 to 8. Q represents either a 5-naphthoquinonediazidesulfonyl group or a hydrogen atom, with the proviso that not all of Qs is a hydrogen atom. The letters a, b, c, d, e, α, β, γ and δ each represent an integer of 0 to 4, with the proviso that α + β + γ + δ ≥ 2. By using the naphthoquinone diazide compound represented by the Formula (6), the sensitivity and resolution in pattern processing are improved.

[0078] The amount of the naphthoquinone diazide compound to be added is not particularly restricted; however, it is preferably 2 to 30 parts by weight, more preferably 3 to 15 parts by weight, compared to 100 parts by weight of the alkali-soluble resin.

5 [0079] When the added amount of the naphthoquinone diazide compound is in the above-described preferred range, the dissolution contrast between an exposed area and a non-exposed area is high enough to allow the composition to exhibit photosensitivity sufficient for practical use. Meanwhile, since the compatibility between the polysiloxane and the naphthoquinone diazide compound is not likely to be deteriorated, whitening of the resulting coating film does not occur and, since
10 coloring of the coating film, which is caused by decomposition of the quinone diazide compound, is not likely to occur, the resulting cured film maintains colorless and transparent properties. Further, in order to attain better dissolution contrast, the amount of the naphthoquinone diazide compound to be added is more preferably not less than 5 parts by weight. In order to obtain a film having higher transparency,
15 the amount of the naphthoquinone diazide compound to be added is more preferably not more than 20 parts by weight, particularly preferably not more than 15 parts by weight, most preferably not more than 10 parts by weight.

[0080] The positive photosensitive composition according to the present invention
20 contains (C) a solvent. The solvent to be used is not particularly restricted; however, a compound having an alcoholic hydroxyl group is preferably used. By using such solvent, the alkali-soluble resin and the quinone diazide compound are uniformly dissolved, so that even when the composition is applied to form a film, the film is not whitened and thus can achieve high transparency.

25 [0081] The above-described compound having an alcoholic hydroxyl group is not particularly restricted; however, it is preferably a compound having a boiling point of 110 to 250°C under atmospheric pressure. When the boiling point is in the above-

described preferred range, excessively fast drying does not occur during coating, so that the surface of the resulting film is not likely to be roughened and good coatability is thus attained, while since the amount of residual solvent in the film is small, film shrinkage during curing is limited and good planarization property can be attained.

[0082] Specific examples of the compound having an alcoholic hydroxyl group include acetol, 3-hydroxy-3-methyl-2-butanone, 4-hydroxy-3-methyl-2-butanone, 5-hydroxy-2-pentanone, 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol), ethyl lactate, butyl lactate, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-n-butyl ether, propylene glycol mono-t-butyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, 3-methoxy-1-butanol, and 3-methyl-3-methoxy-1-butanol. These compounds having an alcoholic hydroxyl group may be used individually, or two or more thereof may be used in combination.

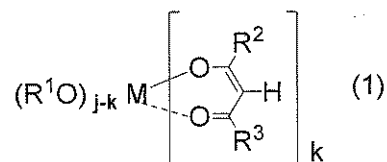
[0083] Further, the positive photosensitive composition according to the present invention may also contain other solvent(s) as long as the effects of the present invention are not adversely affected. Examples of other solvent include esters such as ethyl acetate, n-propyl acetate, iso-propyl acetate, n-butyl acetate, iso-butyl acetate, propylene glycol monomethyl ether acetate, 3-methoxy-1-butyl acetate, 3-methyl-3-methoxy-1-butyl acetate and ethyl acetoacetate; ketones such as methyl iso-butyl ketone, diiso-propyl ketone, diiso-butyl ketone and acetylacetone; ethers such as diethyl ether, diiso-propyl ether, di-n-butyl ether, diphenyl ether, diethylene glycol ethylmethyl ether and diethylene glycol dimethyl ether; γ -butyrolactone; γ -valerolactone; δ -valerolactone; propylene carbonate; N-methylpyrrolidone; cyclopentanone; cyclohexanone; and cycloheptanone.

[0084] The amount of the solvent to be added is not particularly restricted; however,

it is preferably in the range of 100 to 2,000 parts by weight compared to 100 parts by weight of the alkali-soluble resin.

[0085] The photosensitive composition according to the present invention contains (D) a metal chelate compound represented by the following Formula (1).

5 [0086]



[0087] In the metal chelate compound represented by the Formula (1), M is a metal atom; R^1 s, the same or different, each represent hydrogen, an alkyl group, an aryl group, an alkenyl group, or a substitution product thereof; R^2 and R^3 , the same or different, each represent hydrogen, an alkyl group, an aryl group, an alkenyl group, an alkoxy group, or a substitution product thereof; j represents the valency of the metal atom M; and k represents an integer of 0 to j.

15 [0088] By incorporating the above-described metal chelate compound used in the present invention, the adhesion in development and the wet-heat resistance of the resulting cured film are improved.

[0089] In the Formula (1), M is a metal atom and the metal atom is not particularly restricted. From the standpoint of transparency, examples of the metal atom include titanium, zirconium, aluminum, zinc, cobalt, molybdenum, lanthanum, barium, strontium, magnesium and calcium. From the standpoints of adhesion in development and wet-heat resistance, the metal atom is preferably zirconium or aluminum.

25 [0090] Examples of R^1 include methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decanyl group, octadecanyl group, phenyl group, vinyl group, allyl group and oleyl group. Thereamong, since the compound becomes stable, R^1

is preferably an n-propyl group, an n-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, an n-octyl group, an n-nonyl group, an n-decyl group, an n-octadecyl group or a phenyl group. Examples of R^2 and R^3 include hydrogen, methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, t-butyl group, phenyl group, vinyl group, methoxy group, ethoxy group, n-propoxy group, iso-propoxy group, n-butoxy group, sec-butoxy group, n-pentyl group, n-hexyl group, n-heptyl group, n-octyl group, n-nonyl group, n-decyl group, n-octadecyl group and benzoyloxy group. Thereamong, since the compound is easily synthesized and becomes stable, it is preferred that R^2 and R^3 be each a methyl group, a t-butyl group, a phenyl group, a methoxy group, an ethoxy group or an n-octadecyl group.

[0091] Examples of the compound represented by the Formula (1) include, as zirconium compounds, zirconium tetra-n-propoxide, zirconium tetra-n-butoxide, zirconium tetra-sec-butoxide, zirconium tetraphenoxide, zirconium tetraacetylacetonate, zirconium tetra(2,2,6,6-tetramethyl-3,5-heptanedionate), zirconium tetramethylacetoacetate, zirconium tetraethylacetoacetate, zirconium tetramethylmalonate, zirconium tetraethylmalonate, zirconium tetrabenzoylacetonate, zirconium tetradibenzoylmethanate, zirconium mono-n-butoxyacetylacetonate-bis(ethylacetoacetate), zirconium mono-n-butoxyethylacetoacetate-bis(acetylacetonate), zirconium mono-n-butoxy-tris(acetylacetonate), zirconium mono-n-butoxy-tris(acetylacetonate), zirconium di(n-butoxy)bis(ethylacetoacetate), zirconium di(n-butoxy)bis(acetylacetonate), zirconium di(n-butoxy)bis(ethylmalonate), zirconium di(n-butoxy)bis(benzoylacetonate) and zirconium di(n-butoxy)bis(dibenzoylmethanate).

[0092] Further, examples of the compound represented by the Formula (1) include, as aluminum compounds, aluminum tris-iso-propoxide, aluminum tris-n-propoxide, aluminum tris-sec-butoxide, aluminum tris-n-butoxide, aluminum trisphenoxide,

aluminum tris-acetylacetonate, aluminum tris(2,2,6,6-tetramethyl-3,5-heptanedionate), aluminum tris-ethylacetoacetate, aluminum tris-methylacetoacetate, aluminum tris-methylmalonate, aluminum tris-ethylmalonate, aluminum ethylacetate-di(iso-propoxide), aluminum (acetylacetonate)di(iso-propoxide),

5 aluminum methylacetoacetate-di(iso-propoxide), aluminum octadecylacetoacetate di(iso-propylate) and aluminum monoacetylacetonate-bis(ethylacetoacetate).

[0093] Further, examples of the compound represented by the Formula (1) include, as titanium compounds, titanium tetra-n-propoxide, titanium tetra-n-butoxide, titanium tetra-sec-butoxide, titanium tetraphenoxide, titanium tetraacetylacetonate,

10 titanium tetra(2,2,6,6-tetramethyl-3,5-heptanedionate), titanium tetramethylacetoacetate, titanium tetraethylacetoacetate, titanium tetramethylmalonate, titanium tetraethylmalonate, titanium tetrabenzoylacetonate, titanium tetradibenzoylmethanate, titanium mono-n-butoxyacetylacetonate-bis(ethylacetoacetate), titanium mono-n-butoxyethylacetoacetate-bis(acetylacetonate),

15 titanium mono-n-butoxy-tris(acetylacetonate), titanium mono-n-butoxy-tris(acetylacetonate), titanium di(n-butoxy)bis(ethylacetoacetate), titanium di(n-butoxy)bis(acetylacetonate), titanium di(n-butoxy)bis(ethylmalonate), titanium di(n-butoxy)bis(benzoylacetonate), titanium di(n-butoxy)bis(dibenzoylmethanate) and titanium tetra-2-ethylhexyloxide.

20 [0094] Among those compounds described in the above, from the standpoints of solubility to various solvents and/or stability of the compound, the metal chelate compound represented by the Formula (1) is preferably zirconium tetra-n-propoxide, zirconium tetra-n-butoxide, zirconium tetraphenoxide, zirconium tetraacetylacetonate, zirconium tetra(2,2,6,6-tetramethyl-3,5-heptanedionate), zirconium

25 tetramethylmalonate, zirconium tetraethylmalonate, zirconium tetraethylacetoacetate, zirconium di-n-butoxy-bis(ethylacetoacetate), zirconium mono-n-butoxyacetylacetonate-bis(ethylacetoacetate), titanium tetra-n-propoxide, titanium

tetra-n-butoxide, titanium tetraphenoxide, titanium tetraacetylacetonate, titanium tetra(2,2,6,6-tetramethyl-3,5-heptanedionate), titanium tetramethylmalonate, titanium tetraethylmalonate, titanium tetraethylacetoacetate, titanium di-n-butoxy-bis(ethylacetoacetate), titanium mono-n-butoxyacetylacetonate-bis(ethylacetoacetate),
5 aluminum tris-acetylacetonate, aluminum tris(2,2,6,6-tetramethyl-3,5-heptanedionate), aluminum tris-ethylacetoacetate, aluminum tris-methylacetoacetate, aluminum tris-methylmalonate, aluminum tris-ethylmalonate, aluminum ethylacetate-di(iso-propoxide), aluminum (acetylacetonate)di(iso-propoxide), aluminum methylacetoacetate-di(iso-propoxide), aluminum octadecylacetoacetate-di(iso-propylate) or aluminum monoacetylacetonate-bis(ethylacetoacetate). The
10 metal chelate compound represented by the Formula (1) is more preferably a metal complex system.

[0095] In the photosensitive composition according to the present invention, the content of the (D) metal chelate compound is 0.1 to 5 parts by weight compared to
15 100 parts by weight of the (A) alkali-soluble resin. When the content of the (D) metal chelate compound is less than 0.1 part by weight compared to 100 parts by weight of the (A) alkali-soluble resin, there are problems in that the wet-heat resistance and the adhesion in development are poor, while when the content is higher than 5 parts by weight compared to 100 parts by weight of the (A) alkali-soluble resin, there is a problem in that an non-exposed area which should dissolve in
20 a developer is not dissolved and the photosensitivity is thus impaired.

[0096] The content of the (D) metal chelate compound is preferably 0.3 to 4 parts by weight compared to 100 parts by weight of the (A) alkali-soluble resin. However, in cases where a metal having high catalytic activity is used, for example, when the
25 metal atom (M) is aluminum, the content of the (D) metal chelate compound is preferably 0.1 to 1.5 parts by weight, more preferably 0.3 to 1.0 parts by weight.

[0097] The content of the metal chelate compound can be identified and quantified

by performing a fluorescent X-ray analysis, a metal quantitative analysis by inductively-coupled plasma mass spectrometry (ICP-MS) or atomic absorption spectrometry, or an organic analysis by gas chromatography, liquid chromatography, ^1H -NMR and/or ^{13}C -NMR. Further, using the photosensitive composition and the resulting cured film, a metal such as titanium, zirconium, aluminum, zinc, cobalt, molybdenum, lanthanum, barium, strontium, magnesium or calcium can be analyzed by fluorescent X-ray analysis, inductively-coupled plasma mass spectrometry (ICP-MS) or atomic absorption spectrometry. The above-described metal is contained in an amount of 0.005 to 1 part by weight compared to 100 parts by weight of the alkali-soluble resin composition.

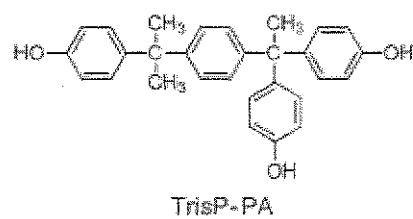
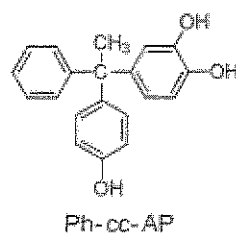
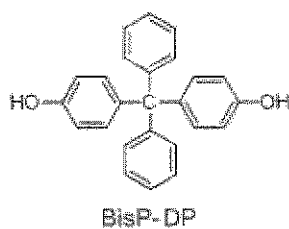
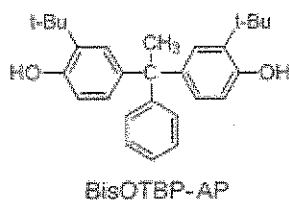
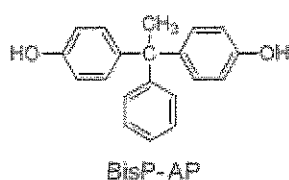
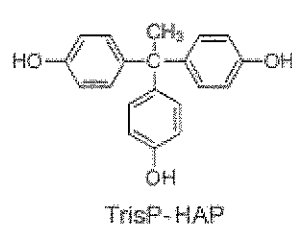
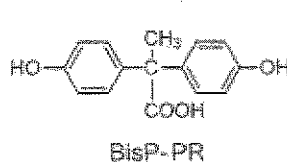
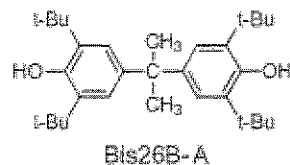
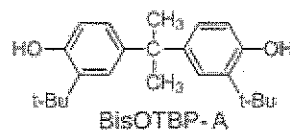
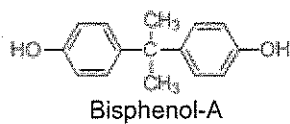
[0098] Further, the positive photosensitive composition according to the present invention may also contain, as required, an additive(s) such as a solubility accelerator, a silane coupling agent, a crosslinking agent, a crosslinking promoter, a sensitizer, a heat radical generator, a dissolution inhibitor, a surfactant, a stabilizer and an antifoaming agent.

[0099] In particular, in order to adjust the solubility in an alkaline developer, it is preferred that the positive photosensitive composition according to the present invention contain a solubility accelerator. Examples of the solubility accelerator include those phenol compounds that are described in the above as specific examples of the compound having a phenolic hydroxyl group; and N-hydroxyimide compounds. An example of the N-hydroxyimide compounds is N-hydroxy-5-norbornene-2,3-hydroxyimide.

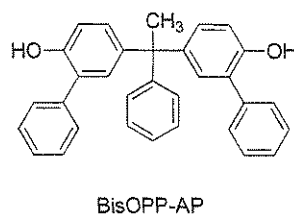
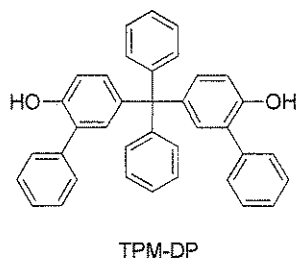
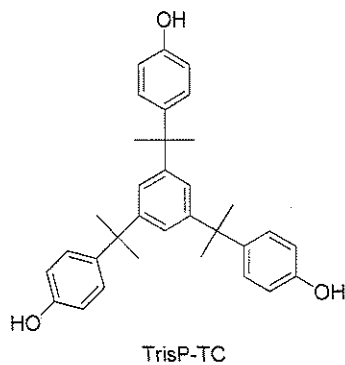
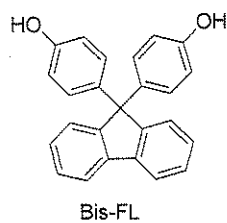
[0100] The phenolic compound is not particularly restricted; however, from the standpoint of transparency, it is preferably a phenol compound used as a starting material of the above-described naphthoquinone diazide compound. That is, a phenolic compound having 2 to 6 benzene rings and 2 to 4 phenolic hydroxyl groups in the molecule is preferred. Further, from the standpoints of heat resistance and

wet-heat resistance, a phenol compound containing no secondary carbon ($-\text{CH}_2-$), tertiary carbon ($-\text{CH}=\text{}$) and cycloalkane group is preferred. Examples of preferred phenol compound are shown below.

[0101]



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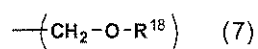


[0102] Surprisingly, by adding a phenol compound to the photosensitive composition according to the present invention, the wet-heat resistance thereof is dramatically improved. It is speculated that the wet-heat resistance is improved due to the hydrophobic barrier effect exerted by the packing property of aromatic rings of the phenol compound. The content of the phenol compound is preferably 1 to 30 parts by weight, more preferably 3 to 15 parts by weight, compared to 100 parts by weight of the alkali-soluble resin. When the content of the phenol compound is in the above-described preferred range compared to 100 parts by weight of the alkali-soluble resin, the effect of wet-heat resistance is sufficiently attained, while since the dissolution-promoting effect does not become excessively large, pattern formation is easily carried out.

[0103] It is also preferred that the positive photosensitive composition according to the present invention contain a crosslinking agent. A crosslinking agent is a compound which cross-links the alkali-soluble resin used in the present invention, a solubility accelerator and the like at the time of heat curing and is incorporated into the resin. By incorporating such crosslinking agent, the resulting cured film has a high degree of crosslinking. Consequently, the chemical resistance and the wet-heat resistance of the cured film are improved and a reduction in the pattern resolution caused by pattern reflow during heat curing is inhibited.

[0104] The crosslinking agent is not particularly restricted; however, preferred examples thereof include compounds having at least two structures selected from the group consisting of the methylol-based structure represented by the Formula (7), epoxy structure and oxetane structure. The combination of the above-described structures is not particularly restricted; however, the structures to be selected are preferably the same.

[0105]



[0106] In the methylol-based compound having at least two methylol-based structures represented by the Formula (7), R^{18} represents either hydrogen or an alkyl group having 1 to 10 carbon atoms. Here, plural R^{18} s in the compound are optionally the same or different. Specific examples of the alkyl group include methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, t-butyl group, n-hexyl group and n-decyl group.

[0107] Specific examples of the methylol-based compound having at least two methylol-based structures include, as ones having two methylol-based structures, DM-BI25X-F, 46DMOC, 46DMOIPP and 46DMOEP (all of which are trade names and manufactured by Asahi Organic Chemicals Industry Co., Ltd.); DML-MBPC, DML-MBOC, DML-OCHP, DML-PC, DML-PCHP, DML-PTBP, DML-34X, DML-EP, DML-POP, DML-OC, Dimethylol-Bis-C, Dimethylol-BisOC-P, DML-BisOC-Z, DML-BisOCHP-Z, DML-PFP, DML-PSBP, DML-MB25, DML-MTrisPC, DML-Bis25X-34XL and DML-Bis25X-PCHP (all of which are trade names and manufactured by Honshu Chemical Industry Co., Ltd.); NIKALAC MX-290 (trade name, manufactured by SANWA CHEMICAL Co., Ltd.); 2,6-dimethoxymethyl-4-t-butylphenol; 2,6-dimethoxymethyl-p-cresol; and 2,6-diacetoxymethyl-p-cresol.

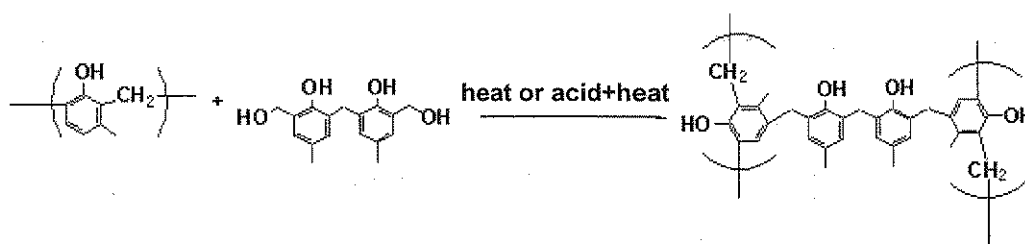
Further, specific examples of methylol-based compound having three methylol-based structures include TriML-P, TriML-35XL and TriML-TrisCR-HAP (all of which are trade names and manufactured by Honshu Chemical Industry Co., Ltd.), and specific examples of methylol-based compound having four methylol-based structures include TM-BIP-A (trade name, manufactured by Asahi Organic Chemicals Industry Co., Ltd.); TML-BP, TML-HQ, TML-pp-BPF, TML-BPA and TMOM-BP (all of which are trade names and manufactured by Honshu Chemical Industry Co., Ltd.); and NIKALAC MX-280 and NIKALAC MX-270 (both of which are trade names and manufactured by SANWA CHEMICAL Co., Ltd.). Specific examples of methylol-based compound having six methylol-based structures include HML-

TPPHBA, HML-TPHAP, HMOM-TPPHBA and HMOM-TPHAP (all of which are trade names and manufactured by Honshu Chemical Industry Co., Ltd.); and NIKALAC MW-390, NIKALAC MW-100LM and NIKALAC 30-HM (all of which are trade names and manufactured by SANWA CHEMICAL Co., Ltd.).

5 [0108] Thereamong, in the present invention, those compounds having at least two heat-crosslinkable groups are preferred, and particularly preferred examples thereof include ones having two heat-crosslinkable groups, such as 46DMOC, 46DMOEP, DML-MBPC, DML-MBOC, DML-OCHP, DML-PC, DML-PCHP, DML-PTBP, DML-34X, DML-EP, DML-POP, Dimethylol-BisOC-P, DML-PFP, DML-PSBP,
10 DML-MTrisPC, NIKALAC MX-290, B-a type benzooxazine, B-m type benzooxazine, 2,6-dimethoxymethyl-4-t-butylphenol, 2,6-dimethoxymethyl-p-cresol and 2,6-diacetoxymethyl-p-cresol; ones having three heat-crosslinkable groups, such as TriML-P and TriML-35XL; ones having four heat-crosslinkable groups, such as TM-BIP-A, TML-BP, TML-HQ, TML-pp-BPF, TML-BPA, TMOM-BP,
15 "NIKALAC" MX-280 and "NIKALAC" MX-270; and ones having six heat-crosslinkable groups, such as HML-TPPHBA, HML-TPHAP, HMOM-TPPHBA and HMOM-TPHAP. Further, more preferred examples include "NIKALAC" MX-280, "NIKALAC" MX-270, "NIKALAC" MW-100LM, "NIKALAC" MW-390 and "NIKALAC" 30HM (all of which are trade names and manufactured by SANWA
20 CHEMICAL Co., Ltd.).

[0109] Among these (e) crosslinking agents, for example, a compound having a methylol group in which a hydrogen atom of a methylol group or that of an alcoholic hydroxyl group is substituted is, as shown below, cross-linked by a reaction mechanism of direct addition to the benzene ring.

25 [0110]



[0111] The structures of representative heat crosslinkable compounds that are particularly preferably used in the photosensitive composition according to the present invention are shown below. Particularly surprisingly, by using a methanol-based compound and the above-described phenol compound in combination in the positive photosensitive composition according to the present invention, the wet-heat resistance of the resulting cured film is further dramatically improved.

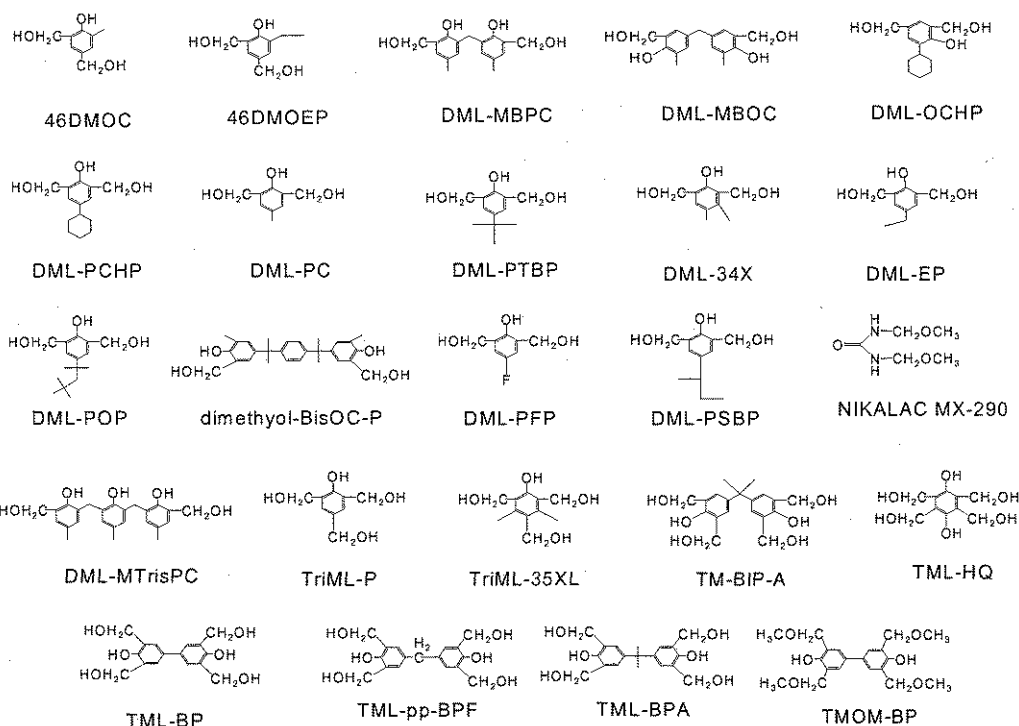
[0112]

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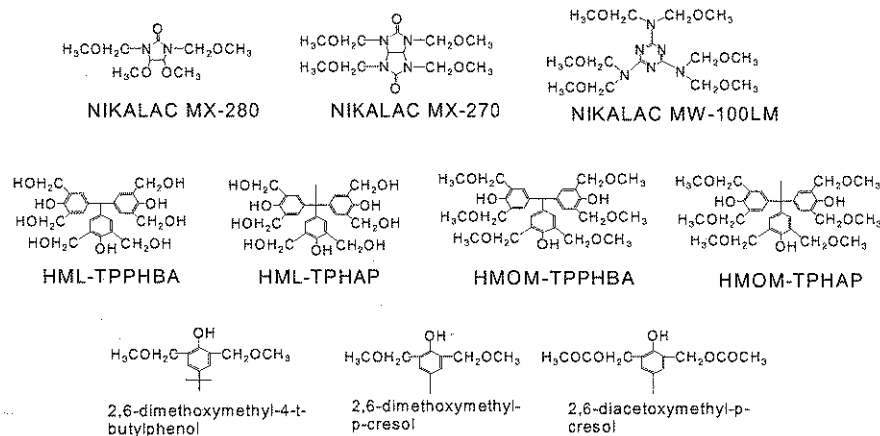
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[0113] Specific examples of the compounds having at least two epoxy structures or oxetane structures include "EPOLITE" 40E, "EPOLITE" 100E, "EPOLITE" 200E, "EPOLITE" 400E, "EPOLITE" 70P, "EPOLITE" 200P, "EPOLITE" 400P, "EPOLITE" 1500NP, "EPOLITE" 80MF, "EPOLITE" 4000 and "EPOLITE" 3002 (all of which are trade names and manufactured by Kyoeisha Chemical Co., Ltd.); "DENACOL" EX-212L, "DENACOL" EX-214L, "DENACOL" EX-216L, "DENACOL" EX-850L and "DENACOL" EX-321L (all of which are trade names and manufactured by Nagase ChemteX Corporation); GAN, GOT, EPPN 502H, NC

3000 and NC 6000 (all of which are trade names and manufactured by Nippon Kayaku Co., Ltd.); "EPICOAT" 828, "EPICOAT" 1002, "EPICOAT" 1750, "EPICOAT" 1007, YX8100-BH30, E1256, E4250 and E4275 (all of which are trade names and manufactured by Japan Epoxy Resins Co., Ltd.); "EPICLON" EXA-9583,
5 "EPICLON" HP4032, "EPICLON" N695 and "EPICLON" HP7200 (all of which are trade names and manufactured by DIC Corporation); "TEPIC" S, "TEPIC" G, and "TEPIC" P (all of which are trade names and manufactured by Nissan Chemical Industries, Ltd.); and "EPOTOHTO" YH-434L (trade name, manufactured by Tohto Kasei Co., Ltd.).

10 [0114] Here, the above-described crosslinking agents may be used individually, or two or more thereof may be used in combination.

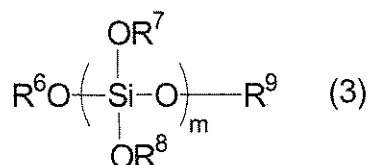
[0115] The amount of the crosslinking agent to be added is not particularly restricted; however, it is preferably in the range of 0.1 to 20 parts by weight compared to 100 parts by weight of the alkali-soluble resin. When the added
15 amount of the crosslinking agent is in the above-described preferred range, the crosslinking effect of the resin is sufficient, while the resulting cured film retains colorless and transparent properties and the composition attains excellent storage stability.

[0116] The positive photosensitive composition according to the present invention
20 may also contain a silane coupling agent. By incorporating a silane coupling agent, the adhesion of the composition with a substrate is improved.

[0117] Specific examples of the silane coupling agent include methyltrimethoxysilane, methyltriethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, n-
25 propyltrimethoxysilane, n-propyltriethoxysilane, n-butyltrimethoxysilane, n-butyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, vinyltrimethoxysilane,

vinyltriethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-methacryloxypropylmethyldiethoxysilane, 3-acryloxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-triethoxysilyl-N-(1,3-dimethyl-butylidene)propylamine, N-phenyl-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, 3-glycidoxypropylmethyldiethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, [(3-ethyl-3-oxetanyl)methoxy]propyltrimethoxysilane, [(3-ethyl-3-oxetanyl)methoxy]propyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-ureidopropyltriethoxysilane, 3-isocyanatepropyltriethoxysilane, 3-trimethoxysilylpropylsuccinic acid, N-t-butyl-3-(3-trimethoxysilylpropyl)succinimide and organosilanes represented by the Formula (3).

[0118]



[0119] (wherein, R⁶ to R⁹ each independently represent hydrogen, an alkyl group having 1 to 6 carbon atoms, an acyl group having 2 to 6 carbon atoms or an aryl group having 6 to 15 carbon atoms; and these alkyl group, acyl group and aryl group are all optionally substituted or unsubstituted).

Specific examples of the organosilane represented by the Formula (3) include tetramethoxysilane; tetraethoxysilane; tetra-n-propoxysilane; tetraiso-propoxysilane; tetra-n-butoxysilane; tetraacetoxysilane; METHYL SILICATE 51 (manufactured by FUSO Chemical Co., Ltd.); M SILICATE 51, SILICATE 40 and SILICATE 45 (which are manufactured by Tama Chemicals Co., Ltd.); and METHYL SILICATE

51, METHYL SILICATE 53A, ETHYL SILICATE 40 and ETHYL SILICATE 48
(which are manufactured by Colcoat Co., Ltd.).

[0120] The organosilane represented by the Formula (3) is preferably 2-(3,4-
epoxycyclohexyl)ethyltrimethoxysilane, 3-ureidopropyltriethoxysilane, N-t-butyl-3-
5 (3-trimethoxysilylpropyl)succinimide, tetramethoxysilane, tetraethoxysilane, tetra-n-
propoxysilane, tetraiso-propoxysilane, tetra-n-butoxysilane, tetraacetoxysilane,
METHYL SILICATE 51 (manufactured by FUSO Chemical Co., Ltd.), M
SILICATE 51, SILICATE 40, SILICATE 45 (manufactured by Tama Chemicals Co.,
Ltd.), METHYL SILICATE 51, METHYL SILICATE 53A, ETHYL SILICATE 40
10 or ETHYL SILICATE 48 (manufactured by Colcoat Co., Ltd.).

[0121] The amount of the silane coupling agent to be added is not particularly
restricted; however, it is preferably in the range of 0.1 to 10 parts by weight
compared to 100 parts by weight of the alkali-soluble resin. When the added
amount of the silane coupling agent is in the above-described preferred range,
15 sufficient adhesion-improving effect is attained, while since condensation reaction of
the silane coupling agent is not likely to occur during storage, the silane coupling
agent is not left undissolved at the time of development.

[0122] The positive photosensitive composition according to the present invention
may also contain a surfactant. By incorporating a surfactant, coating variation is
20 improved, so that a uniform coating film can be obtained. As the surfactant, a
fluorine-based surfactant or a silicone-based surfactant is preferably employed.

[0123] Specific examples of the fluorine-based surfactant include fluorine-based
surfactants that are composed of a compound having a fluoroalkyl or fluoroalkylene
group at least at any one part of the terminals, main chain and side chains, such as
25 1,1,2,2-tetrafluorooctyl(1,1,2,2-tetrafluoropropyl)ether, 1,1,2,2-tetrafluorooctylhexyl
ether, octaethylene glycol di(1,1,2,2-tetrafluorobutyl)ether, hexaethylene glycol
(1,1,2,2,3,3-hexafluoropentyl)ether, octapropylene glycol di(1,1,2,2-

tetrafluorobutyl)ether, hexapropylene glycol di(1,1,2,2,3,3-hexafluoropentyl)ether, sodium perfluorododecylsulfonate, 1,1,2,2,8,8,9,9,10,10-decafluorododecane, 1,1,2,2,3,3-hexafluorodecane, N-[3-(perfluorooctanesulfonamide)propyl]-N,N'-dimethyl-N-carboxymethylene-ammonium betaine, perfluoroalkylsulfonamide
5 propyltrimethylammonium salt, perfluoroalkyl-N-ethylsulfonylglycine salt, bis(N-perfluorooctylsulfonyl-N-ethylaminoethyl)phosphate and monoperfluoroalkyl ethylphosphoric acid ester. Further, examples of commercially available fluorine-based surfactants include "MEGAFAC" F142D, "MEGAFAC" F172, "MEGAFAC" F173, "MEGAFAC" F183, "MEGAFAC" F444, "MEGAFAC" 445, "MEGAFAC" F475 and "MEGAFAC" 477 (all of which are manufactured by DIC Corporation);
10 "EFTOP" EF301, "EFTOP" 303 and "EFTOP" 352 (all of which are manufactured by Shin-Akita Kasei K.K.); "FLUORAD" FC-430 and "FLUORAD" FC-431 (both of which are manufactured by Sumitomo 3M Ltd.); "ASAHI GUARD" AG710, "SURFLON" S-382, "SURFLON" SC-101, "SURFLON" SC-102, "SURFLON" SC-103, "SURFLON" SC-104, "SURFLON" SC-105 and "SURFLON" SC-106 (all of which are manufactured by Asahi Glass Co., Ltd.); BM-1000 and BM-1100 (both of which are manufactured by Yusho Co., Ltd.); and NBX-15, FTX-218 and DFX-218 (all of which are manufactured by NEOS Co., Ltd.).

[0124] Examples of commercially available silicone-based surfactants include
20 SH28PA, SH7PA, SH21PA, SH30PA and SH94PA (all of which are manufactured by Dow Corning Toray Silicone Co., Ltd.); and BYK-333 (BYK Japan K.K.).

[0125] It is generally preferred that the photosensitive composition contain the surfactant in an amount of 0.0001 to 1% by weight.

[0126] The positive photosensitive composition according to the present invention
25 may also contain a crosslinking promoter. A crosslinking promoter is a compound which promotes crosslinking of the alkali-soluble resin during heat curing and, as the crosslinking promoter, a thermal acid generator which generates an acid during heat

curing or a photoacid generator which generates an acid at the time of bleaching exposure performed prior to heat curing is employed. By allowing an acid to exist in the film at the time of heat curing, condensation reaction of unreacted silanol group and epoxy group in the alkali-soluble resin is promoted, so that the resulting cured film attains a high degree of crosslinking. Consequently, the chemical resistance of the cured film is improved and a reduction in the pattern resolution caused by pattern reflow during heat curing is inhibited.

[0127] The thermal acid generator preferably used in the present invention is a compound which generates an acid during heat curing and it is preferred that the thermal acid generator do not generate an acid or generate only a small amount of an acid during prebaking performed after application of the composition. Therefore, the thermal acid generator is preferably a compound which generates an acid at a prebaking temperature or higher, for example, at 100°C or higher. When such a compound which generates an acid at a prebaking temperature or higher is employed, since crosslinking of the alkali-soluble resin does not take place during prebaking, the sensitivity of the composition is not impaired and the composition is not left undissolved at the time of development.

[0128] Specific examples of the thermal acid generator which is preferably used include "SAN-AID" SI-60, SI-80, SI-100, SI-200, SI-110, SI-145, SI-150, SI-60L, SI-80L, SI-100L, SI-110L, SI-145L, SI-150L, SI-160L and SI-180L (all of which are trade names and manufactured by SANSHIN CHEMICAL INDUSTRY Co.,Ltd.); and 4-hydroxyphenyldimethylsulfonium trifluoromethanesulfonate, benzyl-4-hydroxyphenylmethylsulfonium trifluoromethanesulfonate, 2-methylbenzyl-4-hydroxyphenylmethylsulfonium trifluoromethanesulfonate, 4-acetoxyphenyldimethylsulfonium trifluoromethanesulfonate, 4-acetoxyphenylbenzylmethylsulfonium trifluoromethanesulfonate, 4-methoxycarbonyloxyphenyldimethylsulfonium trifluoromethanesulfonate and

benzyl-4-methoxycarbonyloxyphenylmethysulfonium trifluoromethanesulfonate (all of which are manufactured by SANSHIN CHEMICAL INDUSTRY Co.,Ltd.).

These compounds may be used individually, or two or more thereof may be used in combination.

5 [0129] The photoacid generator preferably used in the present invention is a compound which generates an acid at the time of bleaching exposure, that is, a compound which generates an acid upon being irradiated at an exposure wavelength of 365 nm (i-line), 405 nm (h-line) or 436 nm (g-line) or with a mixed light thereof. Therefore, although it is possible that an acid is also generated during pattern
10 exposure where the same light source is used, since the amount of exposure in the pattern exposure is smaller than that in the bleaching exposure, only a small amount of acid is generated and this presents no problem. Further, the acid to be generated is preferably a strong acid such as perfluoroalkylsulfonic acid or p-toluenesulfonic acid. A quinone diazide compound which generates a carboxylic acid does not
15 have such a function of a photoacid generator described in the above and, therefore, does not function as a crosslinking promoter in the present invention.

[0130] Specific examples of the photoacid generator which is preferably used include SI-100, SI-101, SI-105, SI-106, SI-109, PI-105, PI-106, PI-109, NAI-100, NAI-1002, NAI-1003, NAI-1004, NAI-101, NAI-105, NAI-106, NAI-109, NDI-101,
20 NDI-105, NDI-106, NDI-109, PAI-01, PAI-101, PAI-106 and PAI-1001 (all of which are trade names and manufactured by Midori Kagaku Co., Ltd.); SP-077 and SP-082 (both of which are trade names and manufactured by ADEKA Corporation); TPS-PFBS (trade name, manufactured by Toyo Gosei Co., Ltd.); CGI-MDT and CGI-NIT (both of which are trade names and manufactured by Ciba Specialty
25 Chemicals Co., Ltd.); and WPAG-281, WPAG-336, WPAG-339, WPAG-342, WPAG-344, WPAG-350, WPAG-370, WPAG-372, WPAG-449, WPAG-469, WPAG-505 and WPAG-506 (all of which are trade names and manufactured by

Wako Pure Chemical Industries, Ltd.). These compounds may be used individually, or two or more thereof may be used in combination.

[0131] Further, as the crosslinking promoter, the above-described thermal acid generator and photoacid generator can also be used in combination. The amount of the crosslinking promoter to be added is not particularly restricted; however, it is preferably in the range of 0.01 to 5 parts by weight compared to 100 parts by weight of the alkali-soluble resin. When the amount is in the above-described preferred range, sufficient crosslinking-promoting effect is attained, while crosslinking of the polysiloxane is not likely to occur during prebaking and pattern exposure.

[0132] The positive photosensitive composition according to the present invention may also contain a sensitizer. By incorporating a sensitizer, since the reaction of the naphthoquinone diazide compound used as a photosensitizer is promoted, the sensitivity of the composition is improved. Further, when the composition contains a photoacid generator as a crosslinking promoter, reactions in bleaching exposure are promoted, so that the solvent resistance and the pattern resolution of the resulting cured film are improved.

[0133] The sensitizer used in the present invention is not particularly restricted; however, it is preferably a sensitizer which is vaporized by a heat treatment and/or a sensitizer which is discolored by light irradiation. The sensitizer is required to show absorption at a wavelength of 365 nm (i-line), 405 nm (h-line) or 436 nm (g-line), which is the wavelength of light emitted from a light source used in pattern exposure or beaching exposure; however, if the sensitizer showing such absorption remains intact in the resulting cured film, since the cured film acquires absorption in the visible wavelength region, the colorless and transparent properties of the cured film may be deteriorated. Therefore, in order to prevent such deterioration of the colorless and transparent properties caused by the sensitizer, the sensitizer to be used is preferably a compound (sensitizer) which is vaporized by a heat treatment such as

heat curing and/or a compound (sensitizer) which is discolored by light irradiation such as bleaching exposure.

[0134] Specific examples of the above-described sensitizer which is vaporized by a heat treatment and/or sensitizer which is discolored by light irradiation include coumarins such as 3,3'-carbonylbis(diethylaminocoumarin); anthraquinones such as 9,10-anthraquinone; aromatic ketones such as benzophenone, 4,4'-dimethoxybenzophenone, acetophenone, 4-methoxyacetophenone and benzaldehyde; and condensed aromatics such as biphenyl, 1,4-dimethylnaphthalene, 9-fluorenone, fluorene, phenanthrene, triphenylene, pyrene, anthracene, 9-phenylanthracene, 9-methoxyanthracene, 9,10-diphenylanthracene, 9,10-bis(4-methoxyphenyl)anthracene, 9,10-bis(triphenylsilyl)anthracene, 9,10-dimethoxyanthracene, 9,10-diethoxyanthracene, 9,10-dipropoxyanthracene, 9,10-dibutoxyanthracene, 9,10-dipentaoxyanthracene, 2-t-butyl-9,10-dibutoxyanthracene and 9,10-bis(trimethylsilylethynyl)anthracene.

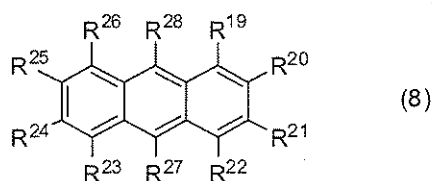
[0135] Among these sensitizers, the sensitizer which is vaporized by a heat treatment is preferably a sensitizer whose thermal decomposition product generated by sublimation, evaporation and/or thermal decomposition is sublimated or evaporated by a heat treatment. Further, the vaporization temperature of the sensitizer is preferably 130°C to 400°C. When the vaporization temperature of the sensitizer is in the above-described preferred range, since the sensitizer remains to be present in the exposure process without being vaporized during prebaking, the sensitivity of the composition can be maintained at a high level. Meanwhile, since the sensitizer is vaporized during heat curing and does not remain in the resulting cured film, the cured film can retain the colorless and transparent properties. In order to prevent the sensitizer from being vaporized during prebaking as much as possible, the vaporization temperature of the sensitizer is more preferably not lower than 150°C. Further, in order to allow the sensitizer to be sufficiently vaporized during heat

curing, the vaporization temperature of the sensitizer is more preferably not higher than 250°C.

[0136] Meanwhile, from the standpoint of transparency, the sensitizer which is discolored by light irradiation is preferably a sensitizer whose absorption in the visible wavelength region is reduced by light irradiation. Further, a more preferred compound which is discolored by light irradiation is a compound which is dimerized by light irradiation. By dimerizing such a compound by light irradiation, since the molecular weight thereof is increased and the compound becomes insolubilized, effects of improving the chemical resistance and heat resistance and reducing the amount of extracts from the resulting transparent cured film can be attained.

[0137] Further, the sensitizer is preferably an anthracene-based compound since a high sensitivity can be attained and the compound is dimerized and discolored by light irradiation. The sensitizer is more preferably a 9,10-disubstituted anthracene-based compound since it is thermally stable. Moreover, from the standpoints of improvement in the solubility of the sensitizer and the reactivity in photodimerization reaction, the sensitizer is still more preferably a 9,10-dialkoxyanthracene-based compound represented by the Formula (8).

[0138]



[0139] In the Formula (8), R¹⁹ to R²⁶ each independently represent hydrogen, an alkyl group, an alkoxy group, an alkenyl group, an aryl group or an acyl group, which has 1 to 20 carbon atoms, or an organic group obtained by substitution of these groups. Specific examples of the alkyl group include methyl group, ethyl group and n-propyl group. Specific examples of the alkoxy group include methoxy group, ethoxy group, propoxy group, butoxy group and pentyloxy group. Specific

examples of the alkenyl group include vinyl group, acryloxypropyl group and methacryloxypropyl group. Specific examples of the aryl group include phenyl group, tolyl group and naphthyl group. Specific examples of the acyl group include acetyl group. From the standpoints of vaporizability of the compound and reactivity in photodimerization, R¹⁹ to R²⁶ are preferably hydrogen or an organic group having 1 to 6 carbon atoms. It is more preferred that R¹⁹, R²², R²³ and R²⁶ be hydrogen.

[0140] In the Formula (8), R²⁷ and R²⁸ each represent an alkoxy group having 1 to 20 carbon atoms or an organic group obtained by substitution thereof. Specific examples of the alkoxy group include methoxy group, ethoxy group, propoxy group, butoxy group and pentyloxy group; however, from the standpoints of solubility of the compound and discoloration reaction by photodimerization, the alkoxy group is preferably a propoxy group or a butoxy group.

[0141] The amount of the sensitizer to be added is not particularly restricted; however, it is preferably in the range of 0.01 to 5 parts by weight compared to 100 parts by weight of the alkali-soluble resin. When the added amount of the sensitizer is in the above-described preferred range, the transparency and the sensitivity are not deteriorated.

[0142] A method forming a cured film using the positive photosensitive composition according to the present invention will now be described. The positive photosensitive composition according to the present invention is coated onto a base substrate by a known method such as a spinner or a slit and the resultant is then prebaked using a heating apparatus such as a hot plate or an oven. It is preferred that this prebaking be performed at a temperature of 50 to 150°C for 30 seconds to 30 minutes so as to form a film having a thickness of 0.1 to 15 μm.

[0143] After the completion of prebaking, using an ultraviolet-visible light exposure machine such as a stepper, a mirror projection mask aligner (MPA) or a parallel-light

mask aligner (PLA), the thus obtained film is exposed through a desired mask at about 10 to 4,000 J/m² (based on the exposure dose at a wavelength of 365 nm) to form a pattern.

[0144] After the exposure, the resulting exposed area can be dissolved by
5 development to obtain a positive pattern. As a development method, it is preferred to immerse the film in a developer for 5 seconds to 10 minutes by a method such as showering, dipping or paddling. As the developer, a known alkaline developer can be employed. Specific examples thereof include aqueous solutions containing one or more of inorganic alkalis such as hydroxide, carbonate, phosphate, silicate and
10 borate of alkali metals, amines such as 2-diethylaminoethanol, monoethanolamine, and diethanolamine, and quaternary ammonium salts such as tetramethylammonium hydroxide and choline. Further, after the development, the resulting film is preferably rinsed with water and, as required, the film can also be dehydrated and dried by baking at a temperature of 50 to 150°C using a heating apparatus such as a
15 hot plate or an oven.

[0145] Thereafter, the film is preferably subjected to bleaching exposure. By performing bleaching exposure, the unreacted naphthoquinone diazide compound remaining in the film is photo-decomposed, so that the optical transparency of the film is further improved. As a method of the bleaching exposure, the entire surface
20 of the film is exposed at about 100 to 20,000 J/m² (based on the exposure dose at a wavelength of 365 nm) using an ultraviolet-visible light exposure machine such as a PLA.

[0146] The film subjected to the bleaching exposure is, as required, soft-baked at a temperature of 50 to 150°C for 30 seconds to 30 minutes using a heating apparatus
25 such as a hot plate or an oven. Then, by curing the thus soft-baked film at a temperature of 150 to 450°C for about 1 hour using a heating apparatus such as a hot plate or an oven, a cured film used as a planarization film for a TFT of a display

device, an interlayer insulation film of a semiconductor element or a core or clad material of an optical waveguide is prepared.

[0147] In the cured film prepared by using the positive photosensitive composition of the present invention, the light transmittance per film thickness of 3 μm at a wavelength of 400 nm is not less than 85%, more preferably not less than 90%. If the light transmittance is less than 85%, when the cured film is used as a planarization film for a TFT substrate of a liquid crystal display device, the color of the film is changed when the backlight passes therethrough, making the white display to be tinged with yellow.

[0148] The above-described transmittance per film thickness of 3 μm at a wavelength of 400 nm can be determined by the following method. The composition is spin-coated onto a TEMPAX glass plate using a spin coater at an arbitrary rotation speed and the resultant is prebaked at 100°C for 2 minutes using a hot plate. Then, for the purpose of performing bleaching exposure, the entire surface of the resulting film is exposed to an ultra-high-pressure mercury lamp at 3,000 J/m² (based on the exposure dose at a wavelength of 365 nm) using a PLA. The thus exposed film is subsequently cured in the air at 220°C for 1 hour using an oven to prepare a cured film having a thickness of 3 μm . Using Multi Spec-1500 manufactured by SHIMADZU Corporation, the ultraviolet and visible absorption spectra of the thus obtained cured film are measured to determine the transmittance at a wavelength of 400 nm.

[0149] This cured film is suitably used as a planarization film for a TFT of a display element, an interlayer insulation film of a semiconductor element, an insulation film or protective film for a touch panel, or a core or clad material of an optical waveguide.

[0150] The element according to the present invention refers to a display device, a semiconductor element or an optical waveguide material, which comprises the

above-described cured film having excellent heat resistance and high transparency. In particular, the element according to the present invention is suitable for a liquid crystal display device, an organic EL display device and a display device equipped with a touch panel, in which the cured film is used as a planarization film for TFT.

5 EXAMPLES

[0151] The present invention will now be described more concretely by way of examples thereof; however, the present invention is not restricted to the following examples. Here, among those compounds that were used, ones that are abbreviated are listed below.

10 [0152] DAA: diacetone alcohol

PGMEA: propylene glycol monomethyl ether acetate

GBL: γ -butyrolactone

EDM: diethylene glycol methylethyl ether

DPM: dipropylene glycol monomethyl ether

15 [0153] Further, the solids concentration of a polysiloxane solution and an acrylic resin solution and the weight-average molecular weight (M_w) of polysiloxane and acrylic resin were determined as follows.

(1) Solids concentration

In an aluminum cup, 1 g of a polysiloxane solution or an acrylic resin solution
20 was weighed and heated at 250°C for 30 minutes by using a hot plate to evaporate the liquid content. Then, the solid content remaining in the aluminum cup after the heating was weighed to determine the solids concentration of the polysiloxane solution or the acrylic resin solution.

(2) Weight-average molecular weight

25 The weight-average molecular weight was determined by GPC (Model 410 RI detector, manufactured by Waters; mobile phase: tetrahydrofuran) based on polystyrene.

(3) Ratio of organosilane structures represented by the Formulae (2) and (3) in polysiloxane

²⁹Si-NMR was measured and, from the overall integral value, the proportions of the integral values corresponding to the respective organosilanes were calculated to determine the ratio of the organosilanes.

[0154] A sample (liquid) was injected into a Teflon (registered trademark) NMR sample tube of 10 mm in diameter and used for measurement. The ²⁹Si-NMR measurement conditions are shown below:

Apparatus: JNM GX-270 manufactured by JEOL Ltd.

Measurement method: gated decoupling method

Measurement nucleus frequency: 53.6693 MHz (²⁹Si nucleus)

Spectrum width: 20,000 Hz

Pulse width: 12 μsec (45° pulse)

Pulse repetition time: 30.0 seconds

Solvent: acetone-D6

Reference material: tetramethylsilane

Measurement temperature: room temperature

Sample rotation speed: 0.0 Hz.

Synthesis Example 1: Synthesis of Polysiloxane Solution (A1-a)

To a 500-mL three-necked flask, 81.72 g (0.60 mol) of methyltrimethoxysilane, 59.49 g (0.30 mol) of phenyltrimethoxysilane, 24.64 g (0.10 mol) of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and 163.1 g of DAA were loaded. Then, to the resulting mixture, an aqueous phosphoric acid solution containing 0.54 g (0.3% by weight compared to the loaded monomer) of phosphoric acid dissolved in 55.8 g of water was added over a period of 10 minutes while stirring the mixture at room temperature. After immersing the flask in a 40°C oil bath and stirring the resulting solution for 30 minutes, the oil bath was heated to

115°C over a period of 30 minutes. The inner temperature of the solution reached 100°C one hour after the start of the heating. From this point, the solution was heated with stirring for 1.5 hours (the inner temperature was 100 to 110°C) to obtain a polysiloxane solution (A1-a). It is noted here that the heating and stirring were
5 performed under nitrogen flow at a rate of 0.05 L (liter)/min. During the reaction, methanol and water, which were by-products, were distilled out in a total amount of 131 g.

[0155] The thus obtained polysiloxane solution (A1-a) had a solids concentration of 43% by weight and the polysiloxane had a weight-average molecular weight of 4,200.
10 Further, the content ratio of phenyl group-substituted silane in the polysiloxane was 30% in terms of molar ratio of Si atom.

Synthesis Example 2: Synthesis of Polysiloxane Solution (A1-b)

To a 500-mL three-necked flask, 54.48 g (0.40mol) of methyltrimethoxysilane, 99.15 g (0.50 mol) of phenyltrimethoxysilane, 24.64 g (0.1
15 mol) of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and 179.5 g of DAA were loaded. Then, to the resulting mixture, an aqueous phosphoric acid solution containing 0.54 g (0.3% by weight compared to the loaded monomer) of phosphoric acid dissolved in 55.8 g of water was added over a period of 10 minutes while stirring the mixture at room temperature. After immersing the flask in a 40°C oil
20 bath and stirring the resulting solution for 30 minutes, the oil bath was heated to 115°C over a period of 30 minutes. The inner temperature of the solution reached 100°C one hour after the start of the heating. From this point, the solution was heated with stirring for 2 hours (the inner temperature was 100 to 110°C) to obtain a polysiloxane solution (A1-b). It is noted here that the heating and stirring were
25 performed under nitrogen flow at a rate of 0.05 L (liter)/min. During the reaction, methanol and water, which were by-products, were distilled out in a total amount of 121 g.

[0156] The thus obtained polysiloxane solution (A1-b) had a solids concentration of 42% by weight and the polysiloxane had a weight-average molecular weight of 3,200. Further, the content ratio of phenyl group-substituted silane in the polysiloxane was 50% in terms of molar ratio of Si atom.

5 Synthesis Example 3: Synthesis of Polysiloxane Solution (A1-c)

To a 500-mL three-necked flask, 27.24 g (0.20mol) of methyltrimethoxysilane, 138.81 g (0.70mol) of phenyltrimethoxysilane, 24.64 g (0.1 mol) of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and 195.89 g of DAA were loaded. Then, to the resulting mixture, an aqueous phosphoric acid solution
10 containing 0.54 g (0.3% by weight compared to the loaded monomer) of phosphoric acid dissolved in 55.8 g of water was added over a period of 10 minutes while stirring the mixture at room temperature. After immersing the flask in a 40°C oil bath and stirring the resulting solution for 30 minutes, the oil bath was heated to 115°C over a period of 30 minutes. The inner temperature of the solution reached
15 100°C one hour after the start of the heating. From this point, the solution was heated with stirring for 3 hours (the inner temperature was 100 to 110°C) to obtain a polysiloxane solution (A1-c). It is noted here that the heating and stirring were performed under nitrogen flow at a rate of 0.05 L (liter)/min. During the reaction, methanol and water, which were by-products, were distilled out in a total amount of
20 125 g.

[0157] The thus obtained polysiloxane solution (A1-c) had a solids concentration of 41% by weight and the polysiloxane had a weight-average molecular weight of 3,000. Further, the content ratio of phenyl group-substituted silane in the polysiloxane was 70% in terms of molar ratio of Si atom.

25 Synthesis Example 4: Synthesis of Polysiloxane Solution (A1-d)

To a 500-mL three-necked flask, 40.86 g (0.30 mol) of methyltrimethoxysilane, 99.15 g (0.5 mol) of phenyltrimethoxysilane, 12.32 g (0.05

mol) of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 17.63 g (0.15 mol) of M
SILICATE 51 (manufactured by Tama Chemicals Co., Ltd.) and 170.77 g of
PGMEA were loaded. Then, to the resulting mixture, an aqueous phosphoric acid
solution containing 0.51 g (0.3% by weight compared to the loaded monomer) of
5 phosphoric acid dissolved in 53.55 g of water was added over a period of 10 minutes
while stirring the mixture at room temperature. After immersing the flask in a 40°C
oil bath and stirring the resulting solution for 30 minutes, the oil bath was heated to
115°C over a period of 30 minutes. The inner temperature of the solution reached
100°C one hour after the start of the heating. From this point, the solution was
10 heated with stirring for 2 hours (the inner temperature was 100 to 110°C) to obtain a
polysiloxane solution (A1-d). It is noted here that the heating and stirring were
performed under nitrogen flow at a rate of 0.05 L (liter)/min. During the reaction,
methanol and water, which were by-products, were distilled out in a total amount of
125 g.

15 [0158] The thus obtained polysiloxane solution (A1-d) had a solids concentration of
43% by weight and the polysiloxane had a weight-average molecular weight of 8,500.
Further, the content ratio of phenyl group-substituted silane in the polysiloxane was
50% in terms of molar ratio of Si atom.

Synthesis Example 5: Synthesis of Polysiloxane Solution (A1-e)

20 To a 500-mL three-necked flask, 24.52 g (0.18 mol) of
methyltrimethoxysilane, 118.98 g (0.60 mol) of phenyltrimethoxysilane, 14.78 g
(0.06 mol) of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 42.30 g (0.36 mol) of
M SILICATE 51 (manufactured by Tama Chemicals Co., Ltd.) and 181.89 g of
PGMEA were loaded. Then, to the resulting mixture, an aqueous phosphoric acid
25 solution containing 0.60 g (0.3% by weight compared to the loaded monomer) of
phosphoric acid dissolved in 62.64 g of water was added over a period of 10 minutes
while stirring the mixture at room temperature. After immersing the flask in a 40°C

oil bath and stirring the resulting solution for 30 minutes, the oil bath was heated to 115°C over a period of 30 minutes. The inner temperature of the solution reached 100°C one hour after the start of the heating. From this point, the solution was heated with stirring for 2 hours (the inner temperature was 100 to 110°C) to obtain a polysiloxane solution (A1-e). It is noted here that the heating and stirring were performed under nitrogen flow at a rate of 0.05 L (liter)/min. During the reaction, methanol and water, which were by-products, were distilled out in a total amount of 150 g.

[0159] The thus obtained polysiloxane solution (A1-e) had a solids concentration of 44% by weight and the polysiloxane had a weight-average molecular weight of 11,400. Further, the content ratio of phenyl group-substituted silane in the polysiloxane was 50% in terms of molar ratio of Si atom.

Synthesis Example 6: Synthesis of Polysiloxane Solution (A1-f)

To a 500-mL three-necked flask, 40.86 g (0.30 mol) of methyltrimethoxysilane, 99.15 g (0.50 mol) of phenyltrimethoxysilane, 49.28 g (0.20 mol) of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and 173.02 g of PGMEA were loaded. Then, to the resulting mixture, an aqueous phosphoric acid solution containing 0.57 g (0.3% by weight compared to the loaded monomer) of phosphoric acid dissolved in 57.60 g of water was added over a period of 10 minutes while stirring the mixture at room temperature. After immersing the flask in a 40°C oil bath and stirring the resulting solution for 30 minutes, the oil bath was heated to 115°C over a period of 30 minutes. The inner temperature of the solution reached 100°C one hour after the start of the heating. From this point, the solution was heated with stirring for 2 hours (the inner temperature was 100 to 110°C) to obtain a polysiloxane solution (A1-f). It is noted here that the heating and stirring were performed under nitrogen flow at a rate of 0.05 L (liter)/min. During the reaction, methanol and water, which were by-products, were distilled out in a total amount of

139 g.

[0160] The thus obtained polysiloxane solution (A1-f) had a solids concentration of 43% by weight and the polysiloxane had a weight-average molecular weight of 8,000. Further, the content ratio of phenyl group-substituted silane in the polysiloxane was 50% in terms of molar ratio of Si atom.

Synthesis Example 7: Synthesis of Polysiloxane Solution (A1-g)

To a 500-mL three-necked flask, 20.43 g (0.15 mol) of methyltrimethoxysilane, 99.15 g (0.50 mol) of phenyltrimethoxysilane, 49.28 g (0.20 mol) of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 17.63 g (0.15 mol) of M
10 SILICATE 51 (manufactured by Tama Chemicals Co., Ltd.) and 170.90 g of PGMEA were loaded. Then, to the resulting mixture, an aqueous phosphoric acid solution containing 0.56 g (0.3% by weight compared to the loaded monomer) of phosphoric acid dissolved in 56.25 g of water was added over a period of 10 minutes while stirring the mixture at room temperature. After immersing the flask in a 40°C
15 oil bath and stirring the resulting solution for 30 minutes, the oil bath was heated to 115°C over a period of 30 minutes. The inner temperature of the solution reached 100°C one hour after the start of the heating. From this point, the solution was heated with stirring for 2 hours (the inner temperature was 100 to 110°C) to obtain a polysiloxane solution (A1-g). It is noted here that the heating and stirring were
20 performed under nitrogen flow at a rate of 0.05 L (liter)/min. During the reaction, methanol and water, which were by-products, were distilled out in a total amount of 139 g.

[0161] The thus obtained polysiloxane solution (A1-g) had a solids concentration of 43% by weight and the polysiloxane had a weight-average molecular weight of 9,500. Further, the content ratio of phenyl group-substituted silane in the polysiloxane was 50% in terms of molar ratio of Si atom.

Synthesis Example 8: Synthesis of Polysiloxane Solution (A1-h)

To a 500-mL three-necked flask, 27.24 g (0.20 mol) of methyltrimethoxysilane, 99.15 g (0.50 mol) of phenyltrimethoxysilane, 73.92 g (0.30 mol) of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and 173.02 g of PGMEA were loaded. Then, to the resulting mixture, an aqueous phosphoric acid solution containing 0.60 g (0.3% by weight compared to the loaded monomer) of phosphoric acid dissolved in 59.40 g of water was added over a period of 10 minutes while stirring the mixture at room temperature. After immersing the flask in a 40°C oil bath and stirring the resulting solution for 30 minutes, the oil bath was heated to 115°C over a period of 30 minutes. The inner temperature of the solution reached 100°C one hour after the start of the heating. From this point, the solution was heated with stirring for 2 hours (the inner temperature was 100 to 110°C) to obtain a polysiloxane solution (A1-h). It is noted here that the heating and stirring were performed under nitrogen flow at a rate of 0.05 L (liter)/min. During the reaction, methanol and water, which were by-products, were distilled out in a total amount of 139 g.

[0162] The thus obtained polysiloxane solution (A1-h) had a solids concentration of 43% by weight and the polysiloxane had a weight-average molecular weight of 9,500. Further, the content ratio of phenyl group-substituted silane in the polysiloxane was 50% in terms of molar ratio of Si atom.

20 Synthesis Example 9: Synthesis of Polysiloxane Solution (A1-i)

To a 500-mL three-necked flask, 27.24 g (0.20 mol) of methyltrimethoxysilane, 99.15 g (0.50 mol) of phenyltrimethoxysilane, 26.64 g (0.10 mol) of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 29.65 g (0.20 mol) of vinyltrimethoxysilane and 164.40 g of PGMEA were loaded. Then, to the resulting mixture, an aqueous phosphoric acid solution containing 0.54 g (0.3% by weight compared to the loaded monomer) of phosphoric acid dissolved in 55.80 g of water was added over a period of 10 minutes while stirring the mixture at room

temperature. After immersing the flask in a 40°C oil bath and stirring the resulting solution for 30 minutes, the oil bath was heated to 115°C over a period of 30 minutes. The inner temperature of the solution reached 100°C one hour after the start of the heating. From this point, the solution was heated with stirring for 2 hours (the inner temperature was 100 to 110°C) to obtain a polysiloxane solution (A1-i). It is noted here that the heating and stirring were performed under nitrogen flow at a rate of 0.05 L (liter)/min. During the reaction, methanol and water, which were by-products, were distilled out in a total amount of 139 g.

[0163] The thus obtained polysiloxane solution (A1-i) had a solids concentration of 43% by weight and the polysiloxane had a weight-average molecular weight of 8,800. Further, the content ratio of phenyl group-substituted silane in the polysiloxane was 50% in terms of molar ratio of Si atom.

Synthesis Example 10: Synthesis of Polysiloxane Solution (A1-j)

To a 500-mL three-necked flask, 68.10 g (0.50 mol) of methyltrimethoxysilane, 99.15 g (0.50 mol) of phenyltrimethoxysilane and 150.40 g of PGMEA were loaded. Then, to the resulting mixture, an aqueous phosphoric acid solution containing 0.50 g (0.3% by weight compared to the loaded monomer) of phosphoric acid dissolved in 54.00 g of water was added over a period of 10 minutes while stirring the mixture at room temperature. After immersing the flask in a 40°C oil bath and stirring the resulting solution for 30 minutes, the oil bath was heated to 115°C over a period of 30 minutes. The inner temperature of the solution reached 100°C one hour after the start of the heating. From this point, the solution was heated with stirring for 2 hours (the inner temperature was 100 to 110°C) to obtain a polysiloxane solution (A1-j). It is noted here that the heating and stirring were performed under nitrogen flow at a rate of 0.05 L (liter)/min. During the reaction, methanol and water, which were by-products, were distilled out in a total amount of 137 g.

[0164] The thus obtained polysiloxane solution (A1-j) had a solids concentration of 43% by weight and the polysiloxane had a weight-average molecular weight of 7,000. Further, the content ratio of phenyl group-substituted silane in the polysiloxane was 50% in terms of molar ratio of Si atom.

5 Synthesis Example 11: Synthesis of Acrylic Resin Solution (A2-a)

To a 500-mL flask, 5 g of 2,2'-azobis(iso-butyronitrile), 5 g of t-dodecanethiol and 180 g of PGMEA were loaded. Then, 40 g of methacrylic acid, 35 g of benzyl methacrylate and 35 g of tricyclo[5.2.1.0^{2,6}]decane-8-yl methacrylate were loaded and the resulting mixture was stirred at room temperature. After
10 replacing the atmosphere inside the flask with nitrogen, the mixture was heated with stirring at 70°C for 5 hours. Thereafter, to the resulting solution, 15 g of glycidyl methacrylate, 1 g of dimethylbenzylamine and 0.2 g of p-methoxyphenol were added, and the resultant was further heated with stirring at 90°C for 4 hours to obtain an acrylic resin solution (A2-a).

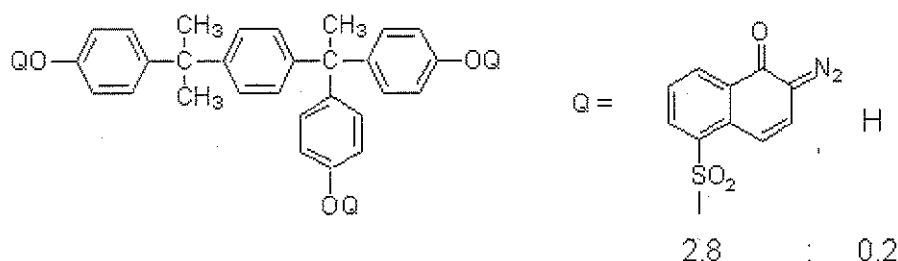
15 [0165] The thus obtained acrylic resin solution (A2-a) had a solids concentration of 40% by weight and the acrylic resin had a weight-average molecular weight of 12,000 and an acid value of 91 mg KOH/g.

Synthesis Example 12: Synthesis of Naphthoquinone Diazide Compound (B-a)

Under dry nitrogen gas flow, 21.23 g (0.05 mol) of TrisP-PA (trade name,
20 manufactured by Honshu Chemical Industry Co., Ltd.) and 37.62 g (0.14 mol) of 5-naphthoquinonediazidesulfonic acid chloride were dissolved in 450 g of 1,4-dioxane, and the temperature of the resulting solution was adjusted to be room temperature. To this solution, 15.58 g (0.154 mol) of triethylamine mixed with 50 g of 1,4-dioxane was added dropwise while maintaining the temperature of the system at
25 lower than 35°C. Thereafter, the resulting solution was stirred at 30°C for 2 hours. Triethylamine salt was filtered out and the filtrate was loaded into water. Then, the resulting precipitate was recovered by filtration. The thus recovered precipitate was

dried in a vacuum dryer to obtain a naphthoquinone diazide compound (B-a) having the following structure.

[0166]



5 [0167] Synthesis Example 13: Synthesis of Naphthoquinone Diazide Compound (B-b)

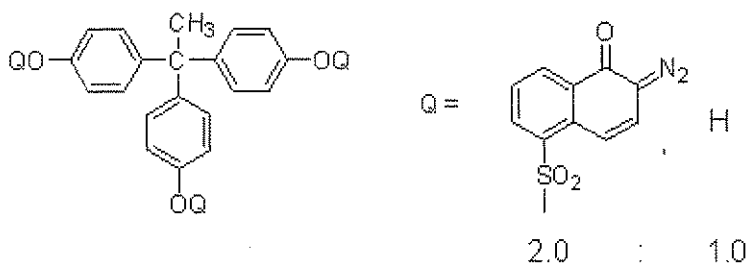
Under dry nitrogen gas flow, 15.32 g (0.05 mol) of TrisP-HAP (trade name, manufactured by Honshu Chemical Industry Co., Ltd.) and 26.87 g (0.1 mol) of 5-naphthoquinonediazidesulfonic acid chloride were dissolved in 450 g of 1,4-dioxane, and the temperature of the resulting solution was adjusted to be room temperature.

10 To this solution, 11.13 g (0.11 mol) of triethylamine mixed with 50 g of 1,4-dioxane was added dropwise while maintaining the temperature of the system at lower than 35°C. Thereafter, the resulting solution was stirred at 30°C for 2 hours.

Triethylamine salt was filtered out and the filtrate was loaded into water. Then, the

15 resulting precipitate was recovered by filtration. The thus recovered precipitate was dried in a vacuum dryer to obtain a naphthoquinone diazide compound (B-b) having the following structure.

[0168]

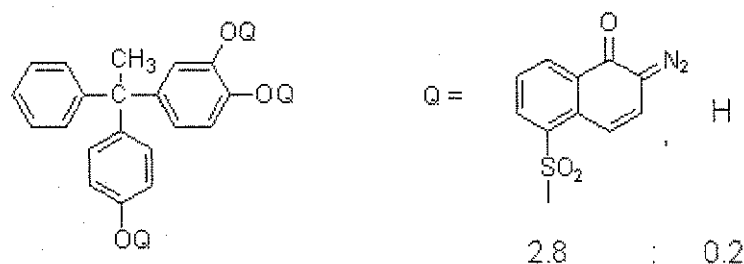


Quinone Diazide Compound (b)

[0169] Synthesis Example 14: Synthesis of Naphthoquinone Diazide Compound (B-c)

Under dry nitrogen gas flow, 15.32 g (0.05 mol) of Ph-cc-AP (trade name,
 5 manufactured by Honshu Chemical Industry Co., Ltd.) and 37.62 g (0.14 mol) of 5-naphthoquinonediazidesulfonic acid chloride were dissolved in 450 g of 1,4-dioxane, and the temperature of the resulting solution was adjusted to be room temperature. To this solution, 15.58 g (0.154 mol) of triethylamine mixed with 50 g of 1,4-dioxane was added dropwise while maintaining the temperature of the system at
 10 lower than 35°C. Thereafter, the resulting solution was stirred at 30°C for 2 hours. Triethylamine salt was filtered out and the filtrate was loaded into water. Then, the resulting precipitate was recovered by filtration. The thus recovered precipitate was dried in a vacuum dryer to obtain a naphthoquinone diazide compound (B-c) having the following structure.

15 [0170]



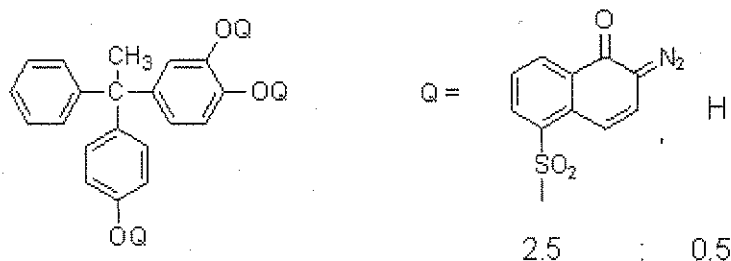
Quinone Diazide Compound (c)

[0171] Synthesis Example 15: Synthesis of Naphthoquinone Diazide Compound (B-

d)

A naphthoquinone diazide compound (B-d) having the following structure was obtained in the same manner as in Synthesis Example 10, except that the amount of 5-naphthoquinonediazidesulfonic acid chloride was changed to 33.59 g (0.125 mol).

[0172]



Quinone Diazide Compound (d)

[0173] (Example 1)

Under a yellow lamp, 15.43 g of the polysiloxane solution (A1-a) obtained in Synthesis Example 1, 0.59 g of the naphthoquinone diazide compound (B-a) obtained in Synthesis Example 7, 3.73 g of DAA as a solvent and 9.84 g of PGMEA were mixed and stirred to prepare a uniform solution. The thus obtained uniform solution was then filtered through a filter having a pore size of 0.45 μm to prepare a composition 1.

[0174] Using a spin coater (1H-360S, manufactured by Mikasa Co., Ltd.) at an arbitrary rotation speed, the composition 1 was spin-coated onto a silicon wafer, an OA-10 glass plate (manufactured by Nippon Electric Glass Co., Ltd.) and a glass substrate having a molybdenum sputtered film, and the resultants were prebaked at 90°C for 2 minutes using a hot plate (SCW-636, manufactured by Dainippon Screen Mfg. Co., Ltd.) to prepare a film having a thickness of 3 μm . Then, using a parallel-light mask aligner (hereinafter, abbreviated as "PLA") (PLA-501F, manufactured by Canon Inc.), the thus prepared film was exposed to an ultra-high-

pressure mercury lamp through a gray-scale mask for sensitivity measurement to form a pattern. Thereafter, using an automatic developing apparatus (AD-2000, manufactured by Takizawa Sangyo Co., Ltd.), the resulting film was developed by 60-second showering of ELM-D (trade name, manufactured by MITSUBISHI GAS
5 CHEMICAL CO., INC.), which is a 2.38%-by-weight tetramethylammonium hydroxide aqueous solution, and then rinsed with water for 30 seconds.

Subsequently, for the purpose of performing bleaching exposure, the entire surface of the resulting film was exposed to an ultra-high-pressure mercury lamp at $3,000 \text{ J/m}^2$ (based on the exposure dose at a wavelength of 365 nm) using a PLA (PLA-501F,
10 manufactured by Canon Inc.).

[0175] Thereafter, the resulting film was soft-baked at 110°C for 2 minutes using a hot plate and then cured in the air at 230°C for 1 hour using an oven (IHPS-222 manufactured by Tabai Espec Corp.) to prepare a cured film.

[0176] The evaluation results of the photosensitive properties and the cured film
15 properties are shown in Table 5. It is noted here that the evaluations of the photosensitive properties and the cured film properties were performed in accordance with the following methods. The following evaluations (4) to (8) were performed on the silicon wafer substrate and the evaluation (9) was performed on the OA-10 glass plate. The evaluations (10) and (11) were performed on the glass substrate
20 having a molybdenum sputtered film.

(4) Measurement of Film Thickness

The film thickness was measured using RAMDA-ACE STM-602 (trade name, manufactured by Dainippon Screen Mfg. Co., Ltd.) at a refractive index of 1.50.

(5) Reduction in Film Thickness of Non-exposed Area during Development

25 The reduction in the film thickness of a non-exposed area during development was calculated by the following equation:

[0177] Reduction in film thickness of non-exposed area = film thickness before

development - film thickness of non-exposed area after development

(6) Determination of Sensitivity

After exposure and development, the exposure dose at which a 10- μ m line-and-space pattern is formed at a width ratio of 1:1 (hereinafter, this exposure dose is referred to as "optimum exposure dose") was adopted as the sensitivity.

(7) Determination of Resolution

The minimum pattern size at the optimum exposure dose after development was adopted as the post-development resolution and the minimum pattern size at the optimum exposure dose after curing was adopted as the post-curing resolution.

10 (8) Heat resistance

The cured film prepared by the method according to Example 1 was scraped off from the substrate and about 10 mg of the scraped film was placed in an aluminum cell. Using a thermogravimetric apparatus (TGA-50, manufactured by SHIMADZU CORPORATION), the film sample was heated to 150°C in a nitrogen atmosphere at a heating rate of 10°C/min. The film sample was maintained at 150°C for 1 hour and then heated to 400°C at a heating rate of 10°C/min. In this process, a temperature Td1% at which the weight loss became 1% was measured and compared. The higher the Td1%, the better the heat resistance.

(9) Measurement of Light Transmittance

20 First, using Multi Spec-1500 (trade name, manufactured by SHIMADZU CORPORATION), the ultraviolet and visible absorption spectra of only the OA-10 glass plate were measured to be used as a reference. Then, a cured film of the composition was formed on an OA-10 glass plate (pattern exposure was not performed) and the resulting sample was measured with a single beam to determine the light transmittance per 3 μ m of the film at a wavelength of 400 nm. The difference between the thus determined light transmittance and the reference was adopted as the light transmittance of the cured film.

(10) Adhesion in Development

The minimum size of the film pattern which was prepared on a glass substrate having a molybdenum sputtered film by the method described in Example 1 and remained on the glass substrate after development was adopted as the adhesion in development. The finer the pattern, the more likely the pattern to be detached during development; therefore, a smaller value means better adhesion in development.

(11) Wet-heat resistance

A cured film was prepared on a glass substrate having a molybdenum sputtered film by the method described in Example 1. The resulting sample was then subjected to a test in which the sample was left to stand for 10 hours or 24 hours in a chamber ("HAST CHAMBER EHS-221MD" (trade name), manufactured by ESPEC Corp.) having a temperature of 121°C, a humidity of 100% and a pressure of 2.1 atm. Thereafter, the degree of change in color of molybdenum was evaluated.

Further, a glass substrate having only a molybdenum sputtered film was also tested at the same time and the change in color of this substrate before and after the test was used as an index to evaluate the wet-heat resistance based on the following criteria.

[0178] 5: No color change was observed in the molybdenum under the cured film between before and after the test.

[0179] 4: As compared to the molybdenum not covered with the cured film, the molybdenum under the cured film showed color change in an area of about one-tenth between before and after the test.

[0180] 3: As compared to the molybdenum not covered with the cured film, the molybdenum under the cured film showed color change in an area of about one-fifth between before and after the test.

[0181] 2: As compared to the molybdenum not covered with the cured film, the molybdenum under the cured film showed color change in an area of about four-

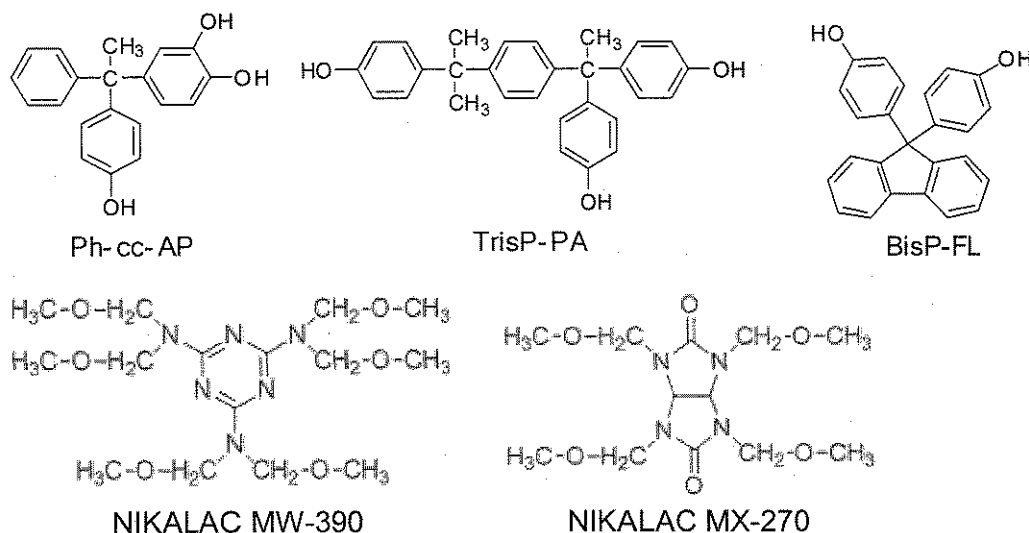
tenth between before and after the test.

[0182] As compared to the molybdenum not covered with the cured film, the molybdenum under the cured film showed color change in an area of not less than about six-tenth between before and after the test.

5 (Examples 2 to 40 and Comparative Examples 1 to 4)

In the same manner as in the case of the composition 1, the compositions 2 to 35 were prepared in accordance with the respective constitutions shown in Tables 1 to 4. It is noted here that KBM303, which was used as a silane coupling agent, is 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane manufactured by Shin-Etsu Chemical
10 Co., Ltd. Those phenol compounds used as solubility accelerators (Phcc-AP, TrisP-PA and BisP-FL; all of which are manufactured by Honshu Chemical Industry Co., Ltd.) and those compounds used as crosslinking agents (NIKALAC MW-390 and NIKALAC MX270; both of which are trade names and manufactured by SANWA CHEMICAL Co., Ltd.) have the following structures.

15 [0183]

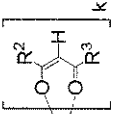


[0184] Further, CGI-MDT (trade name, manufactured by Ciba Specialty Chemicals Co., Ltd.) and WPAG-469 (trade name, manufactured by Wako Pure Chemical

Industries, Ltd.), which were used as crosslinking promoters, were in the form of a 20% PGMEA solution of 4-methylphenyldiphenylsulfonium perfluorobutanesulfonate, and DPA (trade name, manufactured by Kawasaki Kasei Chemicals Ltd.) used as a sensitizer was 9,10-dipropoxyanthracene.

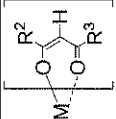
5 [0185] [Table 1]

10

Composition	(D) Zirconium compound (R ¹ O) ₄ M ₂  (1) _k								(A) alkali-soluble resin	(C) solvent	(B) naphthoquinone diazide compound	silane coupling agent	solubility accelerator	crosslinking agent	crosslinking accelerator	sensitizer
	(D) Type of zirconium compound	R ¹	R ²	R ³	j	k	additive amount	additive amount ratio compared to alkali-soluble resin 100 parts by weight (parts by weight)								
Composition 1	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.10g	1.51	polysiloxane solution (A1-a) 15.43g	DAA : 3.73g PGMEA : 9.84g	naphthoquinone diazide compound (B-a) 0.59g		CGI-MDT : 0.05g	DPA : 0.03g		
Composition 2	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.10g	1.57	polysiloxane solution (A1-b) 15.19g	DAA : 3.54g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.64g		CGI-MDT : 0.05g	DPA : 0.03g		
Composition 3	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.09g	1.44	polysiloxane solution (A1-c) 15.29g	DAA : 3.33g PGMEA : 9.84g	naphthoquinone diazide compound (B-d) 0.75g		CGI-MDT : 0.05g	DPA : 0.03g		
Composition 4	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.09g	1.47	polysiloxane solution (A1-d) 14.21g	D A A : 10.13g PGMEA : 3.77g	naphthoquinone diazide compound(B-a) 0.51g	KBM303 : 0.18g				
Composition 5	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.10g	1.51	polysiloxane solution (A1-e) 15.01g	PGMEA : 7.11g EDM : 2.28g D P M : 4.43g	naphthoquinone diazide compound(B-b) 0.45g	KBM303 : 0.18g				
Composition 6	Zirconium dibutoxybis (ethylacetoacetate)	n-butyl group	methyl group	ethoxy group	4	2	0.06g	0.94	polysiloxane solution (A1-b) 15.26g	DAA : 3.51g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.64g		CGI-MDT : 0.05g	DPA : 0.03g		
Composition 7	Zirconium tetrapropoxide	n-propyl group	-	-	4	0	0.03g	0.46	polysiloxane solution (A1-b) 15.50g	DAA : 3.47g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g					
Composition 8	Zirconium tetraphenoxide	phenyl group	-	-	4	0	0.06g	0.93	polysiloxane solution (A1-b) 15.43g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g					
Composition 9	Zirconium tetra(2, 2, 6, 6-tetramethyl-3,5-heptanedionate)	-	t-butyl group	t-butyl group	4	4	0.10g	1.54	polysiloxane solution (A1-b) 15.50g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g		CGI-MDT : 0.05g	DPA : 0.03g		

[0186]

[Table 2]

Composition	(D) Zirconium compound (R ¹ O) _k M  (1) k	(D) Type of zirconium compound	R ¹	R ²	R ³	j	k	additive amount	additive amount ratio compared to alkali-soluble resin 100 parts by weight (parts by weight)	(A) alkali-soluble resin	(C) solvent	(B) naphthoquinone diazide compound	silane coupling agent	solubility accelerator	crosslinking agent	crosslinking accelerator	sensitizer
Composition 10	Zirconium tetramethylmalonate	-	-	methoxy group	methoxy group	4	4	0.10g	1.55	polysiloxane solution (A1-b) 15.35g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g				CGI-MDT : 0.05g	DPA : 0.03g
Composition 11	Zirconium tetrabenzoiacetate	-	-	phenyl group	methyl group	4	4	0.10g	1.55	polysiloxane solution (A1-b) 15.35g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g				CGI-MDT : 0.05g	DPA : 0.03g
Composition 12	Zirconium mono-n-butoxyacetylacetonate-bis (ethylacetoacetate)	n-butyl group	methyl group	methyl group	ethoxy group	4	3	0.06g	0.93	polysiloxane solution (A1-b) 15.35g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g					
					methyl group	4	3										
Composition 13	Aluminum tris-acetylacetonate	-	-	methyl group	methyl group	3	3	0.06g	0.93	polysiloxane solution (A1-b) 15.35g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g				CGI-MDT : 0.05g	DPA : 0.03g
Composition 14	Aluminum tris-propoxide	n-propyl group	-	-	-	3	0	0.02g	0.31	polysiloxane solution (A1-b) 15.35g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g					
Composition 15	Aluminum tris (ethylacetoacetate)	-	-	methyl group	ethoxy group	3	3	0.06g	0.93	polysiloxane solution (A1-b) 15.35g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g					
Composition 16	Aluminum ethylacetoacetate di (iso-propoxide)	iso-propyl group	-	methyl group	ethoxy group	3	2	0.02g	0.31	polysiloxane solution (A1-b) 15.35g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g				CGI-MDT : 0.05g	DPA : 0.03g
Composition 17	Aluminum octadecylacetoacetate di (iso-propoxide)	iso-propyl group	-	methyl group	octadecyl group	3	1	0.06g	0.93	polysiloxane solution (A1-b) 15.35g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g					
Composition 18	Aluminum mono-acetylacetonate-bis (ethylacetoacetate)	-	methyl group	methyl group	methyl group	3	3	0.06g	0.93	polysiloxane solution (A1-b) 15.35g	DAA : 3.50g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.65g					
					ethyl group	3	3										

[0187] [Table 3]

5

Composition	(D) Zirconium compound $(R^1O)_{j-k}M$  (1)						(A) alkali-soluble resin	(C) solvent	(B) naphthoquinone diazide compound	silane coupling agent	solubility accelerator	crosslinking agent	crosslinking accelerator	sensitizer
	(D) Type of zirconium compound	R ¹	R ²	R ³	j	k	additive amount	additive amount ratio compared to alkali-soluble resin 100 parts by weight (parts by weight)						
Composition 19	Titan tetraacetylacetonate	-	methyl group	methyl group	4	4	0.03g	0.47	polysiloxane solution (A1-b) 15.35g	DAA : 4.97g PGMEA : 8.85g	naphthoquinone diazide compound (B-c) 0.55g			
Composition 20	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.17g	1.94	Acryl resin solution (A2-a) 21.91g (MW=12000)	DAA : 5.94g PGMEA : 0.71g	naphthoquinone diazide compound (B-a) 1.17g	NIKALAC MX-270 : 0.18g	WPAC-469 : 0.09g	DPA : 0.04g
Composition 21	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.13g	1.98	polysiloxane solution (A1-b) 15.60g	DAA : 1.86g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.62g			
Composition 22	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.12g	1.83	polysiloxane solution (A1-b) 15.60g	DAA : 1.86g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.62g			
Composition 23	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.18g	2.84	polysiloxane solution (A1-b) 15.10g	DAA : 2.17g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.60g			
Composition 24	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.18g	2.93	polysiloxane solution (A1-b) 14.62g	DAA : 2.44g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.59g			
Composition 25	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.18g	2.84	polysiloxane solution (A1-b) 15.10g	DAA : 2.17g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.60g			
Composition 26	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.18g	2.93	polysiloxane solution (A1-b) 14.62g	DAA : 2.44g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.59g			
Composition 27	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.18g	2.93	polysiloxane solution (A1-b) 14.62g	DAA : 2.44g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.59g			
Composition 28	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.17g	2.88	polysiloxane solution (A1-b) 14.05g	DAA : 2.78g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.56g	NIKALAC MX-270 : 0.28g		
Composition 29	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.17g	2.88	polysiloxane solution (A1-b) 14.05g	DAA : 2.78g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.56g	NIKALAC MW-390 : 0.28g		
Composition 30	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.17g	2.61	polysiloxane solution (A1-b) 14.51g	DAA : 2.51g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.58g	NIKALAC MW-390 : 0.06g		
Composition 31	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.17g	2.88	polysiloxane solution (A1-b) 14.05g	DAA : 2.78g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.56g	NIKALAC MW-390 : 0.28g		
Composition 32	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.16g	2.82	polysiloxane solution (A1-b) 13.52g	DAA : 3.31g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.54g	NIKALAC MW-390 : 0.54g		

[0188] [Table 4]

Composition	(D) Zirconium compound (R ¹ O) _j -(R ² O) _k (1)							(A) alkali-soluble resin	(C) solvent	(B) naphthoquinone diazide compound	silane coupling agent	solubility accelerator	crosslinking agent	crosslinking accelerator	sensitizer
	(D) Type of zirconium compound	R ¹	R ²	R ³	j	k	additive amount	additive amount ratio compared to alkali-soluble resin 100 parts by weight (parts by weight)							
Composition 33	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.20g	3.81	DAA : 3.72g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.50g		TrisP-PA 0.50g	NIKALAC MW-390 : 1.06g		
Composition 34	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.1g	1.57	DAA : 3.54g PGMEA : 9.84g	naphthoquinone diazide compound (B-c) 0.54g	tetramethoxysilane : 0.30g			CGI- MDT : 0.05g	DPA : 0.03g
Composition 35	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.09g	1.47	DAA : 10.13g PGMEA : 3.77g	naphthoquinone diazide compound (B-a) 0.51g	KBM303 : 0.18g tetramethoxysilane : 0.30g				
Composition 36	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.09g	1.47	DAA : 10.13g PGMEA : 3.77g	naphthoquinone diazide compound (B-a) 0.51g	tetramethoxysilane : 0.40g				
Composition 37	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.09g	1.47	DAA : 10.13g PGMEA : 3.77g	naphthoquinone diazide compound (B-a) 0.51g	tetramethoxysilane : 0.30g				
Composition 38	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.09g	1.47	DAA : 10.13g PGMEA : 3.77g	naphthoquinone diazide compound (B-a) 0.51g	methyl silicate 51 : 0.30g				
Composition 39	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.09g	1.47	DAA : 10.13g PGMEA : 3.77g	naphthoquinone diazide compound (B-a) 0.51g	tetramethoxysilane : 0.30g			CGI- MDT : 0.05g	DPA : 0.03g
Composition 40	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.09g	1.47	DAA : 10.13g PGMEA : 3.77g	naphthoquinone diazide compound (B-a) 0.51g				CGI- MDT : 0.05g	DPA : 0.03g
Composition 41							0 g	0.00	DAA : 1.40g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.65g				CGI- MDT : 0.15g	DPA : 0.08g
Composition 42							0 g	0.00	DAA : 5.94g PGMEA : 0.71g (MW = 12000)	naphthoquinone diazide compound (B-a) 1.17g	KBM303 : 0.18g		NIKALAC MX-270 : 0.18g	WPAG- 469 : 0.09g	DPA : 0.04g
Composition 43	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.005g	0.07	DAA : 1.40g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.65g				CGI- MDT : 0.15g	DPA : 0.08g
Composition 44	Zirconium tetraacetylacetonate	-	methyl group	methyl group	4	4	0.5g	7.28	DAA : 1.40g PGMEA : 10.98g	naphthoquinone diazide compound (B-c) 0.65g				CGI- MDT : 0.15g	DPA : 0.08g

[0189] The thus obtained compositions were each evaluated in the same manner as in Example 1. However, in the evaluation of the acrylic resin, development was performed by 60-second showering of 0.4%-by-weight tetramethylammonium hydroxide aqueous solution. The results of the evaluations are shown in Tables 5 and 6. In Comparative Example 4, since the chelate compound was added in an excessively large amount, even when exposure was performed at an exposure dose of 3,000 J/m², resolution was not attained.

[0190] [Table 5]

	Composition	Photosensitive properties				Cured film properties						
		Thickness after prebaking (μm)	Reduction in film thickness of non-exposed area during development (μm)	Sensitivity (Jm ⁻²)	Resolution after development (μm)	Thickness after curing (μm)	Resolution after curing (μm)	Td1% (°C)	Light transmittance (%)	Adhesion in development (μm)	Wet-heat resistance 10 hrs	Wet-heat resistance 24 hrs
Example 1	Composition 1	3.0	0.1	340	2	2.7	2	350	98	2	3	1
Example 2	Composition 2	3.0	0.08	320	2	2.7	2	348	98	2	3	1
Example 3	Composition 3	3.0	0.05	300	2	2.8	2	340	98	2	3	1
Example 4	Composition 4	3.0	0.15	260	2	2.7	2	363	98	2	3	1
Example 5	Composition 5	3.0	0.2	240	2	2.7	2	355	98	2	3	1
Example 6	Composition 6	3.0	0.09	320	2	2.7	2	351	98	2	3	1
Example 7	Composition 7	3.0	0.67	340	2	2.7	2	351	98	2	3	1
Example 8	Composition 8	3.0	0.08	320	2	2.7	2	350	98	2	3	1
Example 9	Composition 9	3.0	0.08	320	2	2.7	2	350	98	2	3	1
Example 10	Composition 10	3.0	0.09	300	2	2.7	2	350	98	2	3	1
Example 11	Composition 11	3.0	0.08	320	2	2.7	2	351	98	2	3	1
Example 12	Composition 12	3.0	0.08	320	2	2.7	2	348	98	2	3	1
Example 13	Composition 13	3.0	0.10	300	2	2.7	2	349	98	2	3	1
Example 14	Composition 14	3.0	0.08	320	2	2.7	2	350	98	2	3	1
Example 15	Composition 15	3.0	0.08	320	2	2.7	2	347	98	2	3	1
Example 16	Composition 16	3.0	0.09	300	2	2.7	2	350	98	2	3	1
Example 17	Composition 17	3.0	0.08	320	2	2.7	2	350	98	2	3	1
Example 18	Composition 18	3.0	0.08	320	2	2.7	2	350	98	2	3	1
Example 19	Composition 19	3.0	0.07	360	2	2.7	2	349	96	2	3	1
Example 20	Composition 20	3.0	0.20	440	6	2.4	6	285	80	2	6	4
Example 21	Composition 21	3.0	0.10	300	2	2.7	2	342	98	2	3	1
Example 22	Composition 22	3.0	0.12	280	2	2.7	2	340	98	2	4	1

10 [0191] [Table 6]

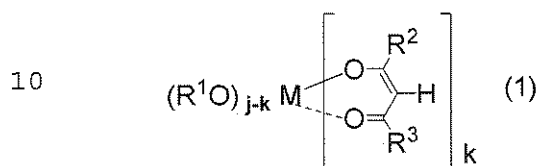
		Photosensitive properties				Cured film properties						
	Composition	Thickness after prebaking (μm)	Reduction in film thickness of non-exposed area during development (μm)	Sensitivity (J/m ²)	Resolution after development (μm)	Thickness after curing (μm)	Resolution after curing (μm)	Td1% (°C)	Light transmittance (%)	Adhesion in development (μm)	Wet-heat resistance 10 hrs	Wet-heat resistance 24 hrs
Example 23	Composition 23	3.0	0.08	320	2	2.7	2	335	97	2	4	2
Example 24	Composition 24	3.0	0.15	280	2	2.7	2	333	96	2	5	2
Example 25	Composition 25	3.0	0.08	320	2	2.7	2	335	97	2	4	2
Example 26	Composition 26	3.0	0.15	280	2	2.7	3	336	95	2	5	2
Example 27	Composition 27	3.0	0.15	280	2	2.7	3	344	95	2	5	2
Example 28	Composition 28	3.0	0.16	260	2	2.7	3	330	95	2	5	3
Example 29	Composition 29	3.0	0.16	260	2	2.7	3	325	95	2	5	4
Example 30	Composition 30	3.0	0.15	280	2	2.7	3	335	96	2	5	3
Example 31	Composition 31	3.0	0.17	240	2	2.7	3	322	95	2	5	4
Example 32	Composition 32	3.0	0.19	220	2	2.7	3	320	94	2	5	5
Example 33	Composition 33	3.0	0.22	200	2	2.6	4	315	93	2	5	5
Example 34	Composition 34	3.0	0.06	300	2	2.7	2	355	99	2	4	1
Example 35	Composition 35	3.0	0.12	270	2	2.7	2	354	98	2	4	2
Example 36	Composition 36	3.0	0.12	240	1	2.7	1	360	99	1	4	2
Example 37	Composition 37	3.0	0.2	200	2	2.6	2	352	99	1	5	2
Example 38	Composition 38	3.0	0.2	200	2	2.6	2	351	98	1	5	3
Example 39	Composition 39	3.0	0.12	240	2	2.7	2	350	98	2	5	3
Example 40	Composition 40	3.0	0.06	320	2	2.7	2	348	98	5	3	1
Comparative Example 1	Composition 41	3.0	0.08	320	2	2.8	4	350	99	40	1	1
Comparative Example 2	Composition 42	3.0	0.2	440	6	2.4	8	280	90	10	3	2
Comparative Example 3	Composition 43	3.0	0.06	320	2	2.8	4	351	99	40	1	1
Comparative Example 4	Composition 44	3.0	0	>3600	unassess- urable	2.8	unassess- urable	358	98	unassess- urable	5	5

INDUSTRIAL APPLICABILITY

[0192] The positive photosensitive composition according to the present invention can be used to form a planarization film for thin-film transistor (TFT) substrate of a liquid crystal display device, an organic EL display device or the like; a protective film or an insulation film for a touch panel; an interlayer insulation film of a semiconductor device; a planarization film or a microlens array pattern for a solid-state image sensing device; or a core or clad material of an optical waveguide.

CLAIM

1. A positive photosensitive composition, which comprises (A) an alkali-soluble polysiloxane and/or an alkali-soluble acrylic resin, (B) a naphthoquinone diazide compound, (C) a solvent and (D) a metal chelate compound, wherein said (D) metal chelate compound has a structure represented by the following Formula (1) and the content of said (D) metal chelate compound is 0.1 to 5 parts by weight compared to 100 parts by weight of said (A) alkali-soluble polysiloxane and/or alkali-soluble acrylic resin:



(wherein, M is a metal atom; R^1 's, the same or different, each represent hydrogen, an alkyl group, an aryl group, an alkenyl group, or a substitution product thereof; R^2 and R^3 , the same or different, each represent hydrogen, an alkyl group, an aryl group, an alkenyl group, an alkoxy group, or a substitution product thereof; j represents the valency of said metal atom M; and k represents an integer of 0 to j).

2. The positive photosensitive composition according to claim 1, wherein said metal atom M in said Formula (1) is any one of a titanium metal atom, a zirconium metal atom and an aluminum metal atom.

20 3. The positive photosensitive composition according to claim 1 or 2, wherein said metal atom M in said Formula (1) is an aluminum metal atom.

4. The positive photosensitive composition according to claim 3, wherein said content of said (D) metal chelate compound is 0.1 to 1.5 parts by weight compared to 100 parts by weight of said (A) alkali-soluble polysiloxane and/or alkali-soluble acrylic resin.

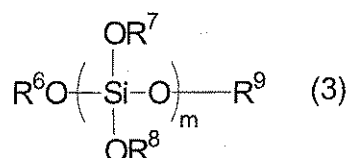
5. The positive photosensitive composition according to claim 1 or 2, wherein said M in said Formula (1) is a zirconium metal atom and said content of said (D)

metal chelate compound is 0.3 to 4 parts by weight compared to 100 parts by weight of said (A) alkali-soluble polysiloxane and/or alkali-soluble acrylic resin.

6. The positive photosensitive composition according to any one of claims 1 to 5, wherein the content ratio of phenyl group in said (A) alkali-soluble polysiloxane is 5 mol% to 70 mol% with respect to Si atom.

7. The positive photosensitive composition according to any one of claims 1 to 5, which is characterized in that the content ratio of epoxy group and/or vinyl group in said (A) alkali-soluble polysiloxane is 1 mol% to 50 mol% with respect to Si atom.

8. The positive photosensitive composition according to any one of claims 1 to 7, which further comprises, as a silane coupling agent, an organosilane represented by the Formula (3):



(wherein, R⁶ to R⁹ each independently represent hydrogen, an alkyl group having 1 to 6 carbon atoms, an acyl group having 2 to 6 carbon atoms or an aryl group having 6 to 15 carbon atoms; and said alkyl group, said acyl group and said aryl group are all optionally substituted or unsubstituted).

9. The positive photosensitive composition according to any one of claims 1 to 8, which is characterized by further comprising a solubility accelerator.

10. The positive photosensitive composition according to claim 9, wherein said solubility accelerator is a phenol compound.

11. The positive photosensitive composition according to any one of claims 1 to 10, which further comprises a crosslinking agent.

12. The positive photosensitive composition according to claim 11, wherein said crosslinking agent comprises a methylol-based compound.

13. A cured film which is formed from the positive photosensitive composition

according to any one of claims 1 to 12, wherein the light transmittance per film thickness of 3 μm at a wavelength of 400 nm is not less than 85%.

14. A cured film which is formed from the positive photosensitive composition according to any one of claims 1 to 12, wherein the content ratio of at least one metal
5 selected from the group consisting of titanium, zirconium, aluminum, zinc, cobalt, molybdenum, lanthanum, barium, strontium, magnesium and calcium is 0.005 to 1 part by weight compared to 100 parts by weight of said (A) alkali-soluble polysiloxane and/or alkali-soluble acrylic resin composition.

15. An element, which comprises the cured film according to claim 13 or 14.