



(51) International Patent Classification:

G03F 7/027 (2006.01)

G03F 7/004 (2006.01)

(21) International Application Number:

PCT/CN2019/089957

(22) International Filing Date:

04 June 2019 (04.06.2019)

(25) Filing Language:

English

(26) Publication Language:

English

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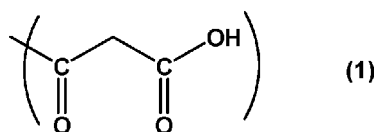
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: CARBOXY GROUP-CONTAINING COMPOUND, CARBOXY GROUP-CONTAINING RESIN, AND PHOTSENSITIVE RESIN COMPOSITION



(57) Abstract: Disclosed is a carboxy group-containing compound having a (meth) acryloyl group and the group represented by the following formula (1); a carboxy group-containing resin having a structural unit based on the carboxy group-containing compound; and a photosensitive resin composition containing the carboxy group-containing resin.



CARBOXY GROUP-CONTAINING COMPOUND, CARBOXY GROUP-CONTAINING RESIN, AND PHOTSENSITIVE RESIN COMPOSITION

DESCRIPTION

Technical Field

The present disclosure relates to a carboxy group-containing compound, a carboxy group-containing resin, and a photosensitive resin composition.

Background Art

In recent years, with the advancement of performance of electronic devices (miniaturization, weight reduction and multifunctionalization), the increase in density of multilayer printed wiring boards by the increase in the number of circuit layers and miniaturization of wiring has progressed. Particularly, the increase in density of semiconductor package substrates such as BGA (ball grid array) and CSP (chip size package) on which semiconductor chips are mounted is remarkable, not only the miniaturization of the wiring but also thinning of the insulating film and further reduction in diameter of a via (also referred to as via hole) for interlayer connection have been required.

An example of a method for manufacturing the printed wiring board adopted conventionally includes the method for manufacturing the multilayer printed wiring board by the buildup method which laminates and forms an interlayer insulation layer and a conductor

circuit layer one by one (for example, refer to Patent Literature 1). On the other hand, along with the miniaturization of circuits, a semi-additive method of forming circuits by plating has become mainstream in manufacturing of multilayer printed wiring boards in recent years.

Citation List

Patent Literature

[Patent Literature 1] JP 07-304931 A

Summary of Invention

Technical Problem

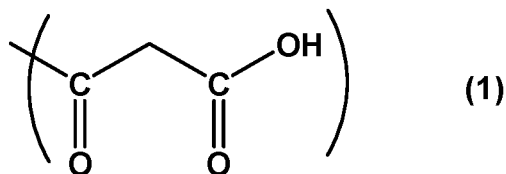
A photosensitive resin composition is used as a material for forming an interlayer insulating layer. In order to improve the alkali developability in forming a resin pattern, the photosensitive resin composition generally contains a component having an acidic group such as a carboxy group. With miniaturization of circuits, multilayer printed wiring boards are required to be excellent in low dielectric characteristics (low dielectric constant and low dielectric loss tangent). However, when a carboxy group is present in a cured film formed by curing the resin pattern, the low dielectric characteristics required for multilayer printed wiring boards tend to be difficult to be obtained. Therefore, the photosensitive resin composition is required to have both alkali developability and low dielectric characteristics.

An object of the present invention is to provide a carboxy group-containing compound, a carboxy group-containing resin, and a photosensitive resin composition capable of forming a cured film having excellent alkali developability and exhibiting low dielectric

characteristics.

Solution to Problem

One aspect of the present invention relates to a carboxy group-containing compound having a (meth) acryloyl group and a group represented by the following formula (1).



The present invention relates, in another aspect, to a carboxy group-containing resin having a structural unit based on the above carboxy group-containing compound.

The present invention relates, in another aspect, to a photosensitive resin composition comprising an alkali-soluble resin, a photopolymerizable compound having an ethylenically unsaturated group, and a photopolymerization initiator, wherein the alkali-soluble resin includes the above carboxy group-containing resin.

Advantageous Effects of Invention

The present invention can provide a carboxy group-containing compound, a carboxy group-containing resin, and a photosensitive resin composition capable of forming a cured film having excellent alkali developability and exhibiting low dielectric characteristics.

Brief Description of Drawings

Figure 1 is a schematic view showing one aspect of a manufacturing process of a multilayer printed wiring board according to the present embodiments.

Description of Embodiments

Hereinafter, embodiments of the present invention will be described in detail. However, the present invention is not limited to the following embodiments

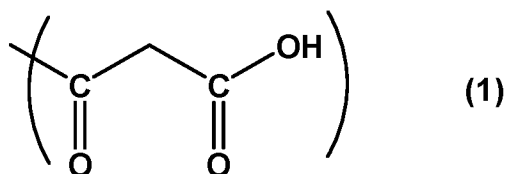
In the present description, the term "step" includes not only an independent step, but also a step that cannot be clearly distinguished from another step as long as the intended effect of the step is achieved. The numerical range shown using "to" shows the range which includes the numerical values described before and after "to" as the minimum value and the maximum value, respectively. The term "layer" includes not only a structure of a shape formed on the entire surface but also a structure of a shape formed in part when it is observed as a plan view. "(Meth)acrylic acid" means at least one of "acrylic acid" and "methacrylic acid" corresponding thereto. The same applies to other similar expressions such as (meth)acryloyl.

In the present description, when a plurality of substances corresponding to each component are present, unless otherwise specified, the amount of each component in the photosensitive resin composition means the total amount of the plurality of the substances present in the photosensitive resin composition. In the numerical range described in the present description, the upper limit value or the lower limit value of the numerical range may be replaced with the value shown in Examples. Moreover, the aspect which arbitrarily combines the matters described in this description is also included in this invention. In the present description, "solids" refers to non-volatile components excluding volatiles such as water and solvents contained in the photosensitive resin composition. That is, "solids" refers to

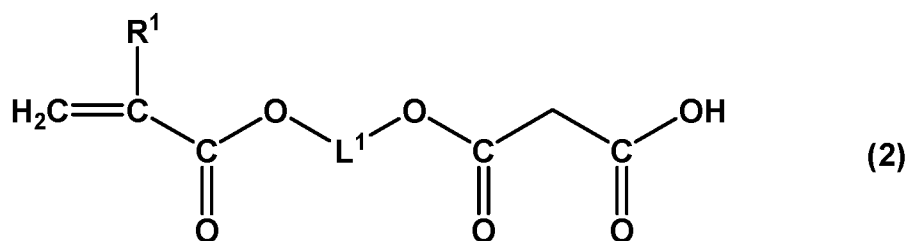
components other than the solvent which remains without volatilization in drying of the photosensitive resin composition described below, and also includes liquid, millet jelly-like, and wax components at room temperature (25°C).

[Carboxy group-containing compound]

The carboxy group-containing compound according to the present embodiments has a (meth)acryloyl group and a group represented by the following formula (1). The group represented by formula (1) may be referred to as a β -ketocarboxy group.



The above carboxy group-containing compound may be a compound having a structure represented by the following formula (2).



In the formula, R^1 represents a hydrogen atom or a methyl group and L^1 represents an alkylene group having 1 to 10 carbon atoms. From the viewpoint of improving the alkali solubility, L^1 is preferable to be an alkylene group having 1 to 6 carbon atoms, more preferable to be an alkylene group having 1 to 4 carbon atoms, and still more preferable to be an alkylene group having 2 or 3 carbon atoms.

The compound represented by formula (2) can be obtained, for example, by reacting a (meth)acryloyl compound having a hydroxyl

group with malonic acid. Examples of the (meth)acryloyl compound having a hydroxyl group include hydroxyalkyl (meth)acrylates such as hydroxymethyl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxypentyl (meth)acrylate, hydroxyhexyl (meth)acrylate, hydroxyheptyl (meth)acrylate, hydroxyoctyl (meth)acrylate, hydroxynonyl (meth)acrylate, and hydroxydecyl (meth)acrylate.

[Carboxy group-containing resin]

The carboxy group-containing resin according to the present embodiments is a resin having a structural unit based on the above carboxy group-containing compound. The carboxy group-containing resin is excellent in the solubility in an alkali aqueous solution because of having the group represented by the above formula (1). The present inventor has found that the carboxy group-containing resin according to the present embodiments is heat-treated at a temperature of 140°C or more, eliminating at least a part of the carboxy group from the group represented by formula (1) to improve low dielectric characteristics after the heat treatment.

From the viewpoint of further improving the solubility in an alkali aqueous solution, the content of the carboxy group-containing compound may be 5% by mass or more, 8% by mass or more, 10% by mass or more, or 12% by mass or more, based on the total amount of the monomers constituting the carboxy group-containing resin. From the viewpoint of further improving the low dielectric characteristics, the content of the carboxy group-containing compound may be 90% by mass or less, 85% by mass or less, 80% by mass or less, or 75% by

mass or less.

From the viewpoint of further improving the low dielectric characteristics, the carboxy group-containing resin may further have a structural unit based on an aromatic vinyl compound. Examples of the aromatic vinyl compound include styrene, α -methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, o-methoxystyrene, m-methoxystyrene, and p-methoxystyrene.

The carboxy group-containing resin according to the present embodiments may further have a structural unit based on a (meth)acrylate. The (meth)acrylate may be a compound having an alkyl group or a hydroxyalkyl group.

Examples of the (meth)acrylate include alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, nonyl (meth)acrylate, and decyl (meth)acrylate; and hydroxyalkyl (meth)acrylates such as hydroxymethyl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxypentyl (meth)acrylate, hydroxyhexyl (meth)acrylate, hydroxyheptyl (meth)acrylate, hydroxyoctyl (meth)acrylate, hydroxynonyl (meth)acrylate, and hydroxydecyl (meth)acrylate.

From the viewpoint of improving heat resistance, the weight average molecular weight (Mw) of the carboxy group-containing resin may be 1000 or more, 2000 or more, or 3000 or more. From the viewpoint of being suitably developable, Mw of the carboxy

group-containing resin may be 30000 or less, 25000 or less, or 18000 or less. Mw can be measured, for example, by gel permeation chromatography (GPC) using a standard polystyrene calibration curve.

[Photosensitive resin composition]

The photosensitive resin composition according to the present embodiments contains (A) an alkali-soluble resin (hereinafter sometimes referred to as "component (A)"), and (B) a photopolymerizable compound having an ethylenically unsaturated group (hereinafter sometimes referred to as "component (B)"), and (C) a photopolymerization initiator (hereinafter sometimes referred to as "component (C)"). Hereinafter, each component which the photosensitive resin composition may contain is explained in detail.

<(A) Alkali-soluble resin>

The component (A) is a resin soluble in an alkali aqueous solution. The alkali aqueous solution is an alkaline aqueous solution such as tetramethyl ammonium hydroxide (TMAH) aqueous solution, metal hydroxide aqueous solution, metal carbonate aqueous solution, and organic amine aqueous solution. The solubility of the component (A) in an alkali aqueous solution can be confirmed, for example, as follows.

A substrate such as a silicon wafer is spin-coated with a varnish obtained by dissolving the component (A) in an arbitrary solvent to form a coating film having about 5 μm thickness. This is immersed in any of TMAH aqueous solution, metal hydroxide aqueous solution, metal carbonate aqueous solution, or organic amine aqueous solution at 20 to 25°C. As a result, when the coating film can be dissolved

uniformly, the component (A) can be regarded as soluble in an alkaline aqueous solution.

The component (A) includes the carboxy group-containing resin according to the present embodiments (hereinafter sometimes referred to as "component (A1)"). The component (A) includes, as the component (A1), a resin having a structural unit based on a carboxy group-containing compound having a (meth)acryloyl group and a group represented by the above formula (1). The component (A1) is contained, thereby improving the solubility of the photosensitive resin composition in an alkali aqueous solution and allowing to form a resin pattern excellent in resolution. The heat treatment of the resin pattern can provide the cured film excellent in the low dielectric characteristics. The component (A1) may be composed of only one resin, or may be composed of two or more resins.

The component (A) may further include an alkali-soluble resin other than the component (A1). The alkali-soluble resin may be a resin having a phenolic hydroxyl group. Examples of the resin having a phenolic hydroxyl group include polyhydroxystyrene, hydroxystyrene-based resins such as copolymers including hydroxystyrene as a monomer unit, phenolic resins, polybenzoxazole precursors such as poly(hydroxyamide), poly(hydroxyphenylene)ether, and polynaphthol.

From the viewpoint of being suitably developable, the acid value of the component (A) may be 30 mg KOH/g or more, 40 mg KOH/g or more, or 50 mg KOH/g or more, and from the viewpoint of improving the adhesion (developer resistance) of the cured product of

the photosensitive resin composition, it may be 250 mg KOH/g or less, 230 mg KOH/g or less, or 200 mg KOH/g or less. The acid value of the component (A) can be adjusted by the content of a structural unit based on the carboxy group-containing compound.

From the viewpoint of further improving the alkali developability, the content of the component (A) may be 50 parts by mass or more, 60 parts by mass or more, or 70 parts by mass or more, per 100 parts by mass in total of the component (A), the component (B), and the component (C). From the viewpoint of improving sensitivity and resolution, the content of the component (A) may be 95 parts by mass or less, 90 parts by mass or less, or 85 parts by mass or less.

<(B) Photopolymerizable compound having ethylenically unsaturated group>

The component (B) is a compound having a functional group having an ethylenically unsaturated bond such as a vinyl group, an allyl group, a propargyl group, a butenyl group, an ethynyl group, a phenyl ethynyl group, a maleimide group, a nadimide group, and a (meth)acryloyl group as a functional group which exhibits photopolymerization. The component (B) is not particularly limited as long as it is a compound having one or more ethylenically unsaturated groups. As a functional group which exhibits photopolymerization, a (meth)acryloyl group is preferable. The component (B) may be used singly or in combination of two or more.

Examples of the photopolymerizable compound having one ethylenically unsaturated group include (meth)acrylic acids, alkyl (meth)acrylates, and phthalic acid-based (meth)acrylate compounds.

Examples of the alkyl (meth)acrylate include methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, and hydroxyethyl (meth)acrylate.

From the viewpoint of suitably improving resolution, adhesion, and resist shape, the component (B) may include a phthalic acid-based compound. Examples of the phthalic acid-based compound include γ -chloro- β -hydroxypropyl- β' -(meth)acryloyloxyethyl-o-phthalate (aka: 3-chloro-2-hydroxypropyl-2-(meth)acryloyloxyethylphthalate), β -hydroxyethyl- β' -(meth)acryloyloxyethyl-o-phthalate, and β -hydroxypropyl- β' -(meth)acryloyloxyethyl-o-phthalate.

Examples of the photopolymerizable compound having two ethylenically unsaturated groups include polyethylene glycol di(meth)acrylate, trimethylolpropane di(meth)acrylate, polypropylene glycol di(meth)acrylate, 2,2-bis(4-(meth)acryloxypolyethoxypolypropoxyphenyl)propane, bisphenol A diglycidyl ether di(meth)acrylate, and alkylene oxide-modified bisphenol A di(meth)acrylate.

From the viewpoint of improving alkali developability and resolution, the component (B) may include an alkylene oxide-modified bisphenol A di(meth)acrylate. Examples of the alkylene oxide modified bisphenol A di(meth)acrylate include 2,2-bis(4-((meth)acryloxypolyethoxy)phenyl)propane (2,2-bis(4-((meth)acryloxypentaethoxy)phenyl)propane or the like), 2,2-bis(4-((meth)acryloxypolypropoxy)phenyl)propane, 2,2-bis(4-((meth)acryloxypolybutoxy)phenyl)propane, and 2,2-bis(4-((meth)acryloxypolyethoxypolypropoxy)phenyl)propane.

Examples of the photopolymerizable compound having 3 or more ethylenically unsaturated groups include (meth)acrylate having a skeleton derived from trimethylolpropane such as trimethylolpropane tri(meth)acrylate; (meth)acrylate having a skeleton derived from tetramethylolmethane such as tetramethylolmethane tri(meth)acrylate and tetramethylolmethane tetra(meth)acrylate; (meth)acrylate having a skeleton derived from pentaerythritol such as pentaerythritol tri(meth)acrylate and pentaerythritol tetra(meth)acrylate; (meth)acrylate having a skeleton derived from dipentaerythritol such as dipentaerythritol penta(meth)acrylate and dipentaerythritol hexa(meth)acrylate; (meth)acrylate having a skeleton derived from ditrimethylolpropane such as ditrimethylolpropane tetra(meth)acrylate; and (meth)acrylate having a skeleton derived from diglycerin. Among them, from the viewpoint of enhancing the chemical resistance after curing (exposure) and increasing the difference in developer resistance between the exposed area and the unexposed area, (meth)acrylate compounds having a skeleton derived from dipentaerythritol are preferable and dipentaerythritol penta(meth)acrylate is more preferable.

From the viewpoint of improving the alkali developability of the unexposed area of the photosensitive resin composition and improving the adhesive strength of the exposed area, the component (B) may include a photopolymerizable compound having an ethylenically unsaturated group and an acid-modified group. Examples of the acidic group to be modified include a carboxy group, a sulfo group, and a phenolic hydroxyl group, and among them, the carboxy group is preferable.

Examples of the photopolymerizable compound having an ethylenically unsaturated group and an acidic group include styrene-maleic acid-based resin and epoxy derivative containing an acid-modified vinyl group.

The styrene-maleic acid-based resin is a hydroxyethyl (meth)acrylate modified product of a styrene-maleic anhydride copolymer. The epoxy derivative containing an acid-modified vinyl group is a compound obtained by reacting a compound having epoxy resin modified with vinyl group-containing organic acid with saturated or unsaturated group-containing polybasic acid anhydride.

The epoxy resin is not particularly limited as long as it is a compound having two or more epoxy groups. Examples of the epoxy resin include a glycidyl ether type epoxy resin, a glycidylamine type epoxy resin, and a glycidyl ester type epoxy resin. Among them, from the viewpoint of reliability in mounting semiconductor chips, a bisphenol novolac type epoxy resin is preferable and a bisphenol F novolac type epoxy resin is more preferable.

The vinyl group-containing organic acid is not particularly limited, and may be a vinyl group-containing monocarboxylic acid. Examples of the vinyl group-containing monocarboxylic acid include acrylic acid derivatives such as acrylic acid, a dimer of acrylic acid, methacrylic acid, β -furfurylacrylic acid, β -styrylacrylic acid, cinnamic acid, crotonic acid, and α -cyanocinnamic acid; a half ester compound which is a reaction product of a hydroxyl group-containing acrylate and a dibasic acid anhydride; and a half ester compound which is a reaction product of a vinyl group-containing monoglycidyl ether or a vinyl

group-containing monoglycidyl ester with a dibasic acid anhydride.

<(C) Photopolymerization initiator>

The component (C) is not particularly limited as long as it is a component capable of polymerizing the component (B), and can be appropriately selected from commonly used photopolymerization initiators. The component (C) can be used singly or in combination of two or more.

Examples of the component (C) include benzoin compounds such as benzoin, benzoin methyl ether, and benzoin isopropyl ether; acetophenone compounds such as acetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-2-phenylacetophenone, 1,1-dichloroacetophenone, 1-hydroxycyclohexyl phenyl ketone, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-1-propanone, and N,N-dimethylaminoacetophenone; anthraquinone compounds such as 2-methyl anthraquinone, 2-ethyl anthraquinone, 2-tert-butyl anthraquinone, 1-chloroanthraquinone, 2-amyl anthraquinone, and 2-aminoanthraquinone; thioxanthone compounds such as 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2-chlorothioxanthone, and 2,4-diisopropylthioxanthone; ketal compounds such as acetophenone dimethyl ketal and benzyl dimethyl ketal; benzophenone compounds such as benzophenone, methylbenzophenone, 4,4'-dichlorobenzophenone, 4,4'-bis(diethylamino)benzophenone, Michler's ketone, and 4-benzoyl-4'-methyl diphenyl sulfide; imidazole compounds such as

2-(o-chlorophenyl)-4,5-diphenylimidazole dimer,
 2-(o-chlorophenyl)-4,5-di(m-methoxyphenyl)imidazole dimer,
 2-(o-fluorophenyl)-4,5-diphenylimidazole dimer,
 2-(o-methoxyphenyl)-4,5-diphenylimidazole dimer,
 2-(p-methoxyphenyl)-4,5-diphenylimidazole dimer,
 2,4-di(p-methoxyphenyl)-5-phenylimidazole dimer, and
 2-(2,4-dimethoxyphenyl)-4,5-diphenylimidazole dimer; acridine
 compounds such as 9-phenylacridine and 1,7-bis(9,9'-acridinyl)heptane;
 acyl phosphine oxide compounds such as 2,4,6-trimethyl benzoyl
 diphenyl phosphine oxide; and oxime ester compounds such as
 1,2-octanedione-1-[4-(phenylthio)phenyl]-2-(O-benzoyloxime),
 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl] ethanone
 1-(O-acetyloxime), and
 1-phenyl-1,2-propanedione-2-[O-(ethoxycarbonyl)oxime].

The content of the component (C) is not particularly limited. From the viewpoint of improving the sensitivity of the resin pattern, the content of the component (C) may be 0.1 parts by mass or more, 0.3 parts by mass or more, or 0.5 parts by mass or more, per 100 parts by mass in total of the total of the component (A), the component (B), and the component (C). From the viewpoint of improving the heat resistance of the resist pattern, the content of the component (C) may be 3 parts by mass or less, 2 parts by mass or less, or 1 part by mass or less.

The photosensitive resin composition according to the present embodiments may contain a photoinitiation auxiliary as component (C') with the component (C). Examples of the photoinitiation auxiliary include tertiary amine compounds such as ethyl

N,N-dimethylaminobenzoate, isoamyl N,N-dimethylaminobenzoate, pentyl-4-dimethylaminobenzoate, triethylamine, and triethanolamine. The component (C') may be used singly or in combination of two or more.

<Other components>

The photosensitive resin composition according to the present embodiments, in addition to the components (A) to (C), may further contain solvent, epoxy resin, elastomer, thermal polymerization initiator, inorganic filler, polymerization inhibitor, thickener, antifoaming agent, silane coupling agent, flame retardant, and the like.

The photosensitive resin composition according to the present embodiments contains a solvent and thereby can be easily applied on a substrate to form a coating film having uniform thickness. Examples of the solvent include ketones such as methyl ethyl ketone and cyclohexanone; aromatic hydrocarbons such as toluene, xylene, and tetramethylbenzene; glycol ethers such as methyl cellosolve, butyl cellosolve, methyl carbitol, butyl carbitol, propylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol diethyl ether, and triethylene glycol monoethyl ether; esters such as ethyl acetate, butyl acetate, propylene glycol monoethyl ether acetate, butyl cellosolve acetate, and carbitol acetate; aliphatic hydrocarbons such as octane and decane; and petroleum solvents such as petroleum ether, petroleum naphtha, hydrogenated petroleum naphtha, and solvent naphtha. The solvents may be used singly or in combination of two or more.

Examples of the epoxy resin include a bisphenol type epoxy

resin, a bisphenol novolac type epoxy resin, a phenol aralkyl type epoxy resin, a biphenyl aralkyl type epoxy resin, a stilbene type epoxy resin, a dicyclopentadiene type epoxy resin, a naphthalene type epoxy resin, a biphenyl type epoxy resin, a biphenylaralkyl type epoxy resin, a xylylene type epoxy resin, a dihydroanthracene type epoxy resin, a dicyclopentadiene type epoxy resin, an alicyclic epoxy resin, an aliphatic chain epoxy resin, and a rubber modified epoxy resin.

Examples of the elastomer include a styrene-based elastomer, an olefin-based elastomer, a polyester-based elastomer, a urethane-based elastomer, a polyamide-based elastomer, an acrylic elastomer, and a silicone-based elastomer.

As the thermal polymerization initiator, an organic peroxide or an azo compound may be used. Examples of the organic peroxide include hydroperoxides such as diisopropylbenzene hydroperoxide, cumene hydroperoxide, and t-butyl hydroperoxide; dialkylperoxides such as α,α -bis(t-butylperoxy-m-isopropyl)benzene, dicumyl peroxide, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane, t-butylcumyl peroxide, di-t-butyl peroxide, and 2,5-dimethyl-2,5-bis(t-butylperoxy)hexyne-3, t-butylperoxy-2-ethylhexanoate; ketone peroxides; peroxyketals such as n-butyl 4,4-di-(t-butylperoxy)valerate; diacyl peroxides; peroxy dicarbonates; and peroxyesters. Examples of the azo compounds include 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-cyclopropylpropionitrile), and 2,2'-azobis(2,4-dimethyl valeronitrile).

Examples of the inorganic filler include silica, alumina, titania, tantalum oxide, zirconia, silicon nitride, barium titanate, barium

carbonate, magnesium carbonate, aluminum hydroxide, magnesium hydroxide, lead titanate, lead zirconate titanate, lead lanthanum zirconate titanate, gallium oxide, spinel, mullite, cordierite, talc, aluminum titanate, yttria-containing zirconia, barium silicate, boron nitride, calcium carbonate, barium sulfate, calcium sulfate, zinc oxide, magnesium titanate, hydrotalcite, mica, calcined kaolin, and carbon.

As a pigment, a coloring agent which develops a desired color can be appropriately selected and used, and examples of the pigment include phthalocyanine blue, phthalocyanine green, iodine green, diazo yellow, crystal violet, titanium oxide, carbon black, and naphthalene black.

Examples of the polymerization inhibitor include hydroquinone, methyl hydroquinone, hydroquinone monomethyl ether, catechol, and pyrogallol. Examples of the thickener include benton and montmorillonite. Examples of the antifoaming agent include silicone-based antifoaming agent, fluorine-based antifoaming agent, and vinyl resin-based antifoaming agent. Examples of the flame retardant include a brominated epoxy compound, an acid-modified brominated epoxy compound, an antimony compound, a phosphate compound, an aromatic condensed phosphate, and a halogen-containing condensed phosphate.

The photosensitive resin composition according to the present embodiments can be prepared by mixing each component with a roll mill, a bead mill, or the like. The photosensitive resin composition according to the present embodiments is excellent in alkali developability and can form a cured film excellent in low dielectric

characteristics. The photosensitive resin composition can be suitably used for forming a resist pattern, and can be particularly suitably used for the method for manufacturing a multilayer printed wiring board described below.

[Photosensitive film]

The photosensitive resin composition according to the present embodiments may be used in the form of a film. The photosensitive film according to the present embodiments includes a support film and the photosensitive layer formed from the above-described photosensitive resin composition. The photosensitive film includes a support film and a photosensitive layer formed on the support film.

The photosensitive film can be prepared by applying the photosensitive resin composition according to the present embodiments on a support film with known coating devices such as a bar coater, a reverse roll coater, a gravure roll coater, a comma coater, a curtain coater, a kiss coater, and a die coater and then by drying a coating film to form a photosensitive layer.

Examples of the support film include polyester films such as polyethylene terephthalate and polybutylene terephthalate and polyolefin films such as polypropylene and polyethylene. The thickness of the support film may be, for example, 5 to 100 μm , 5 to 60 μm , or 15 to 45 μm .

The thickness of the photosensitive layer is not particularly limited, but may be 1 to 100 μm , 1 to 50 μm , or 5 to 40 μm from the viewpoint of thinning the multilayer printed wiring board.

The drying of the coating film can be performed using hot air

drying, or drying using far infrared radiation or near infrared radiation. The drying temperature may be, for example, 60 to 130°C, 70 to 120°C, or 80 to 110°C. The drying time may be, for example, 1 to 60 minutes, 2 to 30 minutes, or 5 to 20 minutes.

The photosensitive film according to the present embodiments can also laminate a protective film on the surface opposite to the surface in contact with the support film of the photosensitive layer. As a protective film, for example, polyolefin films such as polyethylene and polypropylene may be used. The protective film may be the same film as the support film.

[Method for forming resist pattern]

Method for forming a resist pattern according to the present embodiments includes: a step of forming a photosensitive layer using the above-described photosensitive resin composition or photosensitive film; a step of exposing the photosensitive layer to a predetermined pattern; a step of developing and removing the photosensitive layer in the unexposed area with an alkali aqueous solution to obtain a resin pattern; and a step of heat-treating the resin pattern to obtain a cured film (resist pattern), on a substrate.

A substrate such as a copper-clad laminate board is provided, and a photosensitive layer is formed on the substrate. The substrate may be coated with the photosensitive resin composition using methods such as a printing method, a spin coating method, a spraying method, a jet dispensing method, an inkjet method, a roll coating method, a curtain coating method, and an electrostatic coating method. The photosensitive layer can be provided by drying a coating film at 60 to

110°C, the coating film being formed by coating the substrate with the photosensitive resin composition.

The photosensitive layer may also be provided by laminating the photosensitive layer of the photosensitive film on the substrate using a laminator. The lamination may be performed, for example, by preheating the photosensitive film and the substrate, as required, and then performed at a temperature of 70 to 130°C, a pressure of 0.1 to 1.0 MPa, and a reduced pressure of air pressure 20 mmHg (26.7 hPa) or less. The type of the lamination may be batch or continuous by the roll.

The photosensitive layer is exposed to a predetermined pattern through a predetermined mask. The exposure method is not particularly limited, and for example may adopt a method of imagewise irradiating actinic light through a negative or positive mask pattern referred to as artwork (mask exposure method) and may adopt a method of imagewise irradiating actinic light by direct drawing exposure method such as LDI (Laser Direct Imaging) exposure method or DLP (Digital Light Processing) exposure method.

A known light source can be used as a light source of actinic light. Examples of the light source include a light source that effectively emits ultraviolet light or visible light such as gas laser such as carbon arc lamp, mercury vapor arc lamp, high pressure mercury lamp, xenon lamp, and argon laser; solid laser such as YAG laser; and semiconductor laser.

The exposure dose is appropriately selected depending on the light source to be used, the thickness of the photosensitive layer, and the

like. For example, when the thickness of the photosensitive layer is 1 to 100 μm and ultraviolet irradiation from a high-pressure mercury lamp is used, the exposure dose may be 10 to 1000 mJ/cm^2 or 15 to 500 J/m^2 .

After exposure, when a support film is present on the photosensitive layer, the support film is removed and then the unexposed area is removed (developed) with an alkaline developer to obtain a resin pattern. Examples of the development method include methods using a dip method, a paddle method, a spray method, brushing, slapping, scrubbing, swing immersion, or the like. From the viewpoint of improving resolution, a spray method is preferable, and a high pressure spray method is more preferable.

Examples of the alkaline developer include an alkaline aqueous solution in which an alkaline compound such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, tetramethylammonium hydroxide or choline is dissolved in water to a concentration of about 1 to 10% by mass; and ammonia water.

To develop low dielectric characteristics, the resin pattern is heat-treated to obtain a cured film (resist pattern). Heat-treating the resin pattern eliminates at least a part of the carboxy group of the group represented by the above formula (1). Elimination of the carboxy group can enhance the low dielectric characteristics of the cured film. Thus, the heat treatment is performed under the condition of a temperature or more at which the elimination of the carboxy group occurs. For the heating temperature, 140 to 250°C is preferable, 150 to 230°C is more preferable, and 160 to 200°C is still more preferable. For the heating time, about 30 minutes to 10 hours is preferable, 1 hour

to 5 hours is more preferable, and 1.5 hours to 3 hours is still more preferable.

[Multilayer printed wiring board]

The cured product of the photosensitive resin composition of the present embodiments can be suitably used, for example, as a surface protective film (overcoat film) and/or an interlayer insulating film (passivation film) of a semiconductor element, or a solder resist and/or an interlayer insulating layer in a multilayer printed wiring board.

Figure 1 is a view showing a method for manufacturing a multilayer printed wiring board including a cured product of the photosensitive resin composition according to the present embodiments as a solder resist and/or an interlayer insulating film. The multilayer printed wiring board 100A shown in (f) of Figure 1 has a wiring pattern on the surface and inside. The multilayer printed wiring board 100A can be obtained by appropriately forming a wiring pattern by an etching method or a semi-additive method, in addition to laminating a copper-clad laminate, an interlayer insulating film, a metal foil, and the like. Hereinafter, a method for manufacturing the multilayer printed wiring board 100A will be briefly described based on Figure 1.

The interlayer insulating film 103 is formed on both surfaces of the copper-clad laminate 101 having a wiring pattern 102 on the surface (refer to Figure 1(a)). The interlayer insulating film 103 may be formed by printing the above-described photosensitive resin composition using a screen printer or a roll coater, and can also be formed by providing the above-described photosensitive film in advance and bonding the photosensitive layer of the photosensitive film to the

surface of the printed wiring board using a laminator.

The region other than the portion required to be electrically connected to the outside in the interlayer insulating film 103 is exposed and developed to form the opening 104 (refer to Figure 1(b)). Smear (residue) around the opening 104 is removed by desmear treatment. The size (diameter) of the opening 104 is not particularly limited, and can be arbitrarily selected, for example, in the range of 15 to 300 μm . The seed layer 105 is formed on the interlayer insulating film 103 and the opening 104 by the electroless plating method (refer to Figure 1(c)). The thickness of the seed layer 105 may be about 0.1 to 2.0 μm . A photosensitive layer formed from the above-described photosensitive resin composition is formed on the seed layer 105, and predetermined portions are exposed and developed to form the resin pattern 106 (refer to Figure 1(d)). As required, an operation of removing the development residue of the photosensitive layer may be performed using plasma or the like. The wiring pattern 107 is formed by the electro-plating method and the resin pattern 106 is removed by a peeling solution, and then the seed layer 105 between the wirings is removed by etching (refer to Figure 1(e)).

The multilayer printed wiring board 100A can be produced by repeatedly performing the above operation and forming the solder resist 108 including the cured product of the above-described photosensitive resin composition on the outermost surface (refer to Figure 1(f)). In the multilayer printed wiring board 100A obtained in this manner, the semiconductor element is mounted at the corresponding position, and electrical connection can be secured.

[Semiconductor package]

A semiconductor package mounting a semiconductor element can be produced in the printed wiring board according to the present embodiments. The semiconductor package can be manufactured by mounting semiconductor elements such as a semiconductor chip and memory at a predetermined position of the above-described printed wiring board and sealing the semiconductor elements with a sealing resin or the like.

Examples

Hereinafter, the present invention will be specifically described based on Examples, but the present invention is not limited to these Examples.

(1) Carboxy group-containing compound

(Example a1)

Malonic acid (20.8 g, 0.20 mol), 2-hydroxyethyl methacrylate (26.0 g, 0.20 mol), boric acid (4.9 g, 0.08 mol), and 60 mL of acetonitrile were poured into 250 mL three-necked flask equipped with a stirrer, a nitrogen introduction pipe, a reflux condenser, a dropping funnel, and a thermometer to perform the reaction at 75°C for 24 hours under a nitrogen atmosphere.

After removing acetonitrile from the reaction solution with an evaporator, the solution was poured into 100 mL of water, and the separated oily component was collected. 15 mL of chloroform was added to the aqueous solution from which the oily component was removed, and liquid separation operation was performed three times to collect an organic layer. The oily component and the organic layer

were mixed and washed with a saturated saline solution to obtain a chloroform solution of the product. 50 mL (0.16 wt%) of a 0.16% by mass sodium carbonate aqueous solution was added to the chloroform solution of the product to collect the aqueous layer. The collected aqueous layer was washed with chloroform to obtain an aqueous solution of the product.

After 15 g of hydrochloric acid was added to the aqueous solution of the product and the separated oil layer was collected, chloroform was added to the remaining aqueous solution of the product to perform a liquid separation operation, and the chloroform layer was collected. The oil layer and the chloroform layer were mixed, washed by adding water, and then concentrated under reduced pressure to remove chloroform to obtain a carboxy group-containing compound (compound in which R^1 is a hydrogen atom and L^1 is an ethylene group in formula (2), hereinafter referred to as "compound a"). The yield was about 35 to 40%.

(2) Carboxy group-containing resin

(Example A1)

25 g of the compound a, 75 g of 1,4-dioxane, and 0.5 g of 2,2'-azodiisobutyronitrile (AIBN) were poured into 100 mL four-necked flask equipped with a stirrer, a nitrogen introduction pipe, a reflux condenser, a dropping funnel, and a thermometer, and were stirred at 75°C for 6 hours under a nitrogen atmosphere and then cooled to room temperature to obtain a solution of a carboxy group-containing resin (hereinafter referred to as "polymer A").

(Example A2)

139 g of propylene glycol methyl ether (MFG) and 93 g of toluene (TLS) were poured into 400 mL four-necked flask equipped with a stirrer, a nitrogen introduction pipe, a reflux condenser, a dropping funnel, and a thermometer, and were heated to 80°C while stirring under a nitrogen atmosphere. A mixture of 142 g of styrene, 25.2 g of the compound a and 1.41 g of AIBN was dropped for 80 minutes from the dropping funnel, and then a mixed solution of 6 g of MFG, 4 g of TLS, and 0.28 g of AIBN was dropped to perform a reaction. The reaction solution was stirred for 2 hours, heated to 95°C, and stirred for 1.5 hours, and then cooled to room temperature to obtain a solution of a carboxy group-containing resin (hereinafter referred to as "polymer B").

(Example A3)

A solution of a carboxy group-containing resin (hereinafter referred to as "polymer C") was obtained in the same manner as in Example A2, except that a mixture of 36 g of styrene, 84 g of the compound a, and 1.01 g of AIBN was dropped.

(Example A4)

A solution of the polymer B and a solution of the polymer C were mixed at a ratio of 80 parts by mass of the polymer B and 20 parts by mass of the polymer C to obtain a solution of polymer E.

(Example A5)

A solution of the polymer B and a solution of the polymer C were mixed at a ratio of 54 parts by mass of the polymer B and 46 parts by mass of the polymer C to obtain a solution of polymer F.

(Comparative Example B1)

A solution of a carboxy group-containing resin (hereinafter referred to as "polymer D") was obtained in the same manner as in Example A2, except that a mixture of 142 g of styrene, 25.2 g of methacrylic acid, and 1.41 g of AIBN was dropped.

(Acid value)

The acid value of the polymers A to F was calculated from the structure of monomer constituting the polymer and copolymerization ratio.

(Evaluation of alkali solubility)

A solution of the polymers A to F was applied on a substrate using an applicator and dried at 80°C for 10 minutes to form a resin film having a thickness of 10 to 20 μm . The resin film was developed at 30°C for 50 seconds, 80 seconds, and 120 seconds, respectively, using 1.0% by mass of a sodium carbonate aqueous solution. The average dissolution rate of the resin film was calculated from the thickness of the resin film after development. The results are shown in Table 1.

Dissolution rate ($\mu\text{m/s}$) = [thickness before development (μm) - thickness after development (μm)]/development time (s)

[Table 1]

	Example A1	Example A2	Example A3	Example A4	Example A5	Comparative Example A1
Carboxy group-containing resin	Polymer A	Polymer B	Polymer C	Polymer E	Polymer F	Polymer D
Acid value (mg KOH/g)	259	181	38	120	80	70
Dissolution rate ($\mu\text{m/s}$)	1.60	1.40	0.08	0.45	0.14	0.03

(Elimination of carboxy group)

A resin film was formed by using a solution of the polymer A

and drying at 80°C for 10 minutes and then the resin film was heat-treated at 170°C for 2 hours. The infrared absorption spectra of the resin film before and after the heat treatment were measured and the elimination of a carboxy group after the heat treatment was determined by the spectral change derived from the carboxy group.

(3) Photosensitive resin composition

Each component was blended at an amount blended (unit: parts by mass of solids) shown in Table 2, kneaded with a 3-roll mill, and added with carbitol acetate so that the solids concentration was 70 % by mass to produce a photosensitive resin composition.

The details of each material in Table 2 are as follows.

(B) Photopolymerizable compound

FA-321M (trade name):
2,2-bis(4-(methacryloxy-pentaethoxy)phenyl)propane (manufactured by Hitachi Chemical Co., Ltd.)

FA-MECH (trade name):
(2-hydroxy-3-chloro)propyl-2-methacryloyloxyethyl phthalate
(manufactured by Hitachi Chemical Co., Ltd.)

(C) Photopolymerization initiator

BCIM (trade name):
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole (manufactured by Hampford Research Inc.)

(Dielectric loss tangent)

The photosensitive resin composition was applied onto a PET film using an applicator, and dried at 80°C for 15 minutes to form a photosensitive layer having a thickness of 100 to 150 μm. The

photosensitive layer was exposed by irradiating at 100 mJ/cm^2 using an exposure machine (trade name "EXM-1201" manufactured by ORC Manufacturing Co., Ltd.). The photosensitive layer after exposure was peeled from the PET film to obtain a uncured film. The photosensitive layer after exposure was cured at 170°C for 2 hours and peeled from the PET film to obtain a cured film. The Df value of the uncured and cured films were measured by a dielectric loss tangent method using a dielectric constant measurement device (trade name "Concept 40 Dielectric/Impedance Spectrometer" manufactured by Novocontrol Technologies). The results are shown in Table 2.

[Table 2]

		Example B1	Example B2	Example B3	Example B4	Comparative Example B1	Comparative Example B2
Polymer B		13.28	-	-	13.81	-	-
Polymer F		-	13.28	13.81	-	-	-
Polymer D		-	-	-	-	13.28	13.81
FA-321M		1.27	1.27	0.88	0.88	1.27	0.88
FA-MECH		0.32	0.32	0.22	0.22	0.32	0.22
BCIM		0.13	0.13	0.09	0.09	0.13	0.09
Uncured film							
Df	1 MHz	0.023	0.034	0.039	0.023	0.022	0.021
	10 MHz	0.006	0.029	0.032	0.010	0.016	0.027
Cured film							
Df	1 MHz	0.015	0.014	0.019	0.015	0.020	0.023
	10 MHz	0.004	0.004	0.008	0.008	0.016	0.027

A PET film was coated with a solution of the polymer A using an applicator and dried at 80°C for 15 minutes to form a resin film having a thickness of 100 to $150 \mu\text{m}$. The resin film was heat-treated at 170°C for 2 hours. About the resin film before and after the heat

treatment, Df value at 1 MHz was measured by the dielectric loss tangent method. Df value of the polymers B, F and D were calculated by the results of Table 2. The results are shown in Table 3.

[Table 3]

		Example A1	Example A2	Example A5	Comparative Example A1
Carboxy group-containing resin		Polymer A	Polymer B	Polymer F	Polymer D
Df (1 MHz)	Before heat treatment	0.152	-	-	0.049
	After heat treatment	0.090	0.027	0.017	0.049

The resin having the group represented by formula (1) is excellent in the alkali developability, and decarboxylation of at least a part of the carboxy group after the heat treatment can improve the low dielectric characteristics.

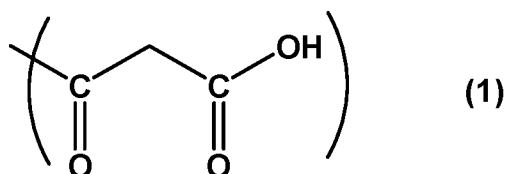
Reference Signs List

100A: multilayer printed wiring board; 101: copper-clad laminate; 102 and 107: wiring pattern; 103: interlayer insulating film; 104: opening; 105: seed layer; 106: resin pattern; 108: solder resist.

CLAIMS

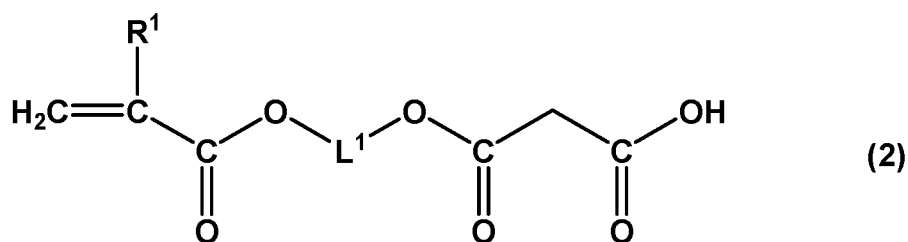
[Claim 1]

A carboxy group-containing compound having a (meth)acryloyl group and a group represented by the following formula (1).



[Claim 2]

The carboxy group-containing compound according to claim 1, the compound having a structure represented by the following formula (2):



wherein R^1 represents a hydrogen atom or a methyl group, and L^1 represents an alkylene group having 1 to 10 carbon atoms.

[Claim 3]

The carboxy group-containing compound according to claim 2, wherein the L^1 represents an alkylene group having 1 to 4 carbon atoms.

[Claim 4]

A carboxy group-containing resin having a structural unit based on the carboxy group-containing compound according to any one of claims 1 to 3.

[Claim 5]

The carboxy group-containing resin according to claim 4,

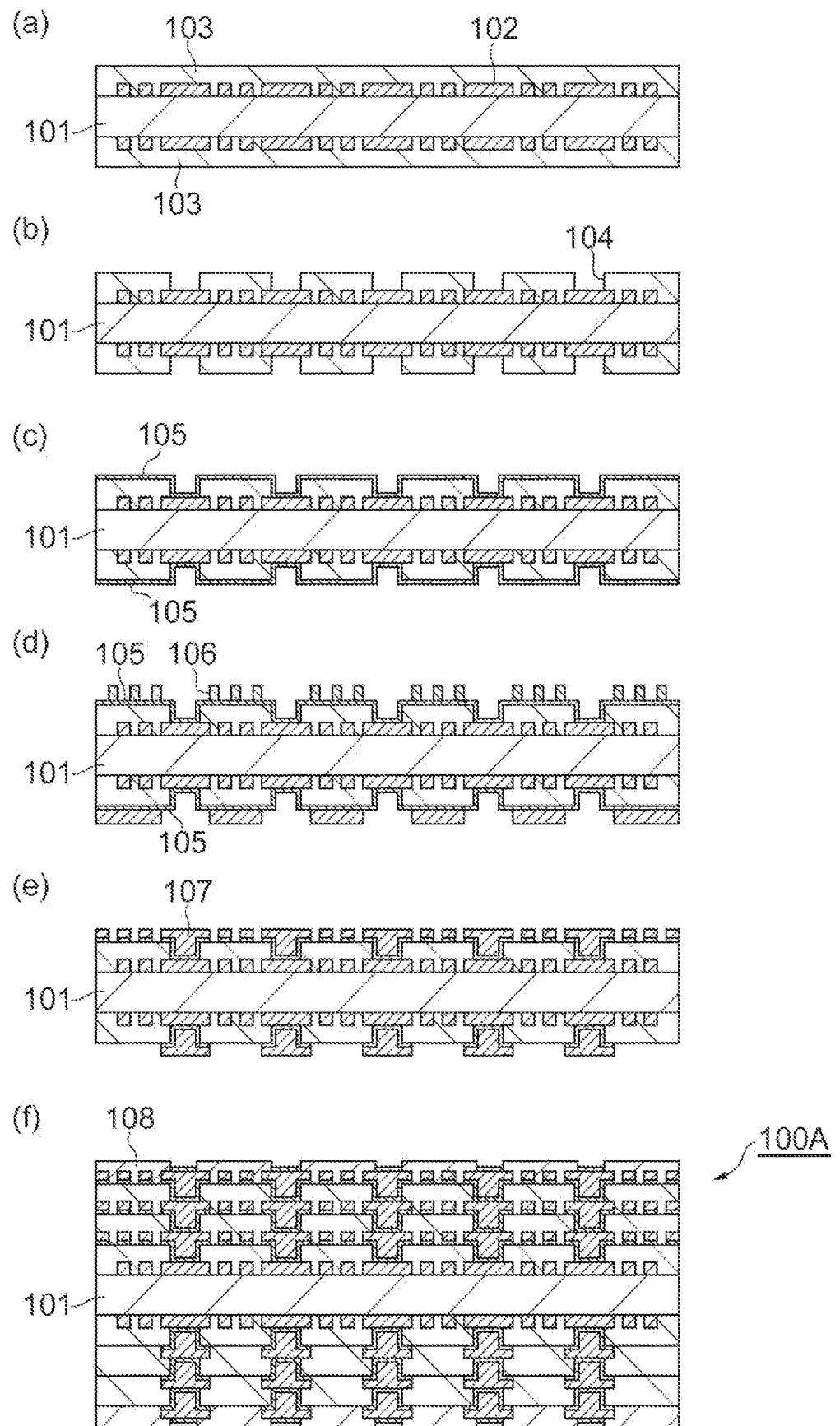
wherein the resin further has a structural unit based on an aromatic vinyl compound.

[Claim 6]

A photosensitive resin composition comprising an alkali-soluble resin, a photopolymerizable compound having an ethylenically unsaturated group, and a photopolymerization initiator,

wherein the alkali-soluble resin comprises the carboxy group-containing resin according to claim 4 or 5.

Fig.1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2019/089957

A. CLASSIFICATION OF SUBJECT MATTER

G03F 7/027(2006.01)i; G03F 7/004(2006.01)i

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)

G03F7/-

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)

CNPAT,DWPI,EPODOC,CNKI: malonic acid, methacrylate, hydroxyalkyl, semiconductor, acryloyl, boric acid, photosensitive

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011112266 A1 (TAKAWAKI, Koichi et al.) 12 May 2011 (2011-05-12) description, paragraphs [0019]-[0025], [0048], [0067], [0079], [0092] and [0097]	1-6
X	CN 105988291 A (DONGWOO FINE CHEM. CO. LTD.) 05 October 2016 (2016-10-05) description, paragraphs [0017]-[0020], [0054], [0055], [0119] and [0123]	1, 4-6
X	US 2015028272 A1 (CHI MEI CORPORATION) 29 January 2015 (2015-01-29) description, paragraphs [0047] and [0048]	1
A	EP 1975707 A1 (FUJIFILM CORPORATION) 01 October 2008 (2008-10-01) description, paragraphs [0014]-[0062]	1-6



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

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“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

20 February 2020

Date of mailing of the international search report

06 March 2020

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2019/089957

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2011112266	A1	12 May 2011	TW	I439475	B	01 June 2014
				KR	20110041491	A	21 April 2011
				EP	2308905	A1	13 April 2011
				CN	102046675	B	24 April 2013
				JP	5367324	B2	11 December 2013
				TW	201012835	A	01 April 2010
				EP	2308905	A4	30 November 2011
				WO	2010010667	A1	28 January 2010
				CN	102046675	A	04 May 2011
				KR	101569955	B1	17 November 2015
				JP	2010031091	A	12 February 2010
CN	105988291	A	05 October 2016	TW	201701072	A	01 January 2017
				KR	20160112506	A	28 September 2016
				KR	102028439	B1	04 October 2019
US	2015028272	A1	29 January 2015	TW	1518459	B	21 January 2016
				TW	201504765	A	01 February 2015
				CN	104345554	A	11 February 2015
EP	1975707	A1	01 October 2008	JP	2008242093	A	09 October 2008
				EP	1975707	B1	19 July 2017
				JP	4860525	B2	25 January 2012
				US	7964334	B2	21 June 2011
				US	2008241744	A1	02 October 2008