

## DESCRIPTION

TITLE OF THE INVENTION: PHOTSENSITIVE RESIN COMPOSITION,  
PHOTSENSITIVE RESIN SHEET, CURED PRODUCT, HOLLOW  
STRUCTURE, ELECTRONIC COMPONENT, AND ELASTIC WAVE FILTER

### TECHNICAL FIELD

[0001]

The present invention relates to a photosensitive resin composition, a photosensitive resin sheet, a cured product, a hollow structure, an electronic component, and an elastic wave filter.

### BACKGROUND ART

[0002]

The photosensitive resin composition is widely used as an insulating film of a wiring board because the composition can be finely processed by a photolithography technique. Further, a material obtained by molding a photosensitive resin composition into a sheet shape has been increasingly applied to a roof material for forming a hollow structure of an electronic component by utilizing the feature of the sheet shape. In recent years, a photosensitive resin sheet used for forming a roof of a hollow structure has been required to have pattern-processability for forming minute through holes and

pressure resistance to withstand a sealing step. A method of adding an inorganic filler for improve pressure resistance to increase an elastic modulus has been proposed. In particular, a technique proposed in Patent Document 1 in which a glass filler of which a refractive index is matched with that of a photosensitive resin composition is expected to suppress scattering of light using exposure and achieve pattern-processability in addition to improving pressure resistance by adding the filler.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0003]

Patent Document 1: Japanese Patent Laid-open  
Publication No. 2015-118194

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0004]

The photosensitive resin composition described in Patent Document 1 has, however, the problem of having insufficient pattern processability and pressure resistance in adapting to roof materials of hollow structures that have demand characteristics increased.

[0005]

The present invention is intended to solve the foregoing problems, and an object of the invention is to provide a photosensitive resin composition that is excellent in pattern processability and pressure resistance.

#### SOLUTIONS TO THE PROBLEMS

[0006]

The present invention for solving the problems mentioned above is as follows.

A photosensitive resin composition including a polymer (A), a radically polymerizable compound (B), a photopolymerization initiator (C), and an inorganic filler (D), wherein the radically polymerizable functional group equivalent of the radically polymerizable compound (B) is 70 g/eq or more and 200 g/eq or less on average.

#### EFFECTS OF THE INVENTION

[0007]

According to the present invention, a finely processed insulating film that is excellent in pressure resistance can be formed. The photosensitive resin composition according to the present invention can be suitable for a substrate required to have a high resolution

and a high elastic modulus, or an electronic component that has a hollow structure also required to have pressure resistance.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

Fig. 1 is a plan schematic view illustrating an aspect in which a convex portion for forming a hollow structure according to the present invention.

Fig. 2 is a schematic view illustrating an example of a method for forming a hollow structure using a photosensitive resin sheet according to the present invention.

#### EMBODIMENTS OF THE INVENTION

[0009]

The present invention is a photosensitive resin composition including a polymer (A), a radically polymerizable compound (B), a photopolymerization initiator (C), and an inorganic filler (D), wherein the radically polymerizable functional group equivalent of the radically polymerizable compound (B) is 70 g/eq or more and 200 g/eq or less on average. Hereinafter, this will be described below in detail.

[0010]

[Polymer (A)]

The photosensitive resin composition according to the present invention contains the polymer (A). By containing the polymer (A), a thick film of the photosensitive resin composition is easily formed, and a film thickness is easily adjusted according to the purpose. The main skeleton of the polymer (A) is not particularly limited, but a (meth)acrylic polymer, an epoxy polymer, a polyurethane, a polybenzoxazine, a polybenzoxazole precursor, a polybenzoxazole, a polyimide precursor, polyimide, and the like can be used. In particular, from the viewpoint of heat resistance, the polymer (A) preferably includes at least one resin selected from the group consisting of a polyimide, a polybenzoxazole, any of precursors thereof, and copolymers thereof, that is, includes a polybenzoxazole precursor, a polybenzoxazole, a polyimide precursor, a polyimide, or a copolymer thereof. The polymer (A) more preferably includes a polyimide precursor or a polyimide, and particularly preferably includes a polyimide from the viewpoint of lowering the heat treatment temperature after pattern processing.

[0011]

The resin included in the polymer (A) is preferably dissolved in a developer, and in particular, preferably has alkali solubility. The alkali solubility as used here

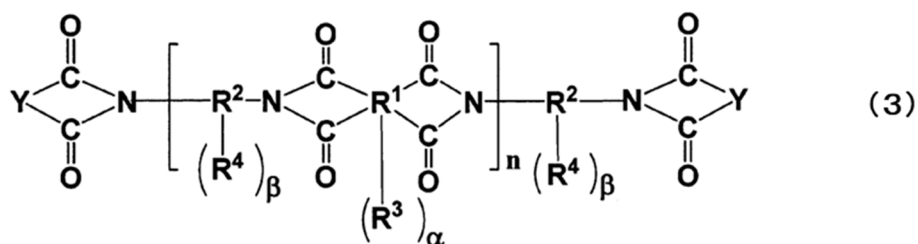
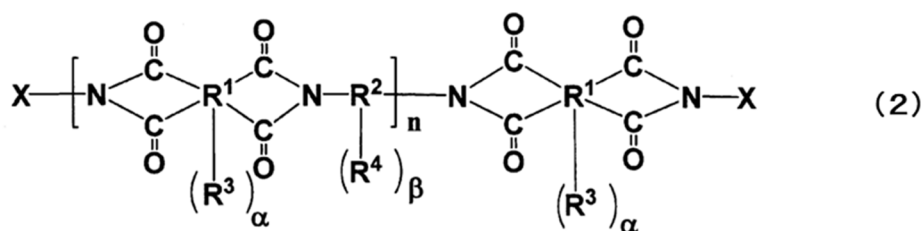
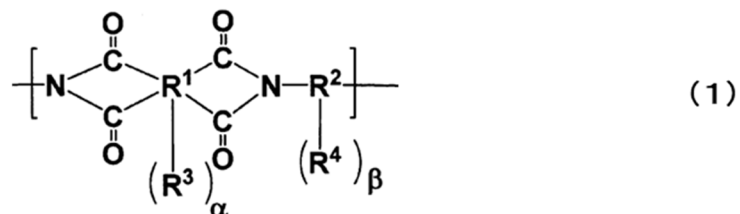
means that solubility in a 2.38% by weight tetramethylammonium hydroxide (TMAH) aqueous solution is 0.1 g/100 mL or more. By imparting alkali solubility to the polymer (A) that is a main component of the photosensitive resin composition, dissolution of the photosensitive resin composition in an alkali developer is promoted, and an excellent pattern can be obtained. Examples of the functional group that imparts alkali solubility to the polymer (A), that is, alkali-soluble group include a phenolic hydroxyl group, a thiol group, a carboxyl group, and a sulfonic acid group, and it is preferable to have any one or both of a phenolic hydroxyl group and a carboxyl group as the alkali-soluble group.

[0012]

As for the polymer (A), a preferred example of the polyimide is described below. In the case of using a polyimide as the polymer (A), the polymer (A) preferably contains one or more polyimides that have a structural unit represented by the following general formula (1), and more preferably contains one or more polyimides represented by the following general formula (2) or (3).

[0013]

[Chem. 1]



[0014]

In the general formulas (1) to (3), X represents a monovalent organic group having at least one of a carboxyl group, a phenolic hydroxyl group, a sulfonic acid group, and a thiol group. Y represents a divalent organic group having at least one of a carboxyl group, a phenolic hydroxyl group, a sulfonic acid group, and a thiol group. X and Y preferably have a phenolic hydroxyl group or a thiol group, and particularly preferably have a phenolic hydroxyl group.

[0015]

In addition,  $R^1$  represents a 4- to 14-valent organic group, and  $R^2$  represents a 2- to 12-valent organic group.  $R^3$  and  $R^4$  each independently represent a carboxyl group, a phenolic hydroxyl group, a sulfonic acid group, or a thiol group.  $R^3$  and  $R^4$  are preferably a phenolic hydroxyl group or a carboxyl group, and particularly preferably a phenolic hydroxyl group.

[0016]

In addition,  $\alpha$  and  $\beta$  each independently represent an integer in the range of 0 to 10. As for such  $\alpha$  and  $\beta$ ,  $\alpha + \beta$  is preferably 1 or more.  $n$  represents the number of repetitions of the structural unit of the polymer. The range of  $n$  is 3 to 200. When  $n$  is 3 or more, the thick film processability of the photosensitive resin composition can be improved. From the viewpoint of improving the thick film processability,  $n$  is preferably 5 or more. In contrast, when  $n$  is 200 or less, the solubility of the alkali-soluble polyimide (a) in an alkaline developer can be improved. From the viewpoint of improving the solubility,  $n$  is preferably 100 or less.

[0017]

In the general formulas (1) to (3),  $R^1$  is a 4- to 14-valent organic group that has a structure derived from a tetracarboxylic acid dianhydride. In particular,  $R^1$  is preferably an organic group having 5 to 40 carbon atoms and

containing an aromatic group or a cycloaliphatic group.

[0018]

Examples of the tetracarboxylic acid dianhydride include aromatic tetracarboxylic acid dianhydrides and aliphatic tetracarboxylic acid dianhydrides. Examples of the aromatic tetracarboxylic dianhydrides include a pyromellitic acid dianhydride, 3,3',4,4'-biphenyltetracarboxylic acid dianhydride, 2,3,3',4'-biphenyltetracarboxylic acid dianhydride, 2,2',3,3'-biphenyltetracarboxylic acid dianhydride, 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride, 2,2',3,3'-benzophenonetetracarboxylic acid dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride, 1,1-bis(3,4-dicarboxyphenyl)ethane dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, bis(2,3-dicarboxyphenyl)methane dianhydride, bis(3,4-dicarboxyphenyl) sulfone dianhydride, bis(3,4-dicarboxyphenyl) ether dianhydride, 1,2,5,6-naphthalenetetracarboxylic acid dianhydride, 9,9-bis(3,4-dicarboxyphenyl)fluorenic acid dianhydride, 9,9-bis{4-(3,4-dicarboxyphenoxy)phenyl}fluorenic acid dianhydride, 2,3,6,7-naphthalenetetracarboxylic acid dianhydride, 2,3,5,6-pyridinetetracarboxylic acid dianhydride, 3,4,9,10-

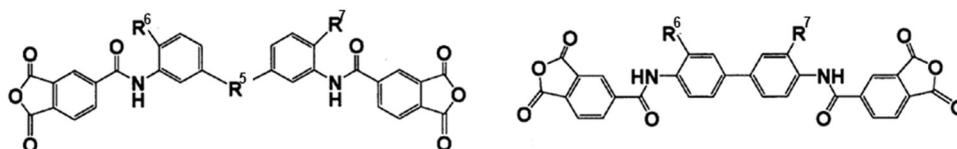
peryleneetetracarboxylic acid dianhydride, and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride. Examples of the aliphatic tetracarboxylic acid dianhydride include a butanetetracarboxylic acid dianhydride and 1,2,3,4-cyclopentanetetracarboxylic acid dianhydride.

[0019]

In addition, examples of the tetracarboxylic acid dianhydride include acid dianhydrides that have the following structure. As the tetracarboxylic acid dianhydride, two or more of the above-described aromatic tetracarboxylic acid dianhydride, aliphatic tetracarboxylic acid dianhydrides, and acid dianhydrides that have the following structure may be used in the present embodiment.

[0020]

[Chem. 2]



[0021]

Here,  $R^5$  represents a group selected from an oxygen atom,  $C(CF_3)_2$ ,  $C(CH_3)_2$ , and  $SO_2$ , and  $R^6$  and  $R^7$  each independently represent a group selected from a carboxyl group, a hydroxyl group, a sulfonic acid group, and a thiol group.

[0022]

In the general formulas (1) to (3),  $R^2$  is a 2- to 12-valent organic group that has a structure derived from a diamine. In particular,  $R^2$  is preferably an organic group having 5 to 40 carbon atoms and containing an aromatic group or a cycloaliphatic group.

[0023]

Examples of the diamine include hydroxyl group-containing diamines, carboxyl group-containing diamines, thiol group-containing diamines, aromatic diamines, compounds where at least some of the hydrogen atoms of the foregoing aromatic rings are substituted with an alkyl group or a halogen atom, and aliphatic diamines.

[0024]

Examples of the hydroxyl group-containing diamines include bis-(3-amino-4-hydroxyphenyl)hexafluoropropane, bis(3-amino-4-hydroxyphenyl)sulfone, bis(3-amino-4-hydroxyphenyl)propane, bis(3-amino-4-hydroxyphenyl)methylene, bis(3-amino-4-hydroxyphenyl)ether, bis(3-amino-4-hydroxy)biphenyl, and bis(3-amino-4-hydroxyphenyl)fluorene. Examples of the carboxyl group-containing diamines include 2,2-bis[3-amino-4-carboxyphenyl]propane, 2,2-bis[4-amino-3-carboxyphenyl]propane, 2,2-bis[3-amino-4-carboxyphenyl]hexafluoropropane, 4,4'-diamino-2,2',5,5'-tetracarboxydiphenylmethane, 3,3'-diamino-4,4'-

dicarboxydiphenyl ether, 4,4'-diamino-3,3'-  
 dicarboxydiphenyl ether, 4,4'-diamino-2,2'-  
 dicarboxydiphenyl ether, 4,4'-diamino-2,2',5,5'-  
 tetracarboxydiphenyl ether, 3,3'-diamino-4,4'-  
 dicarboxydiphenyl sulfone, 4,4'-diamino-3,3'-  
 dicarboxydiphenyl sulfone, 4,4'-diamino-2,2'-  
 dicarboxydiphenylsulfone, 4,4'-diamino-2,2',5,5'-  
 tetracarboxydiphenylsulfone, 2,2-bis[4-(4-amino-3-  
 carboxyphenoxy)phenyl]propane, and 2,2-bis[4-(4-amino-3-  
 carboxyphenoxy)phenyl]sulfone. Examples of the thiol  
 group-containing diamines include a  
 dimercaptophenylenediamine.

[0025]

Examples of the aromatic diamines include 3,3'-  
 diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 4,4'-  
 diaminodiphenyl ether, 3,3'-diaminodiphenylmethane, 3,4'-  
 diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 3,3'-  
 diaminodiphenylsulfone, 3,4'-diaminodiphenylsulfone, 4,4'-  
 diaminodiphenylsulfone, 3,4'-diaminodiphenylsulfide, 4,4'-  
 diaminodiphenylsulfide, 1,4-bis(4-aminophenoxy)benzene,  
 1,3-bis(4-aminophenoxy)benzene, 1,3-bis(3-  
 aminophenoxy)benzene, benzidine, m-phenylenediamine, p-  
 phenylenediamine, 1,5-naphthalenediamine, 2,6-  
 naphthalenediamine, bis(4-aminophenoxyphenyl)sulfone,  
 bis(3-aminophenoxyphenyl)sulfone, bis(4-

aminophenoxy)biphenyl, bis{4-(4-aminophenoxy)phenyl}ether, 1,4-bis(4-aminophenoxy)benzene, 2,2'-dimethyl-4,4'-diaminobiphenyl, 2,2'-diethyl-4,4'-diaminobiphenyl, 3,3'-dimethyl-4,4'-diaminobiphenyl, 3,3'-diethyl-4,4'-diaminobiphenyl, 2,2',3,3'-tetramethyl-4,4'-diaminobiphenyl, 3,3',4,4'-tetramethyl-4,4'-diaminobiphenyl, 2,2'-di(trifluoromethyl)-4,4'-diaminobiphenyl, and 9,9-bis(4-aminophenyl)fluorene.

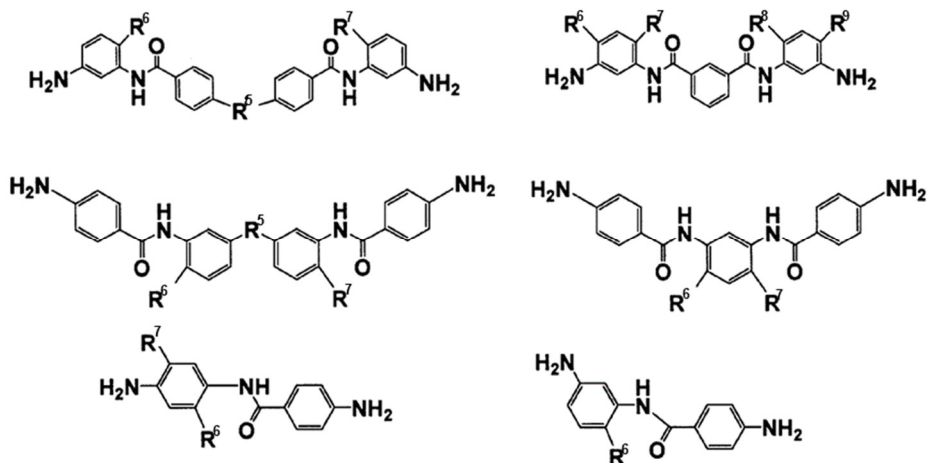
Examples of the aliphatic diamines include a cyclohexyldiamine and a methylenebiscyclohexylamine.

[0026]

In addition, examples of the diamine include a diamine that has the following structure. As the diamine, two or more of the above-described hydroxyl group-containing diamines, carboxyl group-containing diamines, thiol group-containing diamines, aromatic diamine, compounds where at least some of the hydrogen atoms of the foregoing aromatic rings are substituted with an alkyl group or a halogen atom, aliphatic diamines, and diamines that have the following structure may be used in the present embodiment.

[0027]

[Chem. 3]



[0028]

Here,  $R^5$  represents a group selected from an oxygen atom,  $C(CF_3)_2$ ,  $C(CH_3)_2$ , and  $SO_2$ , and  $R^6$  to  $R^9$  each independently represent a group selected from a carboxyl group, a hydroxyl group, a sulfonic acid group, and a thiol group.

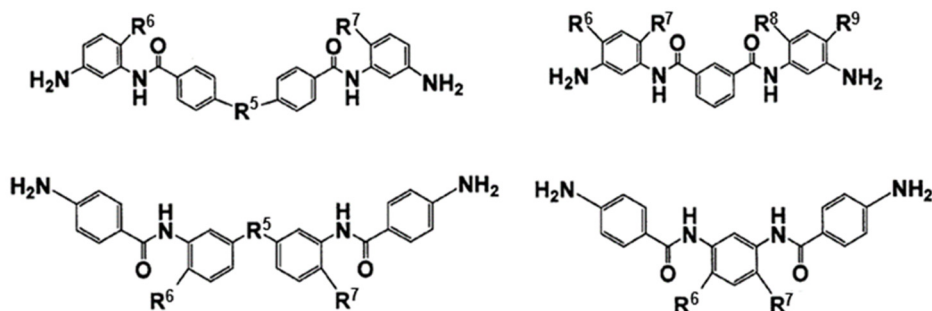
[0029]

Among the diamines described above, preferred are bis-(3-amino-4-hydroxyphenyl)hexafluoropropane, bis(3-amino-4-hydroxyphenyl)sulfone, bis(3-amino-4-hydroxyphenyl)propane, bis(3-amino-4-hydroxyphenyl)methylene, bis(3-amino-4-hydroxyphenyl)ether, bis(3-amino-4-hydroxy)biphenyl, bis(3-amino-4-hydroxyphenyl)fluorene, 2,2-bis[3-amino-4-carboxyphenyl]propane, 2,2-bis[4-amino-3-carboxyphenyl]propane, 2,2-bis[3-amino-4-carboxyphenyl]hexafluoropropane, 4,4'-diamino-2,2',5,5'-

tetracarboxydiphenylmethane, 3,3'-diamino-4,4'-  
 dicarboxydiphenyl ether, 4,4'-diamino-3,3'-  
 dicarboxydiphenyl ether, 4,4'-diamino-2,2'-  
 dicarboxydiphenyl ether, 4,4'-diamino-2,2',5,5'-  
 tetracarboxydiphenyl ether, 3,3'-diamino-4,4'-  
 dicarboxydiphenyl sulfone, 4,4'-diamino-3,3'-  
 dicarboxydiphenyl sulfone, 4,4'-diamino-2,2'-  
 dicarboxydiphenyl sulfone, 4,4'-diamino-2,2',5,5'-  
 tetracarboxydiphenyl sulfone, 2,2-bis[4-(4-amino-3-  
 carboxyphenoxy)phenyl]propane, 2,2-bis[4-(4-amino-3-  
 carboxyphenoxy)phenyl]sulfone, 3,3'-diaminodiphenyl ether,  
 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether,  
 3,3'-diaminodiphenyl methane, 3,4'-diaminodiphenyl methane,  
 4,4'-diaminodiphenyl methane, 3,3'-diaminodiphenyl sulfone,  
 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone,  
 3,4'-diaminodiphenyl sulfide, 4,4'-diaminodiphenyl sulfide,  
 m-phenylenediamine, p-phenylenediamine, 1,4-bis(4-  
 aminophenoxy)benzene, 9,9-bis(4-aminophenyl)fluorene, and a  
 diamine that have the following structure.

[0030]

[Chem. 4]



[0031]

In the general formulas (1) to (3),  $R^3$  and  $R^4$  each independently represent a carboxyl group, a phenolic hydroxyl group, a sulfonic acid group, or a thiol group as described above. Adjusting the amounts of the alkali-soluble groups of  $R^3$  and  $R^4$  changes the dissolution rate of the alkali-soluble polyimide (a) in an aqueous alkali solution, thus allowing a photosensitive resin composition that has a desired dissolution rate to be obtained.

[0032]

Furthermore, in order to improve adhesiveness to a substrate, an aliphatic group having a siloxane structure may be copolymerized with  $R^2$  in a range in which heat resistance is not reduced. Specific examples of the diamine component include those obtained by copolymerizing 1 to 10 mol% of bis(3-aminopropyl)tetramethyldisiloxane, bis(p-amino-phenyl)octamethylpentasiloxane, and the like.

[0033]

In the general formula (2), X is derived from a primary monoamine that is a terminal blocking agent. As

the primary monoamine for use as a terminal blocking agent, 5-amino-8-mercaptoquinoline, 1-hydroxy-7-aminonaphthalene, 1-hydroxy-6-aminonaphthalene, 1-hydroxy-5-aminonaphthalene, 1-hydroxy-4-aminonaphthalene, 2-hydroxy-7-aminonaphthalene, 2-hydroxy-6-aminonaphthalene, 2-hydroxy-5-aminonaphthalene, 1-carboxy-7-aminonaphthalene, 1-carboxy-6-aminonaphthalene, 1-carboxy-5-aminonaphthalene, 2-carboxy-7-aminonaphthalene, 2-carboxy-6-aminonaphthalene, 2-carboxy-5-aminonaphthalene, 2-aminobenzoic acid, 3-aminobenzoic acid, 4-aminobenzoic acid, 4-aminosalicylic acid, 5-aminosalicylic acid, 6-aminosalicylic acid, 2-aminobenzene sulfonic acid, 3-aminobenzene sulfonic acid, 4-aminobenzene sulfonic acid, 3-amino-4,6-dihydroxypyrimidine, 2-aminophenol, 3-aminophenol, 4-aminophenol, 2-aminothiophenol, 3-aminothiophenol, 4-aminothiophenol, and the like are preferable. These are used alone, or two or more thereof are used in combination.

[0034]

In addition, in the general formula (3), Y is derived from a dicarboxylic anhydride that is a terminal blocking agent. As the acid anhydride used as a terminal blocking agent, 4-carboxyphthalic anhydride, 3-hydroxyphthalic anhydride, cis-aconitic anhydride, and the like are preferred. These are used alone, or two or more thereof are used in combination.

[0035]

The alkali-soluble polyimide for use in the present invention may be composed of only a structure represented by the general formula (1) to (3), and may be a mixture with another structure that has alkali-solubility. In this case, it is preferable to contain the alkali-soluble polyimide that has a structure represented by the general formulas (1) to (3) at 30% by weight or more with respect to the total weight of the alkali-soluble polyimide. Furthermore, the content is preferably 60% by weight or more. When the content is 30% by weight or more, shrinkage during thermal curing can be suppressed, which is suitable for producing a thick film. The type and amount of polyimide to be mixed are preferably selected in a range in which the heat resistance of the polyimide obtained by the final heat treatment is not impaired.

[0036]

The alkali-soluble polyimide can be synthesized using a known method by substituting a part of diamine with monoamine that is a terminal blocking agent or by substituting tetracarboxylic dianhydride with dicarboxylic anhydride that is a terminal blocking agent. For example, a polyimide precursor is obtained by using methods such as a method of reacting tetracarboxylic dianhydride, a diamine compound, and monoamine at a low temperature, a method of

reacting tetracarboxylic dianhydride, dicarboxylic anhydride, and a diamine compound at a low temperature, and a method of obtaining a diester from a tetracarboxylic dianhydride and an alcohol and then performing a reaction in the presence of diamine, monoamine, and a condensing agent. Thereafter, polyimide can be synthesized using a method of completely imidizing the resulting polyimide precursor using a known imidization reaction method.

[0037]

In addition, an imidization ratio of the alkali-soluble polyimide can be easily determined, for example, by the following method. Here, the imidization ratio means how many mol% of the polyimide precursor is converted into polyimide in the case of synthesizing polyimide via the polyimide precursor as described above. First, an infrared absorption spectrum of a polymer is measured, and the presence of absorption peaks (near  $1,780\text{ cm}^{-1}$  and near  $1,377\text{ cm}^{-1}$ ) of an imide structure derived from polyimide is confirmed. Next, the polymer is subjected to a heat treatment at  $350^{\circ}\text{C}$  for 1 hour, an infrared spectrum is measured again, and then, peak intensities near  $1,377\text{ cm}^{-1}$  before the heat treatment and after the heat treatment are compared. Assuming that the imidization ratio of the polymer after the heat treatment is 100%, the imidization ratio of the polymer before the heat treatment is

determined. The imidization ratio of the polymer is preferably 90% or more.

[0038]

The terminal blocking agent introduced into the alkali-soluble polyimide can be detected by the following method. For example, the polyimide into which the terminal blocking agent is introduced is dissolved in an acidic solution and decomposed into an amine component and a carboxylic anhydride component that are constituent units of the polyimide, and then, measurement is performed by gas chromatography (GC) or NMR. Alternatively, the terminal blocking agent can also be detected by directly measuring the polyimide into which the terminal blocking agent is introduced using pyrolysis gas chromatograph (PGC) or an infrared spectrum and a  $^{13}\text{C}$ NMR spectrum.

[0039]

The content of the polymer (A) is preferably 20% by mass or more, more preferably 30% by mass or more, still more preferably 40% by mass or more in 100% by mass of the solids of the photosensitive resin composition excluding the inorganic filler (D) described later. The increased content of the polymer (A) allows the storage elastic modulus and pressure resistance of the cured product to be improved. In contrast, the content of the polymer (A) is preferably 80% by mass or less, more preferably 70% by mass

or less, still more preferably 60% by mass or less in 100% by mass of the solids of the photosensitive resin composition excluding the inorganic filler (D) described later. The reduced content of the polymer(A) allows the lamination property of the photosensitive resin sheet to be improved.

[0040]

[Radically Polymerizable Compound (B)]

The photosensitive resin composition according to the present invention contains a (B) radically polymerizable compound. The radically polymerizable compound (B) has, in the molecule, a functional group that exhibits radical polymerizability. Examples of the functional group that exhibits radical polymerizability include a vinyl group, an allyl group, an acryloyl group, a methacryloyl group, and a propargyl group. Among these examples, compounds having the acryloyl group or the methacryloyl group are preferred in view of polymerizability. Hereinafter, a compound having an acryloyl group or a methacryloyl group is referred to as a (meth)acrylic compound.

[0041]

In the present invention, the radically polymerizable functional group equivalent of the radically polymerizable compound (B) is 70 g/eq or more and 200 g/eq or less on average.

[0042]

The radically polymerizable functional group equivalent of the radically polymerizable compound (B) is, on average, 70 g/eq or more, more preferably 80 g/eq or more, still more preferably 90 g/eq or more, particularly preferably 100 g/eq or more. The increased radically polymerizable functional group equivalent allows the elongation of the cured product to be improved, and allows the generation of cracks to be suppressed. In contrast, the radically polymerizable functional group equivalent of the radically polymerizable compound (B) is, on average, 200 g/eq or less, more preferably 180 g/eq or less, still more preferably 160 g/eq or less, particularly preferably 140 g/eq or less. The reduced radically polymerizable functional group equivalent allows the storage elastic modulus and pressure resistance of the cured product to be improved, and allows the shape of the roof to be maintained at the time of a sealing step. In addition, the suppressed pattern swelling derived from the inorganic filler (D) described later allows the formation of a high-resolution pattern. This is presumed to be because the reduced radically polymerizable functional group equivalent improves the crosslinking density at the time of photocuring, and increases the difference in dissolution contrast between the exposed part and the unexposed part.

[0043]

The radically polymerizable functional group equivalent is determined from the following formula.

[0044]

Radically Polymerizable Functional Group Equivalent =  
(Molecular Weight/Number of Functional Groups exhibiting  
Radical Polymerizability in Same Molecule)

In addition, the average is obtained by averaging the radically polymerizable functional group equivalent of each radically polymerizable compound (B) with respect to the ratio of mass.

[0045]

The average number of functional groups of the radically polymerizable compound (B) is preferably 2 or more, more preferably 3 or more. The increased average number of functional groups allows the heat resistance of the cured product to be improved. In contrast, the average number of functional groups of the radically polymerizable compound (B) is preferably 6 or less, more preferably 4 or less. The reduced average number of functional groups allows the generation of cracks in the cured product to be suppressed.

[0046]

The radically polymerizable compound (B) is not particularly limited as long as the radically polymerizable

functional group equivalent is 70 g/eq or more and 200 g/eq or less on average, and examples of the (meth)acrylic compound include a diethylene glycol diacrylate, a triethylene glycol diacrylate, a tetraethylene glycol diacrylate, a diethylene glycol dimethacrylate, a triethylene glycol dimethacrylate, a tetraethylene glycol dimethacrylate, a trimethylolpropane diacrylate, a trimethylolpropane triacrylate, a trimethylolpropane dimethacrylate, a trimethylolpropane trimethacrylate, a butyl acrylate, a butyl methacrylate, an isobutyl acrylate, a hexyl acrylate, an isooctyl acrylate, an isobornyl acrylate, an isobornyl methacrylate, a cyclohexyl methacrylate, a glycidyl methacrylate, 4-hydroxybutyl acrylate glycidyl ether, 1,3-butanediol diacrylate, 1,3-butanediol dimethacrylate, a neopentyl glycol diacrylate, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, 1,9-nonanediol dimethacrylate, 1,10-decanediol dimethacrylate, a dimethyloltricyclodecane diacrylate, a dimethyloltricyclodecane dimethacrylate, 1,3-adamantane diacrylate, 1,3-adamantane dimethacrylate, 1,3,5-adamantane triacrylate, 1,3,5-adamantane trimethacrylate, 5-hydroxy-1,3-adamantane diacrylate, 5-hydroxy-1,3-adamantane dimethacrylate, a pentacyclopentadecane dimethanol diacrylate, a pentacyclopentadecane dimethanol diacrylate,

a pentaerythritol triacrylate, a pentaerythritol tetraacrylate, a pentaerythritol trimethacrylate, a pentaerythritol tetramethacrylate, a dipentaerythritol hexaacrylate, a dipentaerythritol hexamethacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 1,3-diacryloyloxy-2-hydroxypropane, 1,3-dimethacryloyloxy-2-hydroxypropane, 2,2,6,6-tetramethylpiperidinyll methacrylate, 2,2,6,6-tetramethylpiperidinyll acrylate, N-methyl-2,2,6,6-tetramethylpiperidinyll methacrylate, N-methyl-2,2,6,6-tetramethylpiperidinyll acrylate, a dioxane glycol diacrylate, an ethylene oxide-modified bisphenol A diacrylate, an ethylene oxide-modified bisphenol A dimethacrylate, a propylene oxide-modified bisphenol A diacrylate, a propylene oxide-modified bisphenol A methacrylate, propylene oxide-modified bisphenol A, a propoxylated ethoxylated bisphenol A diacrylate, a propoxylated ethoxylated bisphenol A dimethacrylate, an ethylene oxide-modified pentaerythritol tetramethacrylate, a propylene oxide-modified pentaerythritol tetraacrylate, an isocyanuric acid ethylene oxide-modified diacrylate, an isocyanuric acid ethylene oxide-modified dimethacrylate, an isocyanuric acid ethylene oxide-modified triacrylate, and an isocyanuric acid ethylene oxide-modified trimethacrylate. These are used alone, or two or more thereof are used in combination.

[0047]

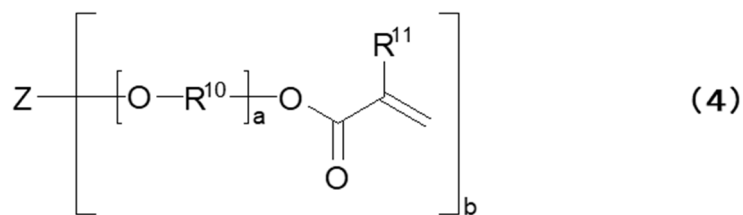
The content of the (B) radically polymerizable compound is preferably 10 parts by mass or more, more preferably 20 parts by mass or more, still more preferably 30 parts by mass or more, particularly preferably 50 parts by mass or more, with respect to 100 parts by mass of the polymer (A). The content is 10 parts by mass or more, thereby allowing the film loss of the exposed part at the time of development to be reduced. In contrast, the content of the radically polymerizable compound (B) is preferably 300 parts by mass or less, more preferably 200 parts by mass or less, still more preferably 100 parts by mass or less, particularly preferably 80 parts by mass or less with respect to 100 parts by mass of the polymer (A). The content is 300 parts by mass or less, thereby allowing the heat resistance of the cured product to be improved.

[0048]

As the radically polymerizable compound (B), a compound represented by the general formula (4) is preferably contained.

[0049]

[Chem. 5]



[0050]

In the general formula (4),  $\text{R}^{10}$  represents a hydrocarbon group having 1 to 5 carbon atoms, and  $\text{R}^{11}$  represents hydrogen or a methyl group. Z represents an organic group. a represents an integer of 0 to 1, and b represents an integer of 2 to 10. a is preferably 0. b is preferably 4 to 8 when Z has no cyclic skeleton, or b is preferably 2 to 4 when Z has a cyclic skeleton, and when Z has a cyclic skeleton, the cyclic skeleton is preferably an alicyclic skeleton.

[0051]

When the total mass of the radically polymerizable compound (B) is regarded as 100% by mass, the content of the compound represented by the following general formula (4) is preferably 70% by mass or more and 100% by mass or less, more preferably 80% by mass or more and 100% by mass or less, still more preferably 90% by mass or more and 100% by mass or less. The content allows the storage elastic modulus and pressure resistance of the cured product to be improved, and allows the shape of the roof to be maintained at the time of a sealing step. In addition, the suppressed

pattern swelling derived from the inorganic filler (D) described later allows the formation of a high-resolution pattern.

[0052]

Furthermore, the radically polymerizable compound (B) in the photosensitive resin composition according to the present invention preferably contains a radically polymerizable compound (B1) that has no cyclic structure and has a radically polymerizable functional group equivalent of 80 to 120 g/eq (hereinafter, referred to as a component (B1)). Containing the component (B1) allows the storage elastic modulus and pressure resistance of the cured product to be improved.

[0053]

The number of functional groups of the component (B1) is preferably 3 or more, more preferably 4 or more. The number of functional groups is 3 or more, thereby allowing the heat resistance of the cured product to be improved. In contrast, the number of functional groups of the component (B1) is preferably 10 or less, more preferably 8 or less. The number of functional groups is 10 or less, thereby allowing the generation of cracks in the cured product to be suppressed.

[0054]

Specific examples of the component (B1) include, but

are not limited to, a trimethylolpropane triacrylate, a trimethylolpropane trimethacrylate, a pentaerythritol triacrylate, a pentaerythritol tetraacrylate, a pentaerythritol trimethacrylate, a pentaerythritol tetramethacrylate, a ditrimethylolpropane tetraacrylate, a ditrimethylolpropane tetramethacrylate, a dipentaerythritol pentaacrylate, a dipentaerythritol pentamethacrylate, a dipentaerythritol pentamethacrylate, a dipentaerythritol hexaacrylate, and a dipentaerythritol hexamethacrylate.

[0055]

The radically polymerizable compound (B) preferably contains a radically polymerizable compound (B2) that has an alicyclic structure and has a radically polymerizable functional group equivalent of 130 to 200 g/eq (hereinafter, referred to as a component (B2)). Containing the component (B2) allows the elongation to be improved while improving the storage elastic modulus and pressure resistance of the cured product.

[0056]

The number of functional groups of the component (B2) is preferably 2 or more. The number of functional groups is 2 or more, thereby allowing the heat resistance of the cured product to be improved. In contrast, the number of functional groups of the component (B2) is preferably 6 or less, more preferably 4 or less. The number of functional

groups is 6 or less, thereby allowing the generation of cracks in the cured product to be suppressed.

[0057]

Specific examples of the component (B2) include, but are not limited to, a dimethyloltricyclodecane diacrylate, a dimethyloltricyclodecane dimethacrylate, 1,3-adamantane diacrylate, 1,3-adamantane dimethacrylate, 1,3,5-adamantane triacrylate, 1,3,5-adamantane trimethacrylate, 5-hydroxy-1,3-adamantane diacrylate, 5-hydroxy-1,3-adamantane dimethacrylate, bis-(2-acryloxyethyl)isocyanurate, and tris-(2-acryloxyethyl)isocyanurate.

[0058]

When the total mass of the radically polymerizable compound (B) is regarded as 100% by mass, the total mass of the component (B1) and component (B2) is preferably 70% by mass or more and 100% by mass or less, more preferably 80% by mass or more and 100% by mass or less, still more preferably 90% by mass or more and 100% by mass or less. The content allows the storage elastic modulus and pressure resistance of the cured product to be improved, and allows the shape of the roof to be maintained at the time of a sealing step. In addition, the suppressed pattern swelling derived from the inorganic filler (D) described later allows the formation of a high-resolution pattern.

[0059]

In addition, in the present invention, when the total mass of the component (B1) and component (B2) is regarded as 100% by mass, the content of the component (B1) is preferably 20% by mass or more and 80% by mass or less. More specifically, when the total mass of the component (B1) and component (B2) is regarded as 100% by mass, the content of the component (B1) is preferably 20% by mass or more, more preferably 30% by mass or more, still more preferably 40% by mass or more. The content is 20% by mass or more, thereby allowing the storage elastic modulus and pressure resistance of the cured product to be improved. In contrast, when the total mass of the component (B1) and component (B2) is regarded as 100% by mass, the content of the component (B1) is preferably 80% by mass or less, more preferably 70% by mass or less, still more preferably 60% by mass or less. The content is 80% by mass or less, thereby allowing the elongation of the cured product to be improved.

[0060]

[Photopolymerization Initiator (C)]

The photosensitive resin composition according to the present invention contains a photopolymerization initiator (C). As the photopolymerization initiator (C) is contained, the radical polymerization of the radically polymerizable compound (B) described above progresses so

that the exposed portion of the film of the resin composition becomes insoluble to the alkaline developer, a negative-type pattern can be formed.

[0061]

Examples of the photopolymerization initiator (C) include benzophenones, glycines, mercaptos, oximes, acylphosphines, and  $\alpha$ -aminoalkylphenones, and in particular, acylphosphines and oximes are suitably used. These photopolymerization initiators may be used alone, or two or more thereof may be used in combination.

[0062]

Specific examples of the photopolymerization initiator (C) include benzophenones such as benzophenone, Michler's ketone, 4,4'-bis(diethylamino)benzophenone, and 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone, benzylidenes such as 3,5-bis(diethylaminobenzylidene)-N-methyl-4-piperidone and 3,5-bis(diethylaminobenzylidene)-N-ethyl-4-piperidone, coumarins such as 7-diethylamino-3-nonylcoumarin, 4,6-dimethyl-3-ethylaminocoumarin, 3,3'-carbonylbis(7-diethylaminocoumarin), 7-diethylamino-3-(1-methylmethylbenzoimidazolyl)coumarin, and 3-(2-benzothiazolyl)-7-diethylaminocoumarin, anthraquinones such as 2-t-butyl anthraquinone, 2-ethyl anthraquinone, and 1,2-benzanthraquinone, benzoin ethers such as benzoin methyl ether, benzoin ethyl ether, and benzoin isopropyl ether,

thioxanthenes such as 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2,4-diisopropylthioxanthone, and 2-isopropylthioxanthone, mercaptos such as ethylene glycol di(3-mercaptopropionate), 2-mercaptobenzthiazole, 2-mercaptobenzoxazole, and 2-mercaptobenzimidazole, glycines such as N-phenylglycine, N-methyl-N-phenylglycine, N-ethyl-N-(p-chlorophenyl)glycine, and N-(4-cyanophenyl)glycine, oximes such as 1-phenyl-1,2-butanedione-2-(o-methoxycarbonyl)oxime, 1-phenyl-1,2-propanedione-2-(o-methoxycarbonyl)oxime, 1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl)oxime, 1-phenyl-1,2-propanedione-2-(o-benzoyl)oxime, bis( $\alpha$ -isonitrosopropiophenone oxime)isophthal, 1,2-octanedione-1-[4-(phenylthio)phenyl]-2-(o-benzoyloxime), and ethanone-1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-1-(o-acetyloxime), acylphosphines such as 2,4,6-trimethylbenzoyl-diphenylphosphine oxide and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide,  $\alpha$ -aminoalkylphenones such as 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butane-1-one and 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, and 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole.

[0063]

In particular, examples of preferred acylphosphines and oximes include 2,4,6-trimethylbenzoyl-diphenyl-

phosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, 1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl)oxime, 1-phenyl-1,2-propanedione-2-(o-benzoyl)oxime, bis( $\alpha$ -isonitrosopropiophenone oxime)isophthal, 1,2-octanedione-1-[4-(phenylthio)phenyl]-2-(o-benzoyloxime)], ethanone-1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-1-(o-acetyloxime), and compounds selected from ADEKA ARKLS (registered trademark) N-1919, NCI-831, and NCI-930 manufactured by ADEKA CORPORATION) and OXE-01, OXE-02, OXE-03, and OXE-04 manufactured by BASF SE.

[0064]

The content of the photopolymerization initiator (C) is preferably 0.5 parts by mass or more, more preferably 1 part by mass or more, still more preferably 2 parts by mass or more in 100 parts by mass of the polymer (A). The content of the photopolymerization initiator (C) is 0.5 parts by mass or more, thereby allowing the sensitivity of the photosensitive resin composition to exposure to be improved. In contrast, the content of the photopolymerization initiator (C) is preferably 30 parts by mass or less, more preferably 20 parts by mass or less, still more preferably 150 parts by mass or less in 100 parts by mass of the polymer (A). The content of the photopolymerization initiator (C) is 30 parts by mass or

less, thereby allowing light to be transmitted deeply, and allowing a favorable pattern shape to be obtained.

[0065]

[Inorganic Filler (D)]

The photosensitive resin composition according to the present invention contains the inorganic filler (D).

Containing the inorganic filler (D) allows mechanical properties such as a storage elastic modulus and chemical resistance to be improved. This allows the shape of the roof to be maintained at the time of a sealing step.

Examples of the inorganic filler (D) include silicon oxides such as talc, amorphous silica, crystalline silica, fused silica, and spherical silica, a titanium oxide, an aluminum oxide, a calcium oxide, a magnesium oxide, a zinc oxide, a calcium carbonate, a magnesium carbonate, fly ash, dehydrated sludge, natural silica, synthetic silica, kaolin, clay, a calcium hydroxide, an aluminum hydroxide, a magnesium hydroxide, mica, hydrotalcite, an aluminum silicate, a magnesium silicate, a calcium silicate, calcined talc, wollastonite, a potassium titanate, a magnesium sulfate, a calcium sulfate, a magnesium phosphate, sepiolite, xonotlite, a boron nitride, aluminum borate, glass, a silica balloon, a glass balloon, iron-making slag, copper, iron, an iron oxide, sendust, an alnico magnet, magnetic powders such as various ferrites,

cement, Neuburg siliceous earth, diatomaceous earth, an antimony trioxide, a magnesium oxysulfate, a hydrated aluminum, a hydrated gypsum, alum, and a barium sulfate. The glass according to the present invention refers to an inorganic substance that has an amorphous property and has multiple inorganic oxides bonded. For example, fused silica exhibits an amorphous property, but is a single inorganic substance, and thus is not included in the glass in the present invention. The amorphous property and the presence or absence of bonds can be confirmed by the fact that peaks of X-ray diffraction are broad. Whether multiple inorganic oxides are present or not can be confirmed by a compositional analysis approach such as a fluorescent X-ray analysis.

[0066]

In particular, the inorganic filler (D) preferably includes a glass filler because adjusting the refractive index suppresses light scattering and allows an improvement in resolution. The glass filler is preferably included at 50% by mass or more, more preferably 90% by mass or more, still more preferably 100% by mass in 100 by mass of the inorganic filler (D).

[0067]

The glass filler preferably has a refractive index of 1.55 to 1.75 at a wavelength of 405 nm from the viewpoint

of refractive index matching with the resin component.

[0068]

The glass filler contains at least two selected from the group consisting of silicon oxide, aluminum oxide, and boron oxide, and preferably further contains a rare earth oxide. By containing the rare earth oxide, elution of a glass component due to humidity described below can be prevented, and a refractive index can be appropriately adjusted. The rare earth oxide contained in the glass filler may have one rare earth oxide, or two or more rare earth oxides used in combination. In the glass filler, the contents of magnesium oxide, calcium oxide, and zinc oxide, which cause elution of the components due to the influence of humidity, are preferably low, and the glass filler more preferably contain none of the oxides. Furthermore, the glass filler more preferably contains no alkali metal oxide from the viewpoint of insulation reliability. In addition, the glass filler is preferably an yttrium oxide or a lanthanoid oxide among rare earth oxides from the viewpoint of ease of mixing with at least two or more oxides of a silicon oxide, an aluminum oxide, and a boron oxide, and it is more preferable to use an yttrium oxide from the viewpoint of accurately adjusting a refractive index of the glass filler.

[0069]

As described above, since the contents of the magnesium oxide, calcium oxide, and zinc oxide are preferably small, the total amount of magnesium ions, calcium ions, and zinc ions detected in an extract obtained by performing an extraction treatment on the glass filler under a saturated water vapor pressure condition at 121°C for 24 hours is preferably 100 ppm (weight basis) or less in the glass filler. It is to be noted that the measurement can be performed by the method described in the examples described below.

[0070]

In order to set the total amount of magnesium ions, calcium ions, and zinc ions detected in the extract obtained by performing the extraction treatment on the glass filler under the saturated water vapor pressure condition at 121°C for 24 hours to 100 ppm (weight basis) or less in the glass filler, and further to obtain the glass filler with a refractive index of 1.55 to 1.75 at 405 nm, the glass filler preferably has the total content of at least two selected from the group consisting of silicon oxide, aluminum oxide, and boron oxide of 65 to 85% by mass, and the total content of rare earth oxides of 15 to 35% by mass, in 100% by mass of the glass filler. More preferably, the glass filler contains 40 to 50% by mass of silicon oxide, 20 to 30% by mass of aluminum oxide, 0 to

10% by mass of boron oxide, and 15 to 35% by mass of a rare earth oxide in 100% by mass of the glass filler. The content of the rare earth oxide contained in the glass filler can be measured by a generally known quantitative method for measuring inorganic elements, and can be measured by combining SEM-EDX, TEM-EDX, ICP-MS, fluorescent X-ray analysis, X-ray diffraction, electron beam diffraction, and the like. It is to be noted that SEM-EDX refers to scanning electron microscope-energy dispersive X-ray spectroscopy, TEM-EDX refers to transmission electron microscope-energy dispersive X-ray spectroscopy, and ICP-MS refers to inductively coupled plasma mass spectrometry.

[0071]

The glass filler in the present invention refers to glass having no sharp peak (half-value width of  $2^\circ$  or less) representing a crystal structure of a specific component in powder X-ray diffraction measurement of  $2\theta-\theta$ .

[0072]

The refractive index of the inorganic filler (D) can be measured by a V block method, and in the present invention, the result of measurement at a wavelength of 405 nm is taken as the refractive index. In the case of a large difference in refractive index between the inorganic filler (D) and the solids of the photosensitive resin composition, reflection or scattering occurs at the

interface, thus decreasing the resolution. For obtaining favorable resolution, the difference between the refractive index of the inorganic filler (D) and the refractive index of the solids of the photosensitive resin composition excluding the inorganic filler (D) preferably has an absolute value of 0.05 or less. The refractive index of the solids of the photosensitive resin composition excluding the inorganic filler (D) mainly depends on the refractive index of the polymer (A), and when the polymer (A) is a polyimide, the refractive index is 1.55 to 1.75. The refractive index of the solids of the photosensitive resin composition excluding the inorganic filler (D) can be determined by preparing only the organic component of the photosensitive resin composition, and then, after application and drying steps, performing a measurement for light with a wavelength of 405 nm at 25°C by an ellipsometry method. The absolute value of the difference between the refractive index of the inorganic filler (D) and the refractive index of the solids of the photosensitive resin composition excluding the inorganic filler (D) is preferably as small as possible, particularly preferably, there is no difference, that is, the absolute value of the difference is 0.

[0073]

The average particle diameter of the inorganic filler

(D) is preferably 0.1 to 3.0  $\mu\text{m}$ , more preferably 0.1 to 2.0  $\mu\text{m}$ . As the average particle diameter is smaller, smoothness of a surface of an insulating film after pattern processing can be more improved. The average particle diameter of the inorganic filler (D) referred to in the present invention is the value of a 50 vol% particle diameter measured with the use a particle size distribution meter (Microtrac particle size analyzer MODEL MT3000) with a laser diffraction scattering method used. The measurement is performed by taking about 1 g of a sample and dispersing the sample in purified water for 1 to 3 minutes with ultrasonic waves having a power of 40 W. In a case where the shape of the inorganic filler (D) is not spherical, the average particle diameter obtained by the laser diffraction scattering method represents a diameter of a volume equivalent shape, but the average particle diameter preferably falls within the range mentioned above, regardless of the shape of the inorganic filler (D). Examples of the shape of the inorganic filler (D) include, but are not limited to, a spherical shape, a needle shape, a fiber shape, an amorphous granular shape, a plate shape, a crushed shape, and the like.

[0074]

The content of the inorganic filler (D) is preferably 30% by mass or more, more preferably 50% by mass or more,

still more preferably 60% by mass or more when the total mass of the solids of the photosensitive resin composition is regarded as 100% by mass, from the viewpoint of improving mechanical properties such as a storage elastic modulus and chemical resistance. In contrast, the content of the inorganic filler (D) is preferably 80% by mass or less with respect to the total mass: 100% by mass of the solids of the photosensitive resin composition, from the viewpoint of improving the elongation.

[0075]

In addition, for dispersing the inorganic filler (D) in the photosensitive resin composition, a surface treatment with a silane coupling agent may be performed, as necessary. As a specific example of the silane coupling agent, vinyltrimethoxysilane (KBM-1003), 3-glycidoxypropyltrimethoxysilane (KBM-403), 3-methacryloxypropyltrimethoxysilane (KBM-503), N-2-(aminoethyl)-3-aminopropyltrimethoxysilane (KBM-603), N-phenyl-3-aminopropyltrimethoxysilane (KBM-573), and the like of Shin-Etsu Chemical Co., Ltd. can be used. The surface treatment for the inorganic filler (D) can be performed by a dry surface treatment of stirring with a silane coupling agent and a small amount of water added to the inorganic filler (D).

[0076]

[Other Components]

The photosensitive resin composition according to the present invention preferably contains a thermal crosslinking agent (E). The thermal crosslinking agent (E) is a component that is cured by a heat treatment after pattern processing, which can improve the mechanical properties and chemical resistance of the cured product. As the thermal crosslinking agent (E), a compound containing at least one of an alkoxymethyl group, a methylol group, and an epoxy group is preferred, and a compound containing at least two of an alkoxymethyl group, a methylol group, and an epoxy group is more preferred.

[0077]

Among the thermal crosslinking agents (E), examples of the compound having an alkoxymethyl or methylol groups include 46DMOC and 46DMOEP (product names, manufactured by ASAHI YUKIZAI CORPORATION), DML-PC, DML-PEP, DML-OC, DML-OEP, DML-34X, DML-PTBP, DML-PCHP, DML-OCHP, DML-PFP, DML-PSBP, DML-POP, DML-MBOC, DML-MBPC, DML-MTrisPC, DML-BisOC-Z, DML-BisOCHP-Z, DML-BPC, DMLBisOC-P, DMOM-PC, DMOM-PTBP, DMOM-MBPC, TriML-P, TriML-35XL, TML-HQ, TML-BP, TML-pp-BPF, TML-BPE, TML-BPA, TML-BPAF, TML-BPAP, TMOM-BP, TMOM-BPE, TMOM-BPA, TMOM-BPAF, TMOM-BPAP, HML-TPPHBA, HML-TPHAP, HMOM-TPPHBA and HMOM-TPHAP (product names, manufactured by Honshu Kagaku Industry Co., Ltd.), and "NIKALAC" registered

trademark) MX-290, "NIKALAC" MX-280, "NIKALAC" MX-270, "NIKALAC" MX-279, "NIKALAC" MW-100LM, and "NIKALAC" MX-750LM (product names, manufactured by Sanwa Chemical Co., Ltd.).

[0078]

Among the thermal crosslinking agents (E), examples of the compound having an epoxy group include a bisphenol A type epoxy resin, a bisphenol F type epoxy resin, a propylene glycol diglycidyl ether, a polypropylene glycol diglycidyl ether, polymethyl(glycidylloxypropyl), and an epoxy group-containing silicone. Specific examples thereof include "EPICLON" (registered trademark) 850-S, "EPICLON" HP-4032, "EPICLON" HP-7200, "EPICLON" HP-820, "EPICLON" HP-4700, "EPICLON" EXA-4710, "EPICLON" HP-4770, "EPICLON" EXA-859 CRP, "EPICLON" EXA-1514, "EPICLON" EXA-4880, "EPICLON" EXA-4850-150, "EPICLON" EXA-4850-1000, "EPICLON" EXA-4816, and "EPICLON" EXA-4822 (product names, manufactured by Dainippon Ink and Chemicals, Inc.), "RIKARESIN" (registered trademark) BEO-60E, "RIKARESIN" BPO-20E, "RIKARESIN" HBE-100, and "RIKARESIN" DME-100 (product names, manufactured by New Japan Chemical Co., Ltd.), EP-4003S and EP-4000S (product names, manufactured by ADEKA Corporation), PG-100, CG-500, and EG-200 (product names, manufactured by Osaka Gas Chemicals Co., Ltd.), NC-3000 and NC-6000 (product names, manufactured by Nippon Kayaku Co., Ltd.), "EPOX"

(registered trademark) -MK R508, "EPOX" -MK R540, "EPOX" -MK R710, "EPOX" -MK R1710, VG3101L, and VG3101M80 (product names, manufactured by Printec Corporation), "CELLOXIDE" (registered trademark) 2021 P, "CELLOXIDE" 2081, "CELLOXIDE" 2083, and "CELLOXIDE" 2085 (product names, manufactured by Daicel Chemical Industries, Ltd.).

For the thermally crosslinking agent (E), two or more of the foregoing examples can be used in combination.

[0079]

The content of the thermal crosslinking agent (E) in the photosensitive resin composition according to the present invention is preferably 1% by mass or more, more preferably 5% by mass or more, with respect to 100% by mass of the polymer (A). The content of the thermal crosslinking agent (E) is 1% by mass or more, thereby allowing the mechanical properties and chemical resistance of the cured product to be improved. In contrast, the content of the thermal crosslinking agent (E) is preferably 50% by mass or less, more preferably 30% by mass or less, with respect to 100% by mass of the polymer (A). The content of the thermal crosslinking agent (E) is 50% by mass or less, thereby allowing the storage stability of the photosensitive resin composition to be improved.

[0080]

In addition, the photosensitive resin composition

according to the present invention may further contain a polymerization inhibitor. By containing the polymerization inhibitor, a concentration of excitons is adjusted, such that a pattern having a rectangular cross-sectional shape can be formed. In addition, excessive photoresponsiveness can be suppressed by the polymerization inhibitor, and an exposure margin can be widened.

[0081]

Examples of the polymerization inhibitor include a phenolic polymerization inhibitor such as hydroquinone, hydroquinone monomethyl ether, or t-butylcatechol, phenothiazine, 2-methoxyphenothiazine, 1-naphthol, 1,4-dihydroxynaphthalene, 4-methoxy-1-naphthol, 1-methoxynaphthalene, 1,4-dimethoxynaphthalene, 2,6-dimethoxynaphthalene, 2,7-dimethoxynaphthalene, 1,4-diethoxynaphthalene, 2,6-diethoxynaphthalene, 2,7-diethoxynaphthalene, 2,6-dibutoxynaphthalene, 2-ethyl-1,4-diethoxynaphthalene, 1,4-dibutoxy naphthalene, 1,4-diphenethyloxynaphthalene, 1,4-naphthoquinone, 2-hydroxy-1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone, 9-butoxyanthracene, 9,10-butoxyanthracene, 9-anthrone, 9,10-anthraquinone, and 2-ethyl-9,10-anthraquinone. These polymerization inhibitors are used alone or in combination of two or more thereof.

[0082]

The photosensitive resin composition according to the present invention may contain a sensitizer, an adhesion improver, a colorant, a dispersant, and the like, as necessary.

[0083]

[Method for Producing Photosensitive Resin Composition]

Next, an example of a method for producing a photosensitive resin composition according to the present invention will be described. One aspect of the photosensitive resin composition according to the present invention is a varnish material obtained by dissolving and diluting various raw materials in a solvent. Examples of the dissolution method include ultrasonic waves, blade stirring, and a ball mill, and filtration with a filter may be performed, as necessary. The filtration method is not particularly limited, but a method of performing filtration by pressure filtration with the use of a filter with a retained particle diameter of 1  $\mu\text{m}$  to 50  $\mu\text{m}$  is preferred. The solvent used for dilution is not particularly limited, and examples thereof include ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, and ethylene glycol dibutyl ether,

acetates such as ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate, propyl acetate, butyl acetate, isobutyl acetate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, methyl lactate, ethyl lactate, and butyl lactate, ketones such as acetone, methyl ethyl ketone, acetyl acetone, methyl propyl ketone, methyl butyl ketone, methyl isobutyl ketone, cyclopentanone, and 2-heptanone, alcohols such as butyl alcohol, isobutyl alcohol, pentanol, 4-methyl-2-pentanol, 3-methyl-2-butanol, 3-methyl-3-methoxy butanol, and diacetone alcohol, aromatic hydrocarbons such as toluene and xylene, N-methyl-2-pyrrolidone, N-cyclohexyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, and  $\gamma$ -butyrolactone.

[0084]

[Photosensitive Resin Sheet]

The photosensitive resin composition according to the present invention constitutes a photosensitive resin sheet that has a layer of the photosensitive resin composition formed on a supporting film (also referred to as a support film) by applying the photosensitive resin composition in the form of the varnish material described above on the support film and drying the photosensitive resin composition. More specifically, the photosensitive resin sheet according to the present invention is a

photosensitive resin sheet including a support film and a layer of the photosensitive resin composition according to the present invention (referred to as a photosensitive resin layer) on the support film.

[0085]

The support film used in the photosensitive resin sheet according to the present invention is not particularly limited, and various films that are commonly commercially available, such as a polyethylene terephthalate (PET) film, a polyphenylene sulfide film, and a polyimide film, can be used. The interface between the support film and the layer of the photosensitive resin may be subjected to a surface treatment with silicone, a silane coupling agent, an aluminum chelating agent, polyurea, or the like in order to improve adhesion and peelability. The thickness of the support film is not particularly limited, and is preferably in a range of 10 to 100  $\mu\text{m}$  from the viewpoint of workability. In exposing the layer of the photosensitive resin composition, the layer can be exposed through the support film, and thus, the haze of the support film is preferably 2.0% or less. When the haze is more than 2.0%, scattering of expose light occurs, resulting in deterioration of pattern-processability.

[0086]

In addition, for protecting the photosensitive resin

sheet, a protective film may be provided on the side of the layer in the photosensitive resin sheet including the layer of the photosensitive resin composition and the support film. Thus, the surface of the layer of the photosensitive resin composition of the photosensitive resin sheet can be protected from contaminants such as dust and dirt in the air. Examples of the protective film include a polyethylene film, a polypropylene (PP) film, a polyester film, and a polyvinyl alcohol film. The protective film is preferably a film such that the layer of the photosensitive resin composition and the protective film are not easily peeled off.

[0087]

Examples of the method for applying the photosensitive resin composition to the support film include methods such as spin coating using a spinner, spray coating, roll coating, screen printing, blade coater, die coater, calender coater, meniscus coater, bar coater, roll coater, comma roll coater, gravure coater, screen coater, and slit die coater. In addition, the film thickness applied varies depending on the application technique, the solid concentration and the viscosity of the composition, and the like, but usually, the film thickness after drying is preferably 3  $\mu\text{m}$  or more and 100  $\mu\text{m}$  or less.

[0088]

For the photosensitive resin sheet according to the present invention, the thickness of the layer of the photosensitive resin composition is preferably 10 to 50  $\mu\text{m}$ . In particular, in the case of using the cured product according to the present invention as a roof material for a hollow structure of an electronic component, the layer of the photosensitive resin composition is preferably 10  $\mu\text{m}$  or more, more preferably 20  $\mu\text{m}$  or more, still more preferably 30  $\mu\text{m}$  or more in thickness from the viewpoint of pressure resistance. In contrast, from the viewpoint of reducing the height of the electronic component, the layer of the photosensitive resin composition is preferably 50  $\mu\text{m}$  or less, more preferably 40  $\mu\text{m}$  or less in thickness. For the drying, an oven, a hot plate, infrared rays, or the like can be used. The drying temperature and the drying time may fall within a range in which an organic solvent can be volatilized, and it is preferable to appropriately set a range in which the photosensitive resin sheet is in an uncured or semi-cured state. Specifically, the drying is preferably performed in a range of 40°C to 120°C for 1 minute to several tens of minutes. In addition, the temperature may be increased stepwise by combining these temperatures, and for example, the heat treatment may be performed at 50°C, 60°C, and 70°C for 1 minute each.

[0089]

For the photosensitive resin sheet according to the present invention, when the photosensitive resin layer is 25  $\mu\text{m}$  in thickness, the visible light transmittance T25 of the photosensitive resin layer is preferably 40% or more and 100% or less, more preferably 50% or more and 100% or less. The visible light transmittance T25 of the photosensitive resin layer is 40% or more when the photosensitive resin layer is 25  $\mu\text{m}$  in thickness, thereby improving the visibility of an alignment mark on the substrate and facilitating the adjustment of the position of a photomask in adjusting the position for exposure. The visible light transmittance T25 can be calculated by averaging the transmittance measured at a wavelength of 400 to 800 nm with an ultraviolet-visible spectrophotometer.

[0090]

[Cured Product]

The cured product according to the present invention is a cured product of the photosensitive resin composition according to the present invention. The cured product according to the present invention can be obtained by photocuring and thermally curing the photosensitive resin composition according to the present invention.

[0091]

The storage elastic modulus at 180°C of the cured product according to the present invention is preferably 10

GPa or more, more preferably 12 GPa or more, still more preferably 13 GPa or more, particularly preferably 14 GPa or more. The storage elastic modulus at 180°C is 10 GPa or more, thereby making it easy to withstand a sealing step in the application as a roof material. In contrast, from the viewpoint of crack suppression, the storage elastic modulus at 180°C of the cured product is preferably 20 GPa or less, more preferably 18 GPa or less, still more preferably 16 GPa or less.

[0092]

The elongation of the cured product obtained by the heat treatment is preferably 0.5% or more, more preferably 1.0% or more, still more preferably 2.0%. The elongation is 0.5% or more, thereby allowing the generation of cracks to be suppressed at the time of a sealing step in the application as a roof material.

[0093]

The cured product according to the present invention preferably satisfies a relationship of  $15 < TG - TE < 25$ , where TE (°C) is a temperature at which the loss elastic modulus reaches a maximum, and TG (°C) is a glass transition temperature. TG - TE is larger than 15, thereby making it easy to withstand a sealing step in the application as a roof material. In contrast, TG - TE is smaller than 25, thereby allowing cracks to be suppressed.

[0094]

The cured product according to the present invention preferably satisfies a relationship of  $1.5 < E_{MAX}/E_{180} < 3.2$ , where  $E_{MAX}$  (GPa) is the maximum value of the loss elastic modulus, and  $E_{180}$  (GPa) is the loss elastic modulus at 180°C.  $E_{MAX}/E_{180}$  is larger than 1.5, thereby making it easy to withstand a sealing step in the application as a roof material. In contrast,  $E_{MAX}/E_{180}$  is smaller than 3.2, thereby allowing cracks to be suppressed.

[0095]

[Hollow Structure]

The hollow structure according to the present invention is a hollow structure including the cured product of the photosensitive resin composition according to the present invention as a roof material. The hollow structure as used here refers to a structure that has a substrate, a convex portion formed on the substrate and provided to surround a part of the surface of the substrate, and a film-shaped material (hereinafter, referred to as a roof material) in contact with a top of the convex portion, has a closed space (hereinafter, referred to as a hollow portion) formed by the substrate, the convex portion, and the roof material, and includes the cured product according to the present invention in the roof material. More specifically, the hollow structure according to the present

invention is a hollow structure that has a substrate, a convex portion formed on the substrate and provided to surround a part of the surface of the substrate, and a film-shaped material (hereinafter, referred to as a roof material) in contact with a top of the convex portion, has a closed space (hereinafter, referred to as a hollow portion) formed by the substrate, the convex portion, and the roof material, with the roof material including the cured product according to the present invention. The convex portion formed on the substrate of the hollow structure may be referred to as a wall or a wall material. In addition, the film-shaped material provided so as to be in contact with the top of the convex portion is referred to as a roof or a roof material.

[0096]

The convex portion of the hollow structure may be formed on a substrate by printing of a resin material or photolithographic processing of a photosensitive material, or a recess may be formed by scraping a substrate by a method such as dry etching to relatively form a convex portion. In a case where the convex portion is formed from a photosensitive material, it is preferable to contain polyimide from the viewpoint of reliability.

[0097]

In the hollow structure according to the present

invention, the convex portion is preferably 5 to 25  $\mu\text{m}$  in thickness, and further, the short side of the substrate in the hollow portion is preferably 200 to 400  $\mu\text{m}$  in width. When the short side of the substrate in the hollow portion is 200  $\mu\text{m}$  or more in width, it is easy to dispose an internal electrode in the hollow portion, and when the width is 400  $\mu\text{m}$  or less, it is easy to maintain the shape of the roof at the time of a sealing step. The inside surrounded by the convex portion may have independent convex portions and convex portions that are continuous with the outer wall. It is to be noted that the width of the short side of the substrate in the hollow portion is the width ( $y_1$  in Fig. 1) of the short side of the inside surrounded by the convex portion of the substrate, and can be measured with a microscope capable of length measurement.

[0098]

For the hollow structure according to the present invention, the roof material preferably has a through hole. The roof material has the through hole, thereby allowing the formation of wiring inside the roof material. This eliminates the need for the formation of wiring on the outer wall of the hollow structure, and allows the electronic component to be reduced in size.

[0099]

A method for forming a hollow structure with the use of the photosensitive resin sheet according to the present invention includes the following steps:

step 1: a step of forming a convex portion on a substrate;

step 2: a step of bonding the photosensitive resin layer side of the photosensitive resin sheet onto the convex portion of the substrate;

step 3: a step of exposing the photosensitive resin layer;

step 4: a step of peeling off the support film;

step 5: a step of developing the photosensitive resin layer; and

step 6: a step of thermally curing the photosensitive resin layer to form a cured product.

[0100]

Each step will be described in detail with reference to Fig. 1 and Fig. 2.

[0101]

First, as described above, the convex portion is formed on the substrate by a method for forming a convex portion by printing a resin material or photolithographic processing of a photosensitive material on a substrate, a method for forming a recess by scraping a substrate by a method such as dry etching to relatively form a convex portion, or the like.

[0102]

Next, the photosensitive resin layer side of the photosensitive resin sheet is bonded onto the convex portion of the substrate. In Fig. 1 and (a) of Fig. 2, as representative examples, the width  $x$  of a convex portion 2 is 50  $\mu\text{m}$ , the high  $z$  of the convex portion 2 is 20  $\mu\text{m}$ , the width  $y_1$  of a short side of a substrate 1 in a hollow portion is 300  $\mu\text{m}$ , and the width  $y_2$  of a short side of the substrate 1 in the hollow portion is 500  $\mu\text{m}$ , but the dimensions are not limited thereto.

[0103]

A protective film is peeled off from the photosensitive resin sheet, a layer 4 of a photosensitive resin composition is disposed so as to face the substrate 1 on which the convex portion 2 is formed, and a roll comes contact with a roll laminator from a support film 3 side so as to bond them together ((b) of Fig. 2). The bonding temperature or pressure depend on the shape of the convex portion formed on the substrate, and are preferably 50 to 80°C and 0.05 to 0.3 MPa, respectively.

[0104]

Subsequently, exposure is performed by a photomask capable of forming a pattern covering the convex portion 2 with an exposure machine including an ultra-high pressure mercury lamp, an LED, a laser, or the like that emits light including ultraviolet rays with a wavelength of 405 nm as a

light source. Examples of the actinic ray to be employed for the exposure to light include ultraviolet ray, visible light, electron beam and X-ray. In the present invention, i-line (365 nm), h-line (405 nm) or g-line (436 nm) of a mercury lamp can be used preferably. The layer 4 of the photosensitive resin composition becomes a layer 5 in which a desired pattern is photocured by exposure ((c) of Fig. 2). Further, post-exposure bake may be performed after the exposure. Performing the post-exposure bake causes the reaction to proceed favorably, thereby allowing the expectation of advantageous effects, such as an improvement in post-development resolution or an increase in the allowable range of development conditions. The post-exposure baking can use an oven, a hot plate, infrared rays, a flash annealing device, a laser annealing device, or the like. The post-exposure bake temperature is preferably 40 to 150°C, more preferably 60 to 150°C. The post-exposure bake time is preferably 10 seconds to several hours.

[0105]

Subsequently, the support film 3 is peeled off ((d) of Fig. 2). The support film may be peeled off before the exposure, may be peeled off immediately after the exposure, or may be peeled off after the heat treatment after the exposure.

Subsequently, the unexposed part is removed with the use of a developing solution ((e) of Fig. 2). Examples of the developer include alkali aqueous solutions such as a tetramethylammonium hydroxide (TMAH) aqueous solution and a sodium carbonate aqueous solution, organic solvents such as cyclohexanone and propylene glycol methyl ether acetate (PGMEA), and can be appropriately selected depending on the solubility of the photosensitive resin layer. The temperature of the developer and the developing time are appropriately set depending on the pattern shape and the like, and are preferably 20 to 30°C and 30 seconds to 10 minutes, respectively. As the developing method, a method of a spray mode, a paddle mode, a dip mode, an ultrasonic mode and the like can be employed.

[0106]

Next, the pattern formed by the development is preferably subjected to a rinsing treatment with distilled water. An alcohol such as ethanol, isopropyl alcohol, an ester such as ethyl lactate, propylene glycol monomethyl ether acetate, or the like may be added to distilled water for the rinsing treatment.

[0107]

Furthermore, a heat treatment is performed to completely cure the photosensitive resin composition, thereby providing a hollow structure including a cured

product 6 of the photosensitive resin composition ((f) of Fig. 2). The photosensitive resin composition is completely cured by the thermal curing, thereby allowing the heat resistance and the chemical resistance to be improved.

[0108]

The heating temperature at which these properties are improved is preferably 150°C or higher, more preferably 180°C or higher. In addition, the heating temperature is preferably 350°C or lower, more preferably 300°C or lower, because the properties are degraded when the photosensitive resin layer is thermally decomposed. This heating treatment is performed for 5 minutes to 5 hours while selecting temperature levels and gradually increasing the temperature, or while selecting a certain temperature range and continuously increasing the temperature. As an example, the heat treatment is performed at each of 150°C and 250°C for 30 minutes. Alternatively, examples thereof include a method of linearly increasing the temperature over 2 hours from room temperature up to 300°C.

[0109]

[Electronic Component, Elastic Wave Filter]

The hollow structure according to the present invention is used for an electronic component including a hollow structure. Examples of the electronic component

including a hollow structure include an elastic wave filter. Similarly, the cured product according to the present invention is used for an electronic component including a cured product, and particularly preferred examples of the electronic component including the cured product according to the present invention include an elastic wave filter. More specifically, the electronic component according to the present invention has the cured product according to the present invention or the hollow structure according to the present invention. In addition, the elastic wave filter according to the present invention has the cured product according to the present invention or the hollow structure according to the present invention.

[0110]

In addition, the cured product according to the present invention can form an insulating film that is excellent in pattern processability and high in reliability, and thus can be suitably used for applications other than an electronic component including a hollow structure.

[0111]

The application of the cured product is not particularly limited, but the cured product can be applied to, for example, a surface protective film built in a substrate and a package for a system using a semiconductor,

such as a mounted substrate and a wafer level package, an interlayer insulating film, a resist such as a wiring protective insulating film for a circuit board, and various electronic components and devices. In addition, due to its excellent heat resistance, the cured product can be suitably used particularly for an adhesive in which a permanent resist, that is, a patterned interlayer insulating film, a pattern formed substrate, glass, a semiconductor element, or the like is subjected to thermocompression bond to an adherend.

#### EXAMPLES

[0112]

The present invention will be described below with reference to examples and the like, but the present invention is not to be considered limited by these examples.

[0113]

<Method for Determining Average of Radically Polymerizable Functional Group Equivalent of Radically Polymerizable Compound (B)>

The radically polymerizable functional group equivalent is determined from the following formula.  
Radically Polymerizable Functional Group Equivalent =  
(Molecular Weight/Number of Functional Groups exhibiting

#### Radical Polymerizability in Same Molecule)

In addition, the average of the radically polymerizable functional group equivalent is obtained by averaging the radically polymerizable functional group equivalent of each radically polymerizable compound (B) with respect to the ratio of mass. Specifically, when B<sub>x</sub>, B<sub>y</sub>, and B<sub>z</sub> are included as the radically polymerizable compound (B); the radically polymerizable functional group equivalents thereof are denoted respectively by R<sub>x</sub>, R<sub>y</sub>, and R<sub>z</sub>; the masses thereof are denoted respectively by W<sub>x</sub>, W<sub>y</sub>, and W<sub>z</sub>; and the total thereof is denoted by W, the average of the radically polymerizable functional group equivalents is  $R_x(W_x/W) + R_y(W_y/W) + R_z(W_z/W)$ .

[0114]

#### <Refractive Index of Inorganic Filler (D)>

The measurement was performed by a V block method. After 50 g of the inorganic filler (D) was melted at 1500°C for 4 hours with the use of a platinum crucible, the melt was poured into a carbon mold and slowly cooled to obtain a block of the inorganic filler (D). The obtained block of the inorganic filler (D) was processed into a rectangular parallelepiped shape of 10 mm or more × 10 mm or more × 10 mm or more, and a refractive index at a wavelength of 405 nm was measured with the use of a precision refractometer KPR-2000 manufactured by Shimadzu Device Corporation.

[0115]

<Refractive Index of Solids of Photosensitive Resin Composition excluding Inorganic Filler (D)>

A solution obtained by removing the inorganic filler (D) from the photosensitive resin composition was prepared, applied onto a silicon wafer, and dried. The refractive index at a wavelength of 405 nm at 25°C was measured by ellipsometry with the use of a spectroscopic ellipsometer SE-2000 manufactured by Semilab Inc.

[0116]

<Evaluation of Storage Elastic Modulus at 180°C, TE, TG, EMAX, and E180>

Protective films of photosensitive resin sheets obtained according to each example and each comparative example were peeled off, layers of the photosensitive resin compositions were each disposed so as to face a silicon wafer, and subjected to roll lamination onto the 4-inch silicon wafer under the conditions of 80°C and 0.3 MPa.

[0117]

The obtained support film and layer of the photosensitive resin composition were exposed at an exposure amount of 400 mJ/cm<sup>2</sup> (with an i-line cut filter used, in terms of h-line) with an exposure machine including an ultra-high pressure mercury lamp as a light source. After the exposure, the support film was peeled

off, and a cured product was formed on the silicon wafer by performing a heat treatment at 200°C for 60 minutes in an inert oven.

[0118]

The cured product obtained was peeled off from the silicon wafer to prepare a single film. This single film was cut into 5 mm × 40 mm with a single blade, and the storage elastic modulus at 180°C, the temperature TE at which the loss elastic modulus reached the maximum, the glass transition temperature TG, the maximum value EMAX of the loss elastic modulus, and the loss elastic modulus E180 at 180°C were measured with a dynamic viscoelasticity measuring device (DMS 6100 manufactured by Hitachi High-Tech Science Corporation).

[0119]

It is to be noted that this measurement was performed under the conditions of test mode: tensile, test temperature: room temperature (23°C) to 350°C, rate of temperature rise: 5 °C/min, test frequency: 1 Hz, distance between chucks: 10 mm, and sample width: 5 mm. The obtained storage elastic modulus at 180°C was used as an evaluation result.

[0120]

<Evaluation of Resolution>

Protective films of photosensitive resin sheets

obtained according to each example and each comparative example were peeled off, layers of the photosensitive resin compositions were each disposed so as to face a silicon wafer, and subjected to roll lamination onto the 4-inch silicon wafer under the conditions of 80°C and 0.3 MPa.

[0121]

The obtained support film and layer of the photosensitive resin composition with a photomask placed thereon, where 20 via patterns with via diameters of 5, 10, 15, and up to 100  $\mu\text{m}$  at intervals of 5  $\mu\text{m}$  were arranged in the photomask, were exposed at an exposure amount of 400  $\text{mJ}/\text{cm}^2$  (with an i-line cut filter used, in terms of h-line) with an exposure machine including an ultra-high pressure mercury lamp as a light source. After the exposure, the support film was peeled off, and heating was performed on a hot plate at 100°C for 5 minutes. Next, the unexposed part was removed by shower development for 480 seconds with the use of an aqueous solution of 2.38% by weight tetramethylammonium hydroxide, a rinsing treatment was performed with water for 60 seconds, and then spin drying was performed. Furthermore, a heat treatment was performed at 200°C for 60 minutes in an inert oven to form, on the silicon wafer, a cured product with the via patterns processed on the silicon wafer.

[0122]

The via patterns were observed with a microscope, and the minimum dimension at which the via was opened was defined as a resolution. The opening of the via as used herein was defined as a via opening when 50% or more of a design value of the photomask was opened. A case where a via of 45  $\mu\text{m}$  or less was opened was rated as A, and a case where a via of 50  $\mu\text{m}$  to 100  $\mu\text{m}$  was opened was rated as B.

[0123]

<Evaluation of Visible Light Transmittance T25 of Photosensitive Resin Layer>

The protective films of the photosensitive resin sheets obtained according to each example and each comparative example were peeled off for use as samples for evaluation. The transmittance of the sample at a wavelength of 400 to 800 nm was measured with the use of an ultraviolet-visible spectrophotometer (U-3900 manufactured by Hitachi High-Tech Science Corporation), and averaged to calculate the visible light transmittance T25.

[0124]

It is to be noted that this measurement was performed under the conditions of reference: support film, scan speed: 300 nm/min, and sampling interval: 0.5 nm. A case where the visible light transmittance T25 was 40% or more was rated as A, and a case where the visible light transmittance T25 is less than 40% was rated as B.

[0125]

<Evaluation of Elongation>

The treatment was performed in accordance with the same method as in the case of the above-described evaluation of the storage elastic modulus at 180°C, thereby preparing a single film of a cured product of the photosensitive resin composition. This single film was cut into 10 mm × 100 mm with a single blade, and the elongation was measured with a tensile tester (manufactured by Baldwin Corporation, UTM-4-100).

[0126]

It is to be noted that this measurement was performed under the conditions of tensile rate of 50 mm/min, distance between chucks of 50 mm, and sample width of 10 mm. A case where the elongation was 2% or more was rated as A, a case where the elongation was 1% or more and less than 2% was rated as B, and case where the elongation was less than 1% was rated as C.

[0127]

<Polymer (A)>

Polyimide 1:

The alkali-soluble polyimide synthesized by the following method was used.

[0128]

Under a dry nitrogen stream, 2,2-bis(3-amino-4

hydroxyphenyl)hexafluoropropane (32.78 g (0.0895 mol)) and 1,3-bis(3-aminopropyl)tetramethyldisiloxane (1.24 g (0.005 mol)) were dissolved in N-methyl-2-pyrrolidone (100 g). Hereinafter, the "N-methyl-2-pyrrolidone" is referred to as "NMP". To the solution, bis(3,4-dicarboxyphenyl)ether dianhydride (31.02 g (0.10 mol)) was added together with NMP (30 g), and the mixture was stirred at 20°C for 1 hour, and then at 50°C for 4 hours. To the stirred solution, 3-aminophenol (1.09 g (0.01 mol)) was added, and the mixture was stirred at 50°C for 2 hours, and then at 180°C for 5 hours to obtain a resin solution. Next, this resin solution was put into water (3 L) to produce a white precipitate. This white precipitate was collected by filtration, washed three times with water, and then dried in a vacuum dryer at 80°C for 5 hours. The imidization ratio of the polyimide obtained was 94%. In addition, the solubility of the polyimide A1 in an aqueous solution of tetramethylammonium (2.38% by mass) at 23°C was 0.5 g/100 g or more.

[0129]

<Radically Polymerizable Compound (B)>

DPE-6A (Kyoisha Chemical Co., Ltd.). Compound name: dipentaerythritol hexaacrylate, radically polymerizable functional group equivalent: 96 g/eq, the number of functional groups: 6. Corresponding to the component (B1).

Corresponding to the general formula (4).

[0130]

M-450 (Toagosei Company, Limited). Compound name: pentaerythritol tetraacrylate, radically polymerizable functional group equivalent: 88 g/eq, the number of functional groups: 4. Corresponding to the component (B1). Corresponding to the general formula (4).

[0131]

DCP-A (Kyoisha Chemical Co., Ltd.). Compound name: dimethyloltricyclodecane diacrylate, radically polymerizable functional group equivalent: 152 g/eq, the number of functional groups: 2. Corresponding to the component (B2). Corresponding to the general formula (4).

[0132]

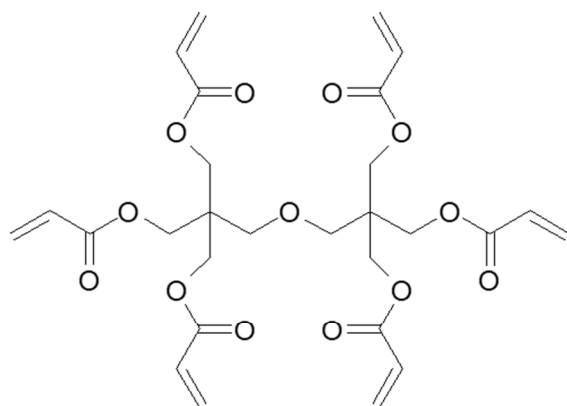
ADDM (Mitsubishi Chemical Corporation). Chemical name: 1,3-adamantane dimethacrylate, radically polymerizable functional group equivalent: 152 g/eq, the number of functional groups: 2. Corresponding to the component (B2). Corresponding to the general formula (4).

[0133]

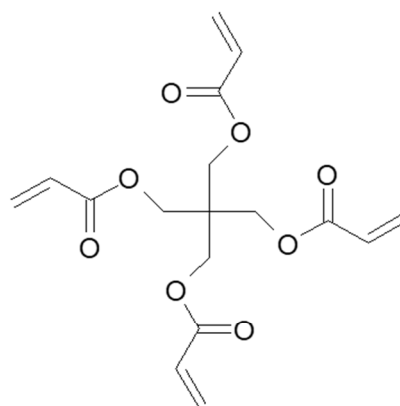
BP-6 EM (Kyoisha Chemical Co., Ltd.). Chemical name: ethylene oxide-modified bisphenol A dimethacrylate, radically polymerizable functional group equivalent: 314 g/eq, the number of functional groups: 2. Not corresponding to the general formula (4).

[0134]

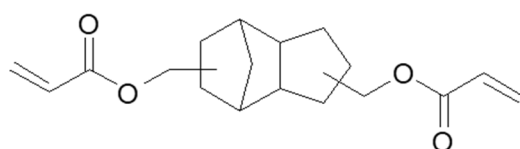
[Chem. 6]



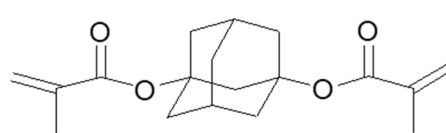
DPE-6A



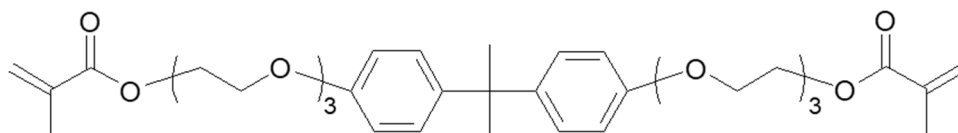
M-450



DCP-A



ADDM



BP-6EM

[0135]

<Photopolymerization Initiator (C)>

OXE-04 (BASF SE). Oxime ester-based photopolymerization initiator.

[0136]

<Inorganic Filler (D)>

Glass Filler 1

A glass filler containing 45% by weight of silicon oxide (hereinafter, also referred to as SiO<sub>2</sub>), 25% by

weight of aluminum oxide (hereinafter, also referred to as  $\text{Al}_2\text{O}_3$ ), 4% by weight of boron oxide (hereinafter, also referred to as  $\text{B}_2\text{O}_3$ ), and 26% by weight of yttrium oxide (hereinafter, also referred to as  $\text{Y}_2\text{O}_3$ ). Refractive index (wavelength of 405 nm): 1.61, average particle diameter: 1.2  $\mu\text{m}$ , extracted ion amount (total amount of magnesium ions, calcium ions, and zinc ions): 7 ppm (weight basis).  
[0137]

#### Silica 1

SO-E2 (Admatechs). Fused silica of 100% by weight silicon oxide. Refractive index (wavelength of 405 nm): 1.47, average particle diameter: 0.5  $\mu\text{m}$ , extracted ion amount (total amount of magnesium ions, calcium ions, and zinc ions): 2 ppm (weight basis).  
[0138]

#### <Thermal Crosslinking Agent (E)>

HMOM-TPHAP (Honshu Chemical Industry Co., Ltd.).  
Chemical name: 4,4',4''-ethylidenetris[2,6-bis(methoxymethyl)phenol].  
[0139]

#### <Polymerization Inhibitor>

Phenothiazine (Tokyo Chemical Industry Co., Ltd.)

#### <Adhesion Improver>

KBM-403 (Shin-Etsu Chemical Co., Ltd.). Chemical name: 3-glycidoxypropyltrimethoxysilane.

[0140]

<Example 1>

The preparation of the photosensitive resin composition according to Example 1 will be described below as an example.

[0141]

The polyimide 1 (35 g) as the polymer (A), DPE-6A (20 g) as the photopolymerizable compound (B), OXE-04 (1.5 g) as the photopolymerization initiator (C), the glass filler 1 (150 g) as the inorganic filler (D), a  $\gamma$ -butyrolactone solution of HMOM-TPHAP (30 g (6 g as a solid)) as the thermal crosslinking agent (E), a phenothiazine (0.01 g) as the polymerization inhibitor, KBM-403 (2 g) as the adhesion improver, and an ethyl lactate (68 g) as a dilution solvent were added, and stirred at room temperature for 120 minutes, and the resulting solution was subjected to pressure filtration with the use of a filter with a retained particle diameter of 10  $\mu\text{m}$  to obtain a photosensitive resin composition.

[0142]

The obtained photosensitive resin composition was applied onto a support film (PET film of 50  $\mu\text{m}$  in thickness) with the use of a comma roll coater, and dried at 65°C for 5 minutes, and then laminated with a PP film of 50  $\mu\text{m}$  in thickness as a protective film to obtain a

photosensitive resin sheet with a photosensitive resin layer of 25  $\mu\text{m}$  in thickness. The obtained photosensitive resin sheet was evaluated by the methods described above, and the evaluation results of Example 1 are shown in Table 1.

[0143]

<Examples 2 to 12, Comparative Examples 1 to 2>

According to Examples 2 to 12 of the present invention and Comparative Examples 1 to 2 against the present invention, photosensitive resin sheets were prepared by performing the treatment in accordance with the same method as in Example 1 except that the above-described composition in Example 1 was changed to the compositions shown in Table 1. The obtained photosensitive resin sheets were used for the evaluations by the methods described above, and the evaluation results of Examples 2 to 12 and Comparative Examples 1 to 2 are shown in Table 1.

[0144]

[Table 1-1]

|                    |                                                                                                                                             |                | Examples |       |       |       |       |       |
|--------------------|---------------------------------------------------------------------------------------------------------------------------------------------|----------------|----------|-------|-------|-------|-------|-------|
|                    |                                                                                                                                             |                | 1        | 2     | 3     | 4     | 5     | 6     |
| Composition        | Polymer (A)                                                                                                                                 | Polyimide 1    | 35       | 35    | 35    | 35    | 35    | 35    |
|                    | Radically Polymerizable Compound (B)                                                                                                        | DPE-6A         | 20       |       |       |       | 10    | 10    |
|                    |                                                                                                                                             | M-450          |          | 20    |       |       |       |       |
|                    |                                                                                                                                             | DCP-A          |          |       | 20    |       | 10    |       |
|                    |                                                                                                                                             | ADDM           |          |       |       | 20    |       | 10    |
|                    |                                                                                                                                             | BP-6EM         |          |       |       |       |       |       |
|                    | Photopolymerization Initiator (C)                                                                                                           | OXE-04         | 1.5      | 1.5   | 1.5   | 1.5   | 1.5   | 1.5   |
|                    | Inorganic Filler (D)                                                                                                                        | Glass Filler 1 | 150      | 150   | 150   | 150   | 150   | 150   |
|                    |                                                                                                                                             | Silica 1       |          |       |       |       |       |       |
|                    | Thermal Crosslinking Agent (E)                                                                                                              | HMOM-TPHAP     | 6        | 6     | 6     | 6     | 6     | 6     |
| Evaluation Results | Polymerization Inhibitor                                                                                                                    | Phenothiazine  | 0.01     | 0.01  | 0.01  | 0.01  | 0.01  | 0.01  |
|                    | Adhesion Improver                                                                                                                           | KBM-403        | 2        | 2     | 2     | 2     | 2     | 2     |
|                    | Average Value of Radically Polymerizable Functional Group Equivalent of Radically Polymerizable Compound (B) [g/eq]                         |                | 96       | 88    | 152   | 152   | 124   | 124   |
|                    | Content (% by mass) of Inorganic Filler (D) in 100% by mass of Solids                                                                       |                | 70       | 70    | 70    | 70    | 70    | 70    |
|                    | Absolute Value of Difference between Refractive Index of Inorganic Filler (D) and Refractive Index of Solids excluding Inorganic Filler (D) |                | ≤0.05    | ≤0.05 | ≤0.05 | ≤0.05 | ≤0.05 | ≤0.05 |
|                    | Storage Elastic Modulus at 180°C [GPa]                                                                                                      |                | 14.4     | 14.1  | 13.0  | 12.9  | 13.9  | 13.8  |
| Evaluation Results | TG-TE                                                                                                                                       |                | 18       | 18    | 21    | 21    | 19    | 19    |
|                    | EMAX/E180                                                                                                                                   |                | 2.8      | 2.7   | 2.0   | 2.0   | 2.5   | 2.5   |
|                    | Resolution                                                                                                                                  |                | A        | A     | A     | A     | A     | A     |
|                    | Visible Light Transmittance T25                                                                                                             |                | A        | A     | A     | A     | A     | A     |
|                    | Elongation                                                                                                                                  |                | C        | C     | A     | A     | B     | B     |

[0145]

[Table 1-2]

|                    |                                                                                                                                             |                | Examples |       |       |       |      |       | Comparative Examples |      |
|--------------------|---------------------------------------------------------------------------------------------------------------------------------------------|----------------|----------|-------|-------|-------|------|-------|----------------------|------|
|                    |                                                                                                                                             |                | 7        | 8     | 9     | 10    | 11   | 12    | 1                    | 2    |
| Composition        | Polymer (A)                                                                                                                                 | Polyimide 1    | 35       | 35    | 35    | 35    | 35   | 35    | 35                   | 35   |
|                    | Radically Polymerizable Compound (B)                                                                                                        | DPE-6A         |          |       |       |       |      | 20    |                      | 20   |
|                    |                                                                                                                                             | M-450          | 5        | 10    | 15    |       |      |       |                      |      |
|                    |                                                                                                                                             | DCP-A          | 15       | 10    | 5     | 15    | 20   |       |                      |      |
|                    |                                                                                                                                             | ADDM           |          |       |       |       |      |       |                      |      |
|                    |                                                                                                                                             | BP-6EM         |          |       |       | 5     |      |       | 20                   |      |
|                    | Photopolymerization Initiator (C)                                                                                                           | OXE-04         | 1.5      | 1.5   | 1.5   | 1.5   | 1.5  | 1.5   | 1.5                  | 1.5  |
|                    | Inorganic Filler (D)                                                                                                                        | Glass Filler 1 | 150      | 150   | 150   | 150   |      | 43    | 150                  |      |
|                    |                                                                                                                                             | Silica 1       |          |       |       |       | 150  |       |                      |      |
|                    | Thermal Crosslinking Agent (E)                                                                                                              | HMOM-TPHAP     | 6        | 6     | 6     | 6     | 6    | 6     | 6                    | 6    |
| Evaluation Results | Polymerization Inhibitor                                                                                                                    | Phenothiazine  | 0.01     | 0.01  | 0.01  | 0.01  | 0.01 | 0.01  | 0.01                 | 0.01 |
|                    | Adhesion Improver                                                                                                                           | KBM-403        | 2        | 2     | 2     | 2     | 2    | 2     | 2                    | 2    |
|                    | Average Value of Radically Polymerizable Functional Group Equivalent of Radically Polymerizable Compound (B) [g/eq]                         |                | 136      | 120   | 104   | 169   | 96   | 96    | 314                  | 96   |
|                    | Content (% by mass) of Inorganic Filler (D) in 100% by mass of Solids                                                                       |                | 70       | 70    | 70    | 70    | 70   | 40    | 70                   | 0    |
|                    | Absolute Value of Difference between Refractive Index of Inorganic Filler (D) and Refractive Index of Solids excluding Inorganic Filler (D) |                | ≤0.05    | ≤0.05 | ≤0.05 | ≤0.05 | 0.15 | ≤0.05 | ≤0.05                | —    |
|                    | Storage Elastic Modulus at 180°C [GPa]                                                                                                      |                | 13.4     | 13.7  | 13.9  | 11.8  | 13.1 | 6.4   | 9.2                  | 3.0  |
|                    | TG-TE                                                                                                                                       |                | 19       | 18    | 18    | 24    | 20   | 29    | 27                   | 31   |
|                    | EMAX/E180                                                                                                                                   |                | 2.4      | 2.5   | 2.6   | 1.6   | 2.0  | 2.8   | 1.2                  | 2.8  |
|                    | Resolution                                                                                                                                  |                | A        | A     | A     | B     | B    | A     | B                    | A    |
|                    | Visible Light Transmittance T25                                                                                                             |                | A        | A     | A     | A     | B    | A     | A                    | A    |
|                    | Elongation                                                                                                                                  |                | A        | A     | B     | A     | A    | A     | A                    | A    |

[0146]

In the tables, the numerical values in the columns of "Composition" each mean mass (g).

[0147]

As shown in Table 1, in Examples 1 to 11 in which the radically polymerizable functional group equivalent of the radically polymerizable compound (B) was 70 g/eq or more and 200 g/eq or less on average, the storage elastic modulus at 180°C was as high as 10 GPa or more, which was a favorable result, as compared with Comparative Example 1 with the same amount of inorganic filler (D). The storage elastic modulus at 180°C and the resolution were favorable in Examples 1 to 9 including the glass filler for the inorganic filler (D) and including only the radically polymerizable compound (B) corresponding to the general formula (4). Examples 5 to 9 including the radically polymerizable compound (B) composed of the component (B1) and the component (B2) exhibited favorable results for both the storage elastic modulus at 180°C and the elongation. The result of Example 1 and Example 12 containing the inorganic filler (D) were higher in elastic modulus at 180°C as compared with Comparative Example 2.

#### INDUSTRIAL APPLICABILITY

[0148]

A cured product that is excellent in pattern-processability and pressure resistance can be formed. The cured product obtained using the photosensitive resin composition according to the present invention is excellent in electrical properties, mechanical properties, and heat resistance, and has high reliability, and thus is useful for a surface protective film and an interlayer insulating film for a semiconductor element and an electronic component, a wiring protective insulating film for a circuit board, and the like. Further, the insulating film is useful for an electronic component having a hollow structure required to have pressure resistance, in particular, for a roof of a hollow structure such as an elastic wave filter or a crystal device.

#### DESCRIPTION OF REFERENCE SIGNS

[0149]

- 1: Substrate
- 2: Convex portion
- 3: Support film
- 4: Layer of photosensitive resin composition
- 5: Photocured layer
- 6: Cured product
- x: Width of convex portion
- y1: Width of short side of inside surrounded by

convex portion of substrate

y2: Width of long side of inside surrounded by convex  
portion of substrate

z: Height of convex portion

## CLAIMS

1. A photosensitive resin composition comprising a polymer (A), a radically polymerizable compound (B), a photopolymerization initiator (C), and an inorganic filler (D),

wherein a radically polymerizable functional group equivalent of the radically polymerizable compound (B) has an average value of 70 g/eq or more and 200 g/eq or less.

2. The photosensitive resin composition according to claim 1, wherein a content of the inorganic filler (D) is 30% by mass or more and 80% by mass or less when a total mass of solids of the photosensitive resin composition is regarded as 100% by mass.

3. The photosensitive resin composition according to claim 1 or 2, wherein a difference between a refractive index of the inorganic filler (D) and a refractive index of solids of the photosensitive resin composition excluding the inorganic filler (D) has an absolute value of 0.05 or less.

4. The photosensitive resin composition according to any one of claims 1 to 3, wherein the inorganic filler (D)

comprises a glass filler.

5. The photosensitive resin composition according to claim 4, wherein the glass filler contains at least two selected from the group consisting of a silicon oxide, an aluminum oxide, and a boron oxide, and further contains a rare earth oxide.

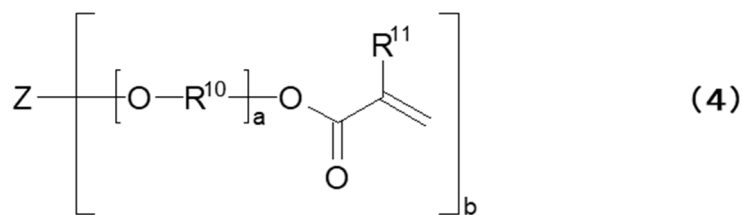
6. The photosensitive resin composition according to any one of claims 1 to 5, wherein the polymer (A) comprises at least one resin selected from the group consisting of a polyimide, a polybenzoxazole, any of precursors thereof, and copolymers thereof.

7. The photosensitive resin composition according to any one of claims 1 to 6, wherein

the radically polymerizable compound (B) comprises a compound represented by the following general formula (4), and

a content of a compound represented by the following general formula (4) is 70% by mass or more and 100% by mass or less when a total mass of the radically polymerizable compound (B) is regarded as 100% by mass:

[Chem. 1]



in which in the general formula (4),  $\text{R}^{10}$  represents a hydrocarbon group having 1 to 5 carbon atoms,  $\text{R}^{11}$  represents hydrogen or a methyl group, Z represents an organic group, a represents an integer of 0 to 1, and b represents an integer of 2 to 10.

8. The photosensitive resin composition according to any one of claims 1 to 7, wherein the radically polymerizable compound (B) comprises a radically polymerizable compound (B1) that has no cyclic structure and has a radically polymerizable functional group equivalent of 80 to 120 g/eq (hereinafter, referred to as a component (B1)).

9. The photosensitive resin composition according to any one of claims 1 to 8, wherein the radically polymerizable compound (B) comprises a radically polymerizable compound (B2) that has an alicyclic structure and has a radically polymerizable functional group equivalent of 130 to 200 g/eq (hereinafter, referred to as a component (B2)).

10. The photosensitive resin composition according to

claim 8 or 9, wherein a total amount of the component (B1) and the component (B2) is 70% by mass or more and 100% by mass or less when a total amount of the radically polymerizable compound (B) is regarded as 100% by mass.

11. The photosensitive resin composition according to claim 9 or 10, wherein a content of the component (B1) is 20% by mass or more and 80% by mass or less when a total mass of the component (B1) and the component (B2) is regarded as 100% by mass.

12. A photosensitive resin sheet comprising: a support film; and a layer (photosensitive resin layer) made of the photosensitive resin composition according to any one of claims 1 to 11 on the support film.

13. The photosensitive resin sheet according to claim 12, wherein the photosensitive resin layer has a visible light transmittance T<sub>25</sub> of 40% or more and 100% or less when the photosensitive resin layer is 25  $\mu\text{m}$  in thickness.

14. A cured product of the photosensitive resin composition according to any one of claims 1 to 11.

15. The cured product according to claim 14, wherein the

cured product has a storage elastic modulus at 180°C of 10 GPa or more and 20 GPa or less.

16. The cured product according to claim 14 or 15, wherein the cured product satisfies a relationship of  $15 < TG - TE < 25$ , where TE (°C) is a temperature at which the cured product reaches a maximum loss elastic modulus, and TG (°C) is a glass transition temperature.

17. The cured product according to any one of claims 14 to 16, wherein the cured product satisfies a relationship of  $1.5 < E_{MAX}/E_{180} < 3.2$ , where EMAX (GPa) is a maximum value of a loss elastic modulus of the cured product, and E180 (GPa) is a loss elastic modulus at 180°C.

18. A hollow structure comprising a substrate, a convex portion formed on the substrate and provided to surround a part of a surface of the substrate, and a film-shaped material (hereinafter, referred to as a roof material) in contact with a top of the convex portion, and

having a closed space (hereinafter, referred to as a hollow portion) formed by the substrate, the convex portion, and the roof material,

wherein the roof material comprises the cured product according to any one of claims 14 to 17.

19. The hollow structure according to claim 18, wherein the roof material has a through hole.

20. The hollow structure according to claim 18 or 19, wherein

the convex portion is 5 to 25  $\mu\text{m}$  in thickness, and a short side of the substrate in the hollow portion is 200 to 400  $\mu\text{m}$  in width.

21. An electronic component comprising the cured product according to any one of claims 14 to 17 or the hollow structure according to any one of claims 18 to 20.

22. An elastic wave filter comprising the cured product according to any one of claims 14 to 17 or the hollow structure according to any one of claims 18 to 20.