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Description

Title of Invention: PHOTSENSITIVE RESIN COMPOSITION, AND DIELECTRIC INSULATING FILM AND ELECTRONIC DEVICE USING THE SAME

Technical Field

- [1] The present invention relates to a photosensitive resin composition forming a dielectric insulating film, a dielectric insulating film using the same, and an apparatus including the same. More specifically, the present invention relates to a photosensitive resin composition forming a dielectric insulating film used during an initial process of a thin film transistor (TFT) for liquid crystal display (LCD).

Background Art

- [2] A TFT substrate used in a liquid crystal display includes an interlayer dielectric insulating film provided between a TFT diode and a transparent conductive film forming a pixel electrode to protect the TFT array diode, and a contact hole through which a drain electrode of the TFT array and a wire formed using the transparent conductive film are connected on a dielectric insulating film.
- [3] A thermally curable photosensitive composition is used as a material of the interlayer dielectric insulating film, and, for example, a composition including an alkali-soluble resin and a 1,2-quinonediazide compound is known as a positive type of photosensitive composition and a photopolymerizable photosensitive composition is known as a negative type of thermally curable composition.
- [4] However, the known positive type of the photosensitive composition including the alkali-soluble resin and the 1,2-quinonediazide compound is thermally decomposed during hard baking after exposure and development to color. Therefore, when light transmittance is reduced in a visible ray region, or the organic dielectric insulating film is exposed to heat at a predetermined temperature or more for a predetermined time or more or absorbs a short wavelength such as ultraviolet rays, a predetermined component of the organic dielectric insulating film is decomposed to cause coloring or generate an impurity, thus forming an afterimage in the liquid crystal display.
- [5] Further, the negative type of photopolymerizable photosensitive composition does not color nor form an impurity due to decomposition of a predetermined component, but may have reduced resolution to an alkali developing solution (KOH, NaOH, and TMAH aq. solns) and reduced adhesion to the substrate due to an increased in molecular weight during photopolymerization.
- [6] Further, a photopolymerization initiator is added to a polymerizable compound having an ethylenically unsaturated bond to prepare the photosensitive composition.

US Patent No. 3558309 proposes an oxime ester derivative and US Patent Nos. 4255513 and 4590145 describe an oxime ester compound as the photopolymerization initiator used in the photosensitive composition. However, when the known oxime ester compounds are used as the photopolymerization initiator, materials decomposed by light during exposure are attached to a mask to form an undesirable pattern during printing and reduce a yield. Further, since the oxime ester compounds have a decomposition temperature of 240°C or less, the photopolymerization initiator may be decomposed to reduce physical properties of the resin during a thermal curing process typically performed at 130 to 240°C after the shape treatment and the thermal curing treatment needs to be performed at a reduced curing temperature. When the thermal curing treatment is performed at high temperatures, the treatment time may be reduced but physical properties of the resin are reduced, accordingly, a photopolymerization initiator having high heat resistance is required.

- [7] Recently, a technology for forming a transmitting film and a semi-transmitting film using a single photon simultaneously has been required to unify processes. The technology includes a method using a halftone mask having a plurality of transmitting regions having different light transmittances on a single mask substrate. The method includes forming the transmitting regions having different light transmittances on a photomask to control the intensity of light radiated on the substrate, on which a thin film pattern is formed, for every unit constituting the substrate to form the thin film pattern having a plurality of thicknesses using a single photolithography process. In the method, a target photosensitive material is exposed in different intensities of light to form a thin film pattern having a multi-stage structure using a single photolithography process.
- [8] However, the method is disadvantageous in that it is difficult to ensure uniformity in the thickness when the film is formed in a region of low transmittance. Accordingly, there is a demand for developing a technology for efficiently forming a photosensitive resin composition layer having a plurality of uniform thicknesses and forming a uniform pattern.
- [9] Further, it is required that characteristics such as transmittance, resolution, and a contrast ratio are continuously increased to apply a material having a resolution at a predetermined level or more and a margin to various processes in practice.

[10]

Disclosure of Invention

Technical Problem

- [11] An object of the present invention is to provide a photosensitive resin composition that can satisfy all requirements such as excellent transmittance and contrast ratio as

compared to the related art, excellent photosensitive characteristics such as a resolution and a remaining rate, excellent adhesion to a substrate at a low exposure dose, excellent resistance to ultraviolet rays, avoiding of a thickness deviation occurring when a composition layer having a plurality of thicknesses is formed, and excellent etching process and exposure process margins.

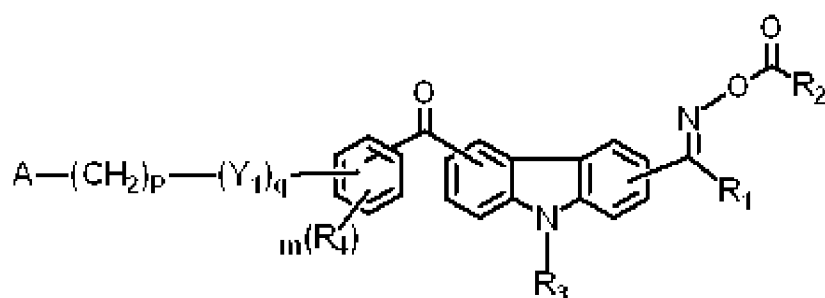
- [12] Another object of the present invention is to provide a negative type of photo-sensitive resin composition having increased transmittance, contrast ratio, and chemical resistance while a predetermined thickness of a thermally cured film is maintained using a novel photopolymerization initiator alone or in combination, a dielectric insulating film prepared using the same, and a liquid crystal display including the dielectric insulating film.

Solution to Problem

- [13] In one general aspect, a photosensitive resin composition includes a) 100 parts by weight of a copolymer formed using polymerization of 5 to 40 mol% of a unsaturated carboxylic acid, unsaturated carboxylic acid anhydride, or a mixture thereof, 5 to 70 mol% of an aromatic unsaturated monomer, 1 to 10 mol% of an unsaturated compound having an epoxy or an oxetane group selected from glycidyl methacrylate, 4-hydroxybutyl acrylate triglycidyl ether, 3-ethyl-3-methyl methacrylate oxetane or a mixture thereof, and 5 to 50 mol% of methyl methacrylate; b) 0.1 to 10 parts by weight of a photopolymerization initiator comprising a compound represented by the following Chemical Formula 1:

- [14] [Chemical Formula 1]

[15]



- [16] wherein

- [17] R_1 to R_4 are independently hydrogen, deuterium, halogen, substituted or unsubstituted (C1-C12)alkyl, substituted or unsubstituted (C2-C12)alkenyl, substituted or unsubstituted halo(C1-C12)alkyl, substituted or unsubstituted (C6-C12)aryl, substituted or unsubstituted (C3-C12)cycloalkyl, substituted or unsubstituted (C1-C12)alkoxy or (C1-C12)ester;

- [18] A is substituted or unsubstituted (C3-C12)heteroaryl or substituted or unsubstituted 5- to 7-membered heterocycloalkyl;

- [19] R_1 to R_4 and A are independently further substituted with one or more substituent

groups selected from a group consisting of halogen, (C1-C12)alkyl substituted or unsubstituted with halogen, (C2-C12)alkenyl, (C6-C12)aryl, (C3-C12)cycloalkyl, (C1-C12)alkoxy, carboxyl, nitro and hydroxyl;

[20] Y_1 is -O-, -S- or -Se-;

[21] m is an integer of 0 to 4, and when m is the integer of 2 or more, R_4 s may be the same or different;

[22] P is an integer of 0 to 5; and

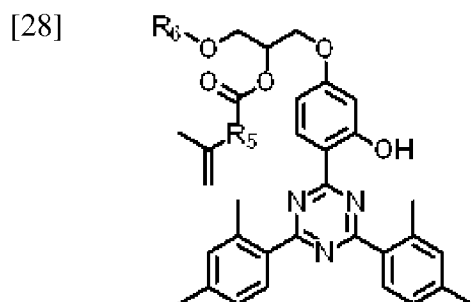
[23] q is an integer of 0 to 1;

[24] c) 1 to 150 parts by weight of a photopolymerizable ethylenically unsaturated monomer compound;

[25] d) 0.5 to 30 parts by weight of a functional silane compound; and

[26] e) 1 to 20 parts by weight of one or more compounds selected from a compound represented by the following Chemical Formula 2, 3 or a mixture thereof:

[27] [Chemical Formula 2]



- [35] R_8 is hydrogen, (C1-C12)alkyl substituted or unsubstituted with (C1-C12)alkyl, (C1-C12)alkyl substituted or unsubstituted with (C2-C12)alkenyl, (C2-C12)alkenyl substituted or unsubstituted with (C1-C12)alkyl, or (C6-C12)aryl substituted or unsubstituted with (C1-C12)alkyl, and
- [36] R_{11} is (C1-C12)alkylene.
- [37] Further, in the composition of each general aspect of the present invention, the copolymer may further include 0.5 to 10 mol% of an imide monomer having a polymerizable unsaturated group to provide a dielectric insulating film having excellent stability during a process and stability in use over a long period of time.
- [38] When the photopolymerization initiator of Chemical Formula 1 according to the present invention is used, the total amount of the photoinitiator used may be reduced due to high sensitivity to reduce absorption of radiated light by the photoinitiator and denaturalization of the photoinitiator by heat, thus increasing transmittance and contrast ratio.
- [39] To be more specific, surprisingly, a large amount of reaction base radicals are rapidly generated even in a small amount as compared to a known photopolymerization initiator to reduce the total amount of a photopolymerization initiator used in a composition having a remaining rate and a resolution, accordingly, a yellowish shift causing discoloration by heat is largely reduced and transmittance and contrast ratio are significantly increased.
- [40] Further, compounds represented by Chemical Formulas 2 and 3 inhibit polymerization on a diffused reflection non-pattern part due to a wavelength of ultraviolet rays generated during exposure.

Advantageous Effects of Invention

- [41] It can be seen that when the photopolymerization initiator according to the present invention was used alone or in a mixture form, the photosensitive resin composition showed the same remaining rate using the photopolymerization initiator even in a relatively small amount to increase the transmittance and contrast ratio while the thickness of the thermally cured film was maintained as compared to the photosensitive resin composition when the photopolymerization initiator according to the present invention was not used.
- [42] Further, the photosensitive resin composition according to the present invention may rapidly generate reaction base radicals in the same exposure amount and significantly reduce a yellowish shift causing discoloration by heat.

Best Mode for Carrying out the Invention

- [43] Hereinafter, the embodiments of the present invention will be described in detail with reference to accompanying drawings.

- [44] A copolymer (a) used in the present invention includes:
- [45] (a1) 5 to 40 mol% of a unsaturated carboxylic acid, unsaturated carboxylic acid anhydride, or a mixture thereof,
- [46] (a2) 5 to 70 mol% of an aromatic unsaturated monomer,
- [47] (a3) 1 to 10 mol% of an unsaturated compound having an epoxy group and/or an oxetane group, and
- [48] (a4) 5 to 50 mol% of a monoolefin-based unsaturated monomer.
- [49] Further, (a5) 0.5 to 10 mol% of an imide monomer compound having a polymerizable unsaturated group may be further used to ensure stability of a process and stability over a long period of time. The composition ratio is based on the total content of only monomers other than a solvent in the entire monomer composition.
- [50] The copolymer according to the present invention may have favorable planarization performance and heat resistance and satisfy all the objects of the present invention only when the content is controlled within the above range in a structural unit thereof. When the copolymer according to the present invention is produced, polymerization is performed using an organic solvent in a content of 50 to 500 parts by weight as a polymerization solvent based on 100 parts by weight of the total content of the monomers.
- [51] A constitution unit derived from (a1) the unsaturated carboxylic acid, unsaturated carboxylic acid anhydride, or the mixture thereof is included in the content of 5 to 40 mol% as a unit constituting the copolymer. When the content is less than 5 mol%, it is difficult to dissolve the copolymer in an alkaline aqueous solution, and when the content is more than 40 mol%, since solubility of the copolymer to the alkaline aqueous solution is excessively increased, it is difficult to control a thickness of a thin film of the copolymer during coating.
- [52] Examples of the monomer may include monocarboxylic acids such as acrylic acids, methacrylic acids, and crotonic acids; dicarboxylic acids such as maleic acids, fumaric acids, citraconic acids, mesaconic acids, and itaconic acids; anhydrides of the dicarboxylic acids; divalent or more, that is, polyvalent mono[(meth)acryloyloxyalkyl]esters of the carboxylic acids such as mono[2-(meth)acryloyloxyethyl] succinates and mono[2-(meth)acryloyloxyethyl] phthalates; and mono(meth)acrylates of a polymer having a carboxyl group and a hydroxyl group at both ends thereof, such as --carboxypolycaprolactone mono(meth)acrylates. Among the examples, the acrylic acids, the methacrylic acids, and the maleic anhydrides are preferably used from the standpoint of copolymerization reactivity, solubility to the alkaline aqueous solution, and ease in buying, and the components are used alone or in combination.
- [53] The aromatic unsaturated monomer as component a2 of the present invention is an aromatic vinyl compound and the content thereof is 5 to 70 mol%. Examples of the

styrene-based monomers such as styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, triethylstyrene, propylstyrene, butylstyrene, hexylstyrene, heptylstyrene, octylstyrene, fluorostyrene, chlorostyrene, bromostyrene, dibromostyrene, iodostyrene, nitrostyrene, acetylstyrene, methoxystyrene, and divinylbenzene, and nitrogen-containing aromatic vinyls such as vinylpyridine and vinylcarbazole.

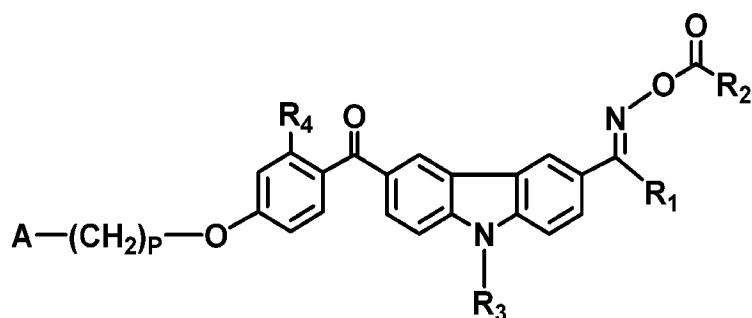
- [54] It is preferable that unsaturated compound a3 having the epoxy group or the oxetane group used in the present invention includes an epoxy-based monomer copolymerized with the unsaturated carboxylic acid, unsaturated carboxylic acid anhydride, or the mixture thereof.
- [55] Examples of the unsaturated compound having the epoxy group may include glycidyl methacrylate, and 4-hydroxybutyl acrylate glycidyl ether, and examples of the unsaturated compound having the oxetanyl group may include 3-ethyl-3-methyl methacrylate oxetane, but are not limited thereto.
- [56] The photosensitive resin composition obtained using the components increases a process margin and heat resistance of a pattern to be formed, and is used alone or in combination.
- [57] It is preferable that component a3 of the present invention is included in the content of 1 to 10 mol% based on the total monomer composition, and when the content is within the above range, copolymerization reactivity and attachment force of the obtained pattern are increased. On the other hand, when the component is obtained in the content of less than 1 mol%, heat resistance of the obtained pattern is reduced, and when the content is more than 10 mol%, storage stability of the copolymer is reduced.
- [58] Specific examples of the monoolefin-based unsaturated compound of component a4 of the present invention may include methyl methacrylate but are not limited thereto. When the component is used in the content of 5 to 50 mol%, the reactivity of the copolymer is controlled and solubility to the alkaline aqueous solution is increased to significantly improve a coating characteristic.
- [59] The copolymer according to the present invention may further include an imide monomer a5 having a polymerizable unsaturated group to additionally ensure stability over a long period of time or prevent defects of the dielectric insulating film during heat treatment at high temperatures in a process, and examples thereof include phenyl-maleimide, cyclohexylmaleimide, benzylmaleimide, N-succinimidyl-3-maleimide benzoate, N-succinimidyl-4-maleimide butyrate, N-succinimidyl-6-maleimide caproate, N-succinimidyl-3-maleimide propionate and N-(9-acridinyl)maleimide.
- [60] Examples of the organic solvent used to prepare the copolymer of the present invention may include ethylene glycol monoalkyl ether acetates such as ethylene glycol monomethyl ether acetate, and ethylene glycol monoethyl ether acetate;

propylene glycol monoalkyl ethers such as propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monopropyl ether, and propylene glycol monobutyl ether; propylene glycol dialkyl ethers such as propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol dipropyl ether, and propylene glycol dibutyl ether; propylene glycol monoalkyl ether acetates such as propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, and propylene glycol monobutyl ether acetate; cellosolves such as ethyl cellosolve and butyl cellosolve; carbitols such as butyl carbitol; ester lactates such as methyl lactate, ethyl lactate, n-propyl lactate, and isopropyl lactate; aliphatic ester carboxylates such as ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, n-amyl acetate, isoamyl acetate, isopropyl propionate, n-butyl propionate, and isobutyl propionate; esters such as 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-ethoxy methyl propionate, 3-ethoxy ethyl propionate, methyl pyruvate, and ethyl pyruvate; aromatic hydrocarbons such as toluene and xylene; ketones such as 2-heptanone, 3-heptanone, 4-heptanone, and cyclohexanone; amides such as N-dimethylformamide, N-methylacetamide, N,N-dimethylacetamide, and N-methylpyrrolidone; and lactones such as γ -butyrolactone, but are not limited thereto. The organic solvents may be used alone or in combination of two or more solvents. The components are typically used in the content of 5 to 70 wt% and preferably 10 to 50 wt% based on the solid concentration.

- [61] Copolymer a used in the present invention has a polystyrene-reduced weight average molecular weight Mw of favorably 5,000 to 50,000 and preferably 7,000 to 30,000. The film obtained using the Mw of less than 7,000 has a reduced developing property and remaining rate or undesirable pattern shape and heat resistance, and when the Mw is more than 30,000, sensitivity is reduced or the pattern shape is undesirable.
- [62] The photopolymerization initiator b initiating polymerization of the crosslinking monomers using the wavelength of visible rays, ultraviolet rays, or far ultraviolet rays used in the present invention includes Chemical Formula 1, and Chemical Formula 1 is represented by the following Chemical Formula 4.

[63] [Chemical Formula 4]

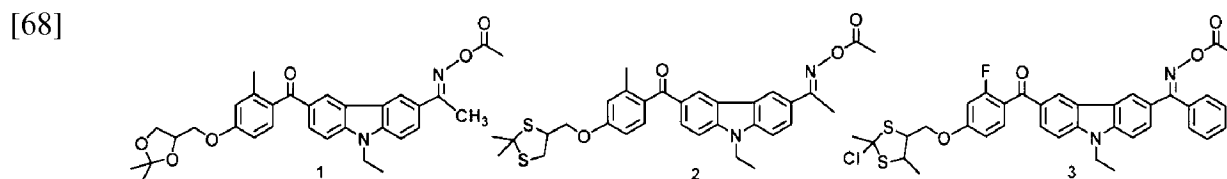
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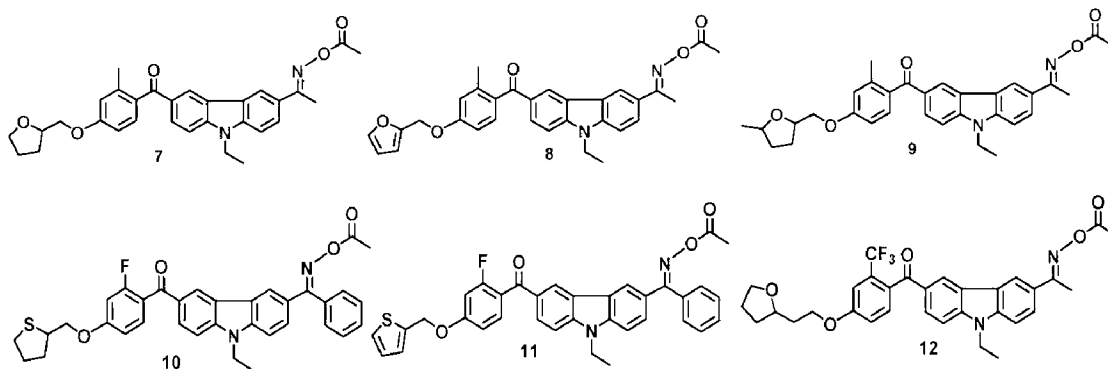


[65] [wherein R₁ to R₄, P and A are the same as defined in Chemical Formula 1]

[66] A substituent including "alkyl" of the present invention and another "alkyl" includes both straight- or branched chained forms, and the term "cycloalkyl" includes a single cycle system and various cyclic hydrocarbons such as substituted or unsubstituted adamantyl or substituted or unsubstituted (C7-C12)bicycloalkyl. The term "aryl" described in the present invention is an organic radical derived from aromatic hydrocarbon from which one hydrogen is removed, and includes a single or fused ring system including appropriately 4 to 7 and preferably 5 or 6 ring atoms in each ring, and also a plurality of aryls connected using a single bond. Specific examples thereof include phenyl, naphthyl, biphenyl, anthryl, indenyl, fluorenyl, phenanthryl, triphenylenyl, pyrenyl, perylenyl, crycenyl, naphthacenyl, and fluoranthenyl, but are not limited thereto. The term "heteroaryl" described in the present invention means an aryl group including one to four heteroatoms selected from B, N, O, S, P, P (= O), Si, and Se as an aromatic cyclic atom and the residual aromatic cyclic atom formed of carbon, 5- or 6-membered monocyclic heteroaryl, and polycyclic heteroaryl condensed with one or more benzene cycles, and may be partially saturated. The heteroaryl group having a heteroatom oxidized or forming four members in a ring includes, for example, a divalent aryl group forming N-oxide or quaternary salt. Specific examples thereof include monocyclic heteroaryl such as furyl, thienyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, thiadiazolyl, isothiazolyl, isoxazolyl, oxazolyl, oxadiazolyl, triazinyl, tetrazinyl, triazolyl, tetrazolyl, furazanyl, pyridyl, pyrazinyl, pyrimidinyl, and pyridazinyl, polycyclic heteroaryl such as benzofuryl, benzothienyl, isobenzofuryl, benzoimidazolyl, benzothiazolyl, benzoisothiazolyl, benzoisoxazolyl, benzooxazolyl, isoindolyl, indolyl, indazolyl, benzothiadiazolyl, quinolyl, isoquinolyl, cinnolyl, quinazolinyl, quinoliziny, quinoxaliny, carbazolyl, phenantridinyl, benzodioxolyl, naphthylidinyl, dibenzofuryl, and dibenzothiophenyl, N-oxides corresponding thereto (for example, pyridyl N-oxide and quinolyl N-oxide), and quaternary salts thereof, but are not limited thereto.

[67] More specific examples of the photopolymerization initiator of Chemical Formula 1 may include the following compounds, but the present invention is not limited by the following compounds.





[69]

[70] The photopolymerization initiator of Chemical Formula 1 may be mixed with other photopolymerization initiators, specifically, one or more initiators selected from the group consisting of an acetophenone-based initiator, a benzophenone-based initiator, a benzoin-based initiator, a benzoyl-based initiator, a xanthone-based initiator, a triazine-based initiator, a halomethyloxadizole-based initiator and a lophine dimer-based initiator may be further included and mixed therewith, and the mixing of the photopolymerization initiators is not limited as long as the photopolymerization initiators are used in the art.

[71] More specific examples of the initiators used in the mixing may include p-dimethylaminoacetophenon, 2-hydroxy-2-methyl-1-phenyl-propane-1-one, benzylidimethylketal, benzophenon, benzoin propyl ether, diethylthioxanthone, 2,4-bis(trichloromethyl)-6-p-methoxyphenyl-s-triazine, 2-trichloromethyl-5-styryl-1,3,4-oxodiazol, 9-phenylacridine, 3-methyl-5-amino-((s-triazine-2-yl)amino)-3-phenylcoumarin, 2-(o-chlorophenyl)-4,5-diphenylimidazolyl dimers, 1-phenyl-1,2-propanedion-2-(o-ethoxycarbonyl)oxime, 1-[4-(phenylthio)phenyl]-octane-1,2-dion-2-(o-benzoyloxime), o-benzoyl-4'-(benzmercapto)benzoyl-hexyl-ketoxime, 2,4,6-trimethylphenylcarbonyl-diphenylphosphonyl oxide, hexafluorophosphor-tri-alkylphenylsulfonium salts, 2-mercaptobenzimidazole, or 2,2'-benzothiazolyl disulfide, but are not limited thereto.

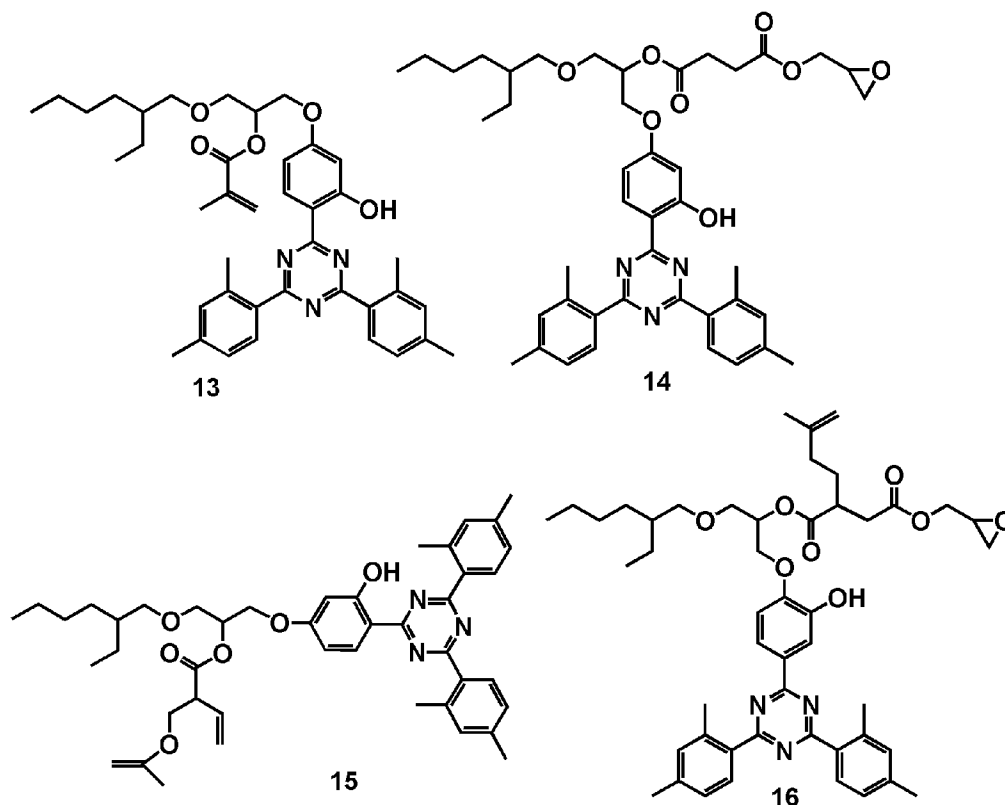
[72] It is preferable that the mixture of photopolymerization initiator b is included in an amount of 0.1 to 10 parts by weight based on 100 parts by weight of the copolymer composition, and that the mixing content of photopolymerization initiator b of Chemical Formula 1 is 40 to 100 parts by weight based on 100 parts by weight of the total content of the photopolymerization initiators. When the content is less than 40 parts by weight, since the degree of curing is reduced, the total content of the photopolymerization initiator needs to increase to maintain a predetermined remaining rate after the composition is applied, accordingly, it is difficult to increase transmittance

and avoid a yellowish shift.

- [73] Ethylenically unsaturated monomer compound c of the present invention may be a (metha)acrylic acid derivative, and specific examples thereof may include 2-hydroxyethyl (metha)acrylate, 2-hydroxypropyl (metha)acrylate, 1,4-butanediol mono(metha)acrylate, carbitol (metha)acrylate, acryloyl morpholine, half ester obtained using a reaction of hydroxyl group-containing (metha)acrylate and a di-carboxylic acid compound, polyethyleneglycol di(metha)acrylate, tripropyleneglycol di(metha)acrylate, trimethylolpropane tri(metha)acrylate, trimethylolpropanepolyethoxy tri(metha)acrylate, glycerinpolypropoxy tri(metha)acrylate, di(metha)acrylate (for example, KAYARAD DPHA, KAYARAD HX-220, and HX-620 manufactured by Nippon Gunpowder, Co., Ltd.) obtained using a reaction of neopentylglycol hydroxypivalate and ϵ -caprolactone, pentaerythritol tetra(metha)acrylate, poly(metha)acrylate obtained using a reaction of dipentaerythritol and ϵ -caprolactone, or dipentaerythritol poly(metha)acrylate.
- [74] Further, it is preferable that the composition ratio of ethylenically unsaturated photopolymerizable monomer compound c be 1 to 150 parts by weight based on 100 parts by weight of the copolymer to maintain a predetermined transmittance, increase an attachment property and surface finish, and ensure favorable workability.
- [75] Compound c may be used alone or in a mixture form of two or more compounds, and the content thereof is preferably 1 to 150 parts by weight and more preferably 50 to 120 parts by weight based on 100 parts by weight of copolymer a.
- [76] Further, functional silane compound d of the present invention may be added to increase adhesion of a protective film to be formed and the substrate. The compound may include a functional silane compound having a reactive substituent group. Examples of the reactive substituent group may include a carboxyl group, a methacryloyl group, an isocyanate group, an epoxy group, an imidazole group, a thiol group, and an amine group.
- [77] Specific examples thereof may include trimethoxysilylbenzoic acid, Υ -methacryloxypropyltrimethoxysilane, vinyltriacetoxysilane, vinyltrimethoxysilane, Υ -isocyanatopropyltriethoxysilane, Υ -glycidoxypropyltrimethoxysilane, Υ -glycidoxypropyltriethoxysilane and β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, but are not limited thereto.
- [78] Component d is used in the content of preferably 0.5 to 30 parts by weight and more preferably 1 to 20 parts by weight based on 100 parts by weight of the copolymer. When the content of component d is more than 30 parts by weight, storage stability of the composition is reduced.
- [79] Further, in the present invention, one or more compounds e selected from Chemical Formulas 2 and 3 and a mixture thereof may be preferably used.

[80] The compounds represented by Chemical Formulas 2 and 3 may be added to increase chemical resistance during a process of TFT-LCD, and specific examples thereof may include the following compounds, but the present invention is not limited by the following compounds.

[81]



[82] The compounds represented by Chemical Formulas 2 and 3 are used in the content of preferably 1 to 20 parts by weight and more preferably 5 to 10 parts by weight based on 100 parts by weight of the copolymer. When the content is less than 1 part by weight, light resistance is insufficient, and when the content is more than 20 parts by weight, sensitivity is reduced to hinder formation of the pattern.

[83] In the present invention, if necessary, a surfactant may be further included to improve a coating ability of the resin composition. Examples of the surfactant may include a fluorine-based surfactant, a silicon-based surfactant, a nonion-based surfactant, and other surfactants.

[84] Examples thereof include fluorine-based and silicon-based surfactants such as BM-1000 and BM-1100 (manufactured by BM CHEMIE, Co., Ltd.), Mega Fac F142D, Mega Fac F172, Mega Fac F173, and Mega Fac F183 (manufactured by Dainippon Ink & Chemicals, Incorporated), Florad FC-135, Florad FC-170 C, Florad FC-430, and Florad FC-431 (manufactured by Sumitomo 3M Limited), SURFLON S-112, SURFLON S-113, SURFLON S-131, SURFLON S-141, SURFLON S-145, SURFLON S-382, SURFLON SC-101, SURFLON SC-102, SURFLON SC-103,

SURFLON SC-104, SURFLON SC-105, and SURFLON SC-106 (manufactured by Asahi Glass, Co., Ltd.), FTOP EF301, FTOP 303, and FTOP 352 (manufactured by Shin Akita Kasei, Co., Ltd.), and SH-28 PA, SH-190, SH-193, SZ-6032, SF-8428, DC-57, and DC-190 (manufactured by Tore Silicon Corporation); nonion-based surfactants such as polyoxyethylene alkyl ethers such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, and polyoxyethylene oleyl ether, polyoxyethylene aryl ethers such as polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, and polyoxyethylene dialkyl esters such as polyoxyethylene dilaurate and polyoxyethylene distearate; organosiloxane polymer KP341 (manufactured by Shin-Etsu Chemical, Co., Ltd.), and (meth)acrylic acid-based copolymer Polyflow Nos. 57 and 95 (manufactured by Kyoeisha Chemical, Co., Ltd.).

- [85] The content of the surfactant added is preferably 5 parts by weight or less and more preferably 0.5 to 2 parts by weight based on 100 parts by weight of the polymer.
- [86] The photosensitive resin composition according to the present invention may be cured to produce the dielectric insulating film, and the dielectric insulating film may be used as an electronic device.
- [87] Further, the dielectric insulating film produced using the photosensitive resin composition of the present invention may be used in a liquid crystal display.
- [88] The transmittance of the photosensitive resin composition including the photoinitiator according to the present invention was 90 to 95%, as a result of measurement at a wavelength of 400 nm through ultraviolet ray/visible ray spectra, and the contrast ratio of black and white of the thermally cured film formed on the glass wafer was measured according to an operation of the fixed and rotating polarizing plate using a contrast ratio measurement apparatus (trademark: CT-1), and the result was 19700 to 22000.
- [89] From the results, it could be seen that the transmittance and the contrast ratio were 10 to 20% higher than those of the known photosensitive resin composition.
- [90] Accordingly, the photosensitive resin composition of the present invention has excellent transmittance and contrast ratio, excellent photosensitive characteristics such as a resolution and a remaining rate, excellent adhesion to a substrate at a low exposure dose, and excellent resistance to ultraviolet rays, prevents a thickness deviation from occurring when a composition layer having a plurality of thicknesses is formed, and has excellent etching process and exposure process margins and light resistance. The photosensitive resin composition having excellent chemical resistance may be used to produce a dielectric insulating film and a liquid crystal display including the dielectric insulating film.
- [91] A better understanding of the present invention may be obtained in light of the following Examples which are set forth to illustrate, but are not to be construed to limit

the present invention.

[92] [Test example]

[93] 1. **Evaluation of the developing property**

[94] The photosensitive resin composition was applied to the silicon wafer using spin coating and then subjected to preliminary baking on the high temperature plate at 105°C for 90 sec to form the dried coat having the thickness of 5 μm .

[95] The composition film was exposed using the aligner (trademark MA6) emitting the wavelength of 200 to 450 nm at the intensity of about 100 mJ based on 365 nm for a predetermined time, and the developing solution including 2.38 wt% of the tetramethylammonium hydroxide aqueous solution was sprayed using the spray nozzle at 23°C to develop the composition film. The obtained exposed film was heated in the convection oven at 220°C for 1 hour to obtain the thermally cured film. The developing property was evaluated using the shape of the developed fine pattern.

[96] 2. **Evaluation of the remaining rate**

[97] The thickness of the thermally cured film to the initial coat thickness (5 μm) of the thermally cured film was evaluated using the contact type of film thickness evaluating apparatus (Surface-profiler, trademark: ALPHA-STEP IQ) and the remaining rate was expressed as a percentage.

[98] 3. **Resolution**

[99] The image of the thermally cured film was observed using the optical microscope, and the line width (μm) of the resolved minimum contact hole was expressed by the resolution.

[100] 4. **Formation of the step difference**

[101] The film thickness of the exposed region was measured using the halftone mask having a plurality of transmitting regions of the thermally cured film to check the region having the thickness of 1.3 μm after the development. The case where the thickness of the halftone region was 1.3 μm was evaluated by o, and the case of more than 30% was evaluated by x.

[102] 5. **Shape of the pattern**

[103] The shape of the pattern formed in the contact hole having the line width of 10 μm of the thermally cured film was observed using the scanning microscope to evaluate according to the following criteria.

[104] A : The rectangle is favorable and there is no tailing

[105] B : The rectangle is favorable but tailing slightly occurs

[106] C : Poor rectangle or no resolution

[107] 6. **Evaluation of the transmittance**

[108] The transmittance of the thermally cured film formed on the glass wafer instead of the silicon wafer was measured at the wavelength of 400 nm using measurement of an

ultraviolet ray/visible ray spectra, and a comparison was performed.

[109] 7. **Evaluation of the contrast ratio**

[110] The contrast ratio of black and white of the thermally cured film formed on the glass wafer was measured according to operation of the fixed and rotating polarizing plate using the contrast ratio measurement apparatus (trademark: CT-1).

[111] 8. **Evaluation of adhesion**

[112] The cross-cut test was performed using the substrate produced in the evaluation of the photosensitive properties according to ASTM D3359, and attachment force was evaluated according to the following criteria.

[113] OB : Broken into flakes by 65% or more

[114] 1B : The end and the lattice of the cut portion are removed and the removal area is 35 to 65%

[115] 2B : The end and a portion of the lattice of the cut portion are removed and the removal area is 15 to 35%

[116] 3B : A small region of the lattice of the cut portion is removed and the removal area is 5 to 15%

[117] 4B : A portion of the lattice of the cut portion is removed and the removal area is 5% or less

[118] 5B : The end of the cut portion is rounded and the lattice is not removed

[119] 9. **Evaluation of light fastness**

[120] The cured film was formed using the same procedure as the example, except that the entire surface thereof was exposed using the aligner (trademark: MA6) emitting the wavelength of 200 to 450 nm based on 365 nm at the intensity of about 50 J for a pre-determined time without the photomask, and a change in transmittance at 300 to 400 nm was evaluated (o 1 to 3%, Δ 3 to 5%, and x 5 to 10%).

[121] 10. **Chemical resistance**

[122] The thermally cured film was immersed in the 20 wt% hydrochloric acid at 40°C for 20 min to perform evaluation according to the following criteria.

[123] o : The hole and the surface roughness (unevenness) are not found when the surface is observed using the optical microscope

[124] x : The hole or the surface roughness (unevenness) is found when the surface is observed using the optical microscope, or cloudiness is found by the naked eye

[125] 11. **Storage stability**

[126] The composition solution obtained in the example was stored in the low temperature incubator at 23°C, and a change in viscosity of the composition solution was measured.

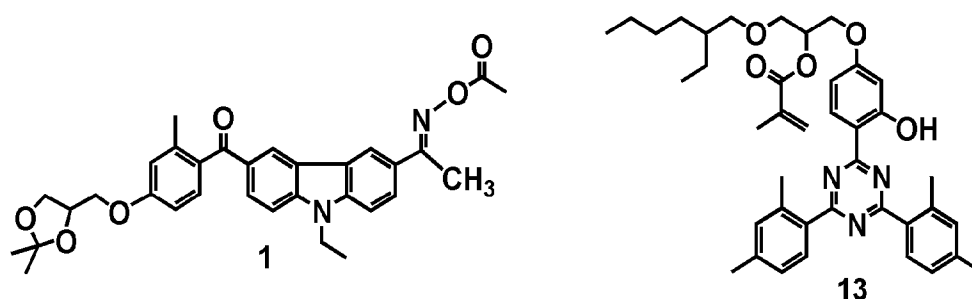
[128] [Preparation example 1]

[129] 100 parts by weight of the monomer mixture including styrene, methyl methacrylate, methacrylic acid, and glycidyl methacrylate at the composition ratio of 50 : 20 : 25 : 5 (mol%) was dissolved in 150 parts by weight of the methyl 3-methoxypropionate solvent while 4 parts by weight of azobisisobutyronitrile was used as the polymerization initiator, and subjected to solution polymerization at 65°C for 6 hours to obtain copolymer A having the weight average molecular weight of 15,300.

[130] [Example 1]

[131] 90 parts by weight of KAYARAD DPHA, 2.5 parts by weight of the photopolymerization initiator of the following compound 1, 1 part by weight of γ -glycidoxypropyltriethoxysilane, and 3 parts by weight of the following compound 13 were mixed based on 100 parts by weight of photopolymerizable copolymer A, and filtered using the filter having a hole diameter of 0.5 μm to prepare the photosensitive resin composition, physical properties described in the test example were evaluated using the photosensitive resin composition, and the results are described in the following Table 1.

[132]



[133] (compound 1) (compound 13)

[134] [Example 2]

[135] The same procedure as example 1 was repeated except that 2 parts by weight of compound 1 and 1 part by weight of 2,4-bis(trichloromethyl)-6-p-methoxyphenyl-s-triazine were mixed and used instead of the photopolymerization initiator of example 1, and the results are described in the following Table 1.

[136] [Example 3]

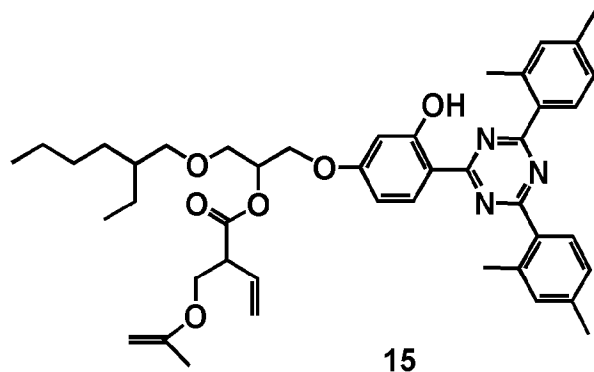
[137] The same procedure as example 1 was repeated except that 2 parts by weight of compound 1 and 2 part by weight of 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone were mixed and used instead of the photopolymerization initiator of example 1, and the results are described in the following Table 1.

[138] [Example 4]

[139] The same procedure as example 1 was repeated except that compound 15 was used

instead of compound 13 of example 1, and the results are described in the following Table 1.

[140]



[141] (compound 15)

[142] [Example 5]

[143] The same procedure as example 2 was repeated except that compound 15 was used instead of compound 13 of example 2, and the results are described in the following Table 1.

[144] [Example 6]

[145] The same procedure as example 3 was repeated except that compound 15 was used instead of compound 13 of example 3, and the results are described in the following Table 1.

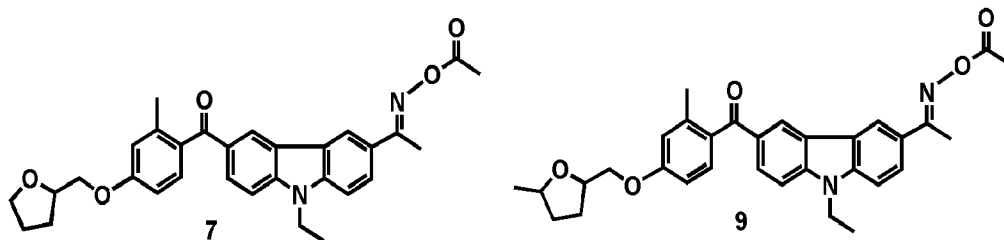
[146] [Example 7]

[147] The same procedure as example 1 was repeated except that compound 7 was used instead of compound 1 as the photopolymerization initiator of example 1, and the results are described in the following Table 1.

[148] [Example 8]

[149] The same procedure as example 1 was repeated except that compound 9 was used instead of compound 1 as the photopolymerization initiator of example 1, and the results are described in the following Table 1.

[150]



[151] (compound 7) (compound 9)

[152] [Comparative Example 1]

[153] The same procedure as example 2 was repeated except that compound 1 of the photopolymerization initiator of example 2 was not used and 5 parts by weight of 2,4-bis(trichloromethyl)-6-p-methoxyphenyl-s-triazine was used, and the results are

described in the following Table 1.

[154] [Comparative Example 2]

[155] The same procedure as example 5 was repeated except that compound 1 of the photopolymerization initiator of example 5 was not used and 5 parts by weight of 2,4-bis(trichloromethyl)-6-p-methoxyphenyl-s-triazine was used, and the results are described in the following Table 1.

[156] [Comparative Example 3]

[157] The same procedure as example 3 was repeated except that compound 1 of the photopolymerization initiator of example 3 was not used and 7 parts by weight of 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl) phenyl]-1-butanone was used, and the results are described in the following Table 1.

[158] [Comparative Example 4]

[159] The same procedure as example 6 was repeated except that compound 1 of the photopolymerization initiator of example 6 was not used and 7 parts by weight of 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl) phenyl]-1-butanone was used, and the results are described in the following Table 1.

[160] [Table 1] Comparison of physical property data

[161]

	Example								Comparative Example			
	1	2	3	4	5	6	7	8	1	2	3	4
Remaining rate (%)	80	80	80	80	80	80	80	80	80	80	80	80
Resolution (μm)	10	10	10	10	10	10	10	10	10	10	12	11
Forming of step difference	○	○	○	○	○	○	○	○	○	○	○	○
Pattern shape	A	A	A	A	A	A	A	A	A	A	A	A
Transmittance (%)	92	92	91	91	91	90	92	92	81	82	79	80
Contrast ratio	21000	19960	19870	20900	19830	19780	20982	20956	18504	18430	18405	18320
Adhesion	5B	5B										

- [162] From Table 1, it can be seen that when the photopolymerization initiator of compound 1 according to the present invention was used alone or in a mixture form, the photosensitive resin composition showed the same remaining rate using the photopolymerization initiator even in a relatively small amount to increase the transmittance and contrast ratio while the thickness of the thermally cured film was maintained as compared to the photosensitive resin composition when the photopolymerization initiator of compound 1 was not used.

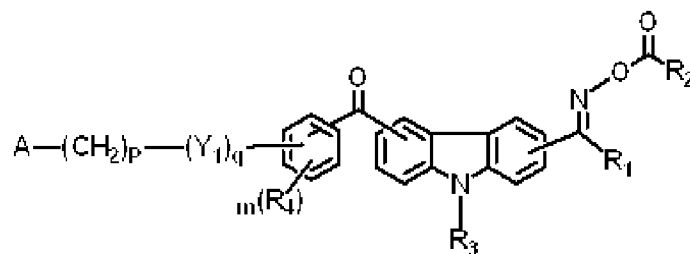
Claims

[Claim 1]

A photosensitive resin composition comprising:

- a) 100 parts by weight of a copolymer formed using polymerization of 5 to 40 mol% of an unsaturated carboxylic acid, an unsaturated carboxylic acid anhydride, or a mixture thereof, 5 to 70 mol% of an aromatic unsaturated monomer, 1 to 10 mol% of an unsaturated compound having an epoxy or an oxetane group selected from glycidyl methacrylate, 4-hydroxybutyl acrylate triglycidyl ether, 3-ethyl-3-methyl methacrylate oxetane or a mixture thereof, and 5 to 50 mol% of methyl methacrylate;
- b) 0.1 to 10 parts by weight of a photopolymerization initiator comprising a compound represented by the following Chemical Formula 1:

[Chemical Formula 1]



wherein

R_1 to R_4 are independently hydrogen, deuterium, halogen, substituted or unsubstituted (C1-C12)alkyl, substituted or unsubstituted (C2-C12)alkenyl, substituted or unsubstituted halo(C1-C12)alkyl, substituted or unsubstituted (C6-C12)aryl, substituted or unsubstituted (C3-C12)cycloalkyl, substituted or unsubstituted (C1-C12)alkoxy or (C1-C12)ester;

A is substituted or unsubstituted (C3-C12)heteroaryl or substituted or unsubstituted 5- to 7-membered heterocycloalkyl;

R_1 to R_4 and A are independently further substituted with one or more substituent groups selected from a group consisting of halogen, (C1-C12)alkyl substituted or unsubstituted with halogen, (C2-C12)alkenyl, (C6-C12)aryl, (C3-C12)cycloalkyl, (C1-C12)alkoxy, carboxyl, nitro and hydroxyl;

Y_1 is -O-, -S- or -Se-;

m is an integer of 0 to 4, and when m is the integer of 2 or more, R_4 s may be the same or different;

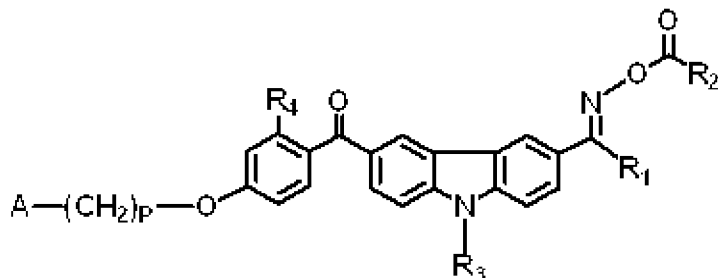
(C1-C12)alkyl, and

R₁₁ is (C1-C12)alkylene.

[Claim 2]

The photosensitive resin composition of claim 1, wherein Chemical Formula 1 is represented by the following Chemical Formula 4:

[Chemical Formula 4]

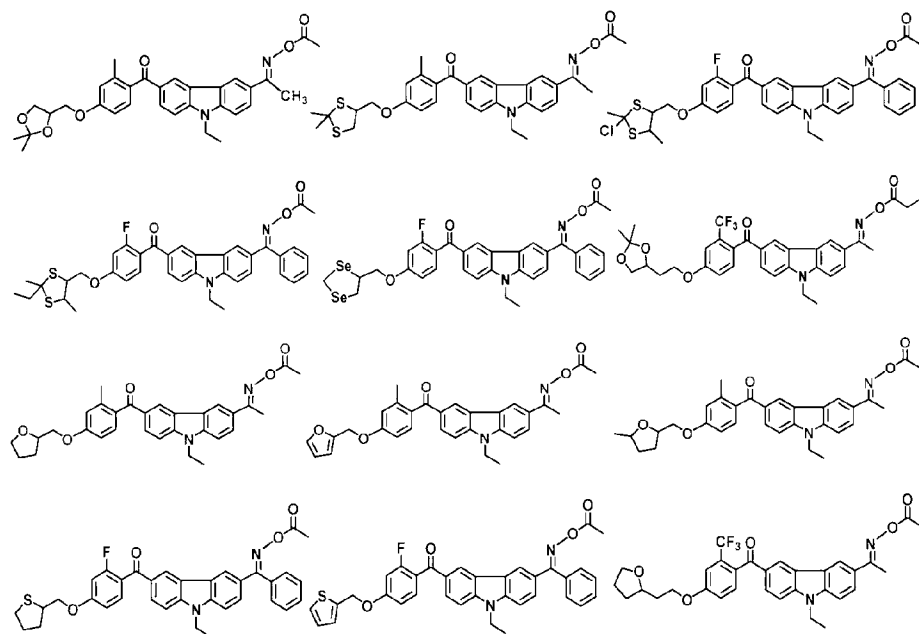


wherein

R₁ to R₄, P and A are the same as defined in Chemical Formula 1.

[Claim 3]

The photosensitive resin composition of claim 2, which Chemical Formula 4 is selected from the following compounds:



[Claim 4]

The photosensitive resin composition of claim 1, wherein the photopolymerization initiator further comprises one or more initiators selected from the group consisting of an acetophenone-based initiator, benzophenone-based initiator, a benzoin-based initiator, a benzoyl-based initiator, a xanthone-based initiator, a triazine-based initiator, a halomethyloxadiazole-based initiator and a lophine dimer-based initiator.

[Claim 5]

The photosensitive resin composition of claim 1, wherein the copolymer further comprises 0.5 to 10 mol% of an imide monomer

having an unsaturated group.

- [Claim 6] The photosensitive resin composition of claim 5, wherein the imide monomer is one or more selected from the group consisting of phenylmaleimide, cyclohexylmaleimide, benzylmaleimide, N-succinimidyl-3-maleimide benzoate, N-succinimidyl-4-maleimide butyrate, N-succinimidyl-6-maleimide caproate, N-succinimidyl-3-maleimide propionate and N-(9-acridinyl)maleimide.
- [Claim 7] The photosensitive resin composition of claim 1, wherein the functional silane compound is a silane compound having a reactive substituent group selected from a carboxyl group, a methacryloyl group, an isocyanate group, an epoxy group, an imidazole group, a thiol group or an amine group.
- [Claim 8] The photosensitive resin composition of claim 7, wherein the functional silane compound is one or more selected from the group consisting of trimethoxysilylbenzoic acid, Υ -methacryloxypropyltrimethoxysilane, vinyltriacetoxysilane, vinyltrimethoxysilane, Υ -isocyanatopropyltriethoxysilane, Υ -glycidoxypropyltrimethoxysilane, Υ -glycidoxypropyltriethoxysilane and β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane.
- [Claim 9] A dielectric insulating film prepared by curing the photosensitive resin composition of any one of claims 1 to 8.
- [Claim 10] An electronic device having the dielectric insulating film of claim 9.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2011/008453

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C08F 2/46 (2006.01) **G03F 7/004** (2006.01) **G03F 7/033** (2006.01)
C08G 2/02 (2006.01) **G03F 7/027** (2006.01)
C08L 33/10 (2006.01) **G03F 7/028** (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC: IPC marks—(IC/EC C08F2/46, G03F7/004, G03F7/027, G03F7/028, G03F7/033, C08L33/10, C08G2/02) & keywords: photosensitive, resin, polymer, acrylic, acrylates, epoxy, styrene, silane and like terms; Esp@cenet, Google Patents, Patent Lens, ScienceDirect & Google Scholar (including NPL) using similar keywords.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010/0261815 A1 (CHO et al.) 14 October 2010 Abstract; paragraph [0069]; claims 14-15	1-10
A	US 2008/0233515 A1 (ITO et al.) 25 September 2008 Abstract; paragraphs [0001], [0006], [0010], [0027]-[0039], [0063], [0145]-[0147], [0172]-[0178], [0211]-[0219]; claims 1-6	1-10
A	US 7267929 B2 (TAKAHASHI et al.) 11 September 2007 Abstract; col. 1, lines 11-16; col. 3, line 20-col. 4, line 58; col. 5, line 11-col. 6, line 52; col. 11, line 25 –col. 12, line 53; col. 14, lines 15-19; claims 1-2	1-10



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2011/008453

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.