

DESCRIPTION

TITLE OF THE INVENTION: RESIN COMPOSITION, RESIN LAYER,
PERMANENT ADHESIVE, ADHESIVE FOR TEMPORARY BONDING,
LAMINATED FILM, PROCESSED WAFER, AND METHOD FOR
MANUFACTURING ELECTRONIC COMPONENT OR SEMICONDUCTOR DEVICE

TECHNICAL FIELD

[0001]

The present invention relates to a resin composition, a resin layer, a permanent adhesive, an adhesive for temporary bonding, a laminated film, a processed wafer, and a method for manufacturing an electronic component or a semiconductor device.

BACKGROUND ART

[0002]

In recent years, substrates have been thinned in order to reduce the weight and thickness of an electronic component and a semiconductor device. A thin substrate is used in a processed wafer in which the thin substrate is fixed to a supportive support substrate such as a silicon substrate, a glass substrate, and a film with an adhesive for temporary bonding because a thin substrate warps largely, is difficult to form a circuit, and cracks and

breaks easily. When the processed wafer is subjected to a heat treatment such as circuit formation processing, the adhesive for temporary bonding is required to have heat resistance enough to withstand the heat treatment.

[0003]

For example, in an electronic component, a capacitor or the like is required to be thinned. To solve such a problem, an electronic circuit formation substrate is required to be thinned, and thus, investigations have been made to reduce the thickness of an electronic circuit formation substrate to 1 μm or more and 100 μm or less. Because an electronic circuit formation substrate having a thickness of 1 μm or more and 100 μm or less warps largely and is difficult to form a circuit, the electronic circuit formation substrate is fixed to a supportive support substrate such as a silicon substrate, a glass substrate, and a film to form a processed wafer, and is subjected to the circuit formation processing, and then the electronic circuit formation substrate on which a circuit is formed is peeled off. An adhesive for temporary bonding is used as a bonding layer to fix the electronic circuit formation substrate to a support substrate. After a step of peeling the electronic circuit formation substrate from the support substrate, the adhesive layer remaining on the electronic circuit formation substrate and the support substrate as

well as the residue of the adhesive layer may be reworked with an organic solvent or an alkaline aqueous solution.

[0004]

The adhesive for temporary bonding used in the manufacture of an electronic component is required to have heat resistance enough to withstand the circuit forming step, and in particular, is required to have heat resistance enough to withstand the circuit forming step in an electronic circuit formation substrate having a thickness of 1 μm or more and 100 μm or less. The adhesive for temporary bonding is required to be easily peeled off after the completion of the circuit forming step.

[0005]

In a semiconductor device, techniques of laminating semiconductor chips with the semiconductor chips connected with a through-silicon via (TSV) have been developed in order to achieve higher levels of integration and higher packaging density of a semiconductor device. In the field of power semiconductors, reduction of conduction loss is required for energy saving. In order to achieve such an object, the thickness of the package has to be reduced. Thus, investigations have been made to reduce the thickness of a semiconductor circuit formation substrate to 1 μm or more and 100 μm or less. A surface of the semiconductor circuit formation substrate not having a circuit (a

backside) is polished to be thinned, and a back electrode is formed on the backside. In order to prevent cracking of the semiconductor circuit formation substrate during processes such as polishing, back circuit formation processing and the like, the semiconductor circuit formation substrate is fixed to a supportive support substrate such as a silicon substrate, a glass substrate, and a film to form a processed wafer, and is subjected to polishing, back circuit formation processing and the like, and then the polished and back circuit formation-processed semiconductor circuit formation substrate is peeled from the support substrate. For fixing the semiconductor circuit formation substrate to the support substrate, an adhesive for temporary bonding is used as an adhesive layer. After the step of peeling the semiconductor circuit formation substrate from the support substrate, the adhesive layer remaining on the semiconductor circuit formation substrate and the support substrate as well as the residue of the adhesive layer may be reworked with an organic solvent or an alkaline aqueous solution.

[0006]

The adhesive for temporary bonding used in manufacture of the semiconductor device is required to have heat resistance enough to withstand polishing and the backside circuit forming step, and in particular, is required to

have heat resistance enough to withstand the backside circuit forming step after polishing and thinning of the surface not having a circuit (a backside) of the semiconductor circuit formation substrate. The adhesive for temporary bonding is required to be easily peeled off after the completion of polishing and the backside circuit forming step.

[0007]

As such an adhesive for temporary bonding, for example, there has been proposed an adhesive which produces a polyamide- or polyimide-based heat-resistant bonding layer, and which is peeled off by being heated to change the adhesive force (see, for example, Patent Document 1). There has also been proposed an adhesive for temporary bonding which produces a structure including two types of adhesive layers, that is, a heat-resistant thermoplastic organopolysiloxane-based adhesive layer and a heat-resistant curable modified siloxane-based adhesive layer, which has an adhesive force that makes the adhesive layer peelable from both a semiconductor circuit formation substrate and a support substrate, and which is peeled off by a mechanical force applied at room temperature (for example, Patent Document 2). There has also been proposed an adhesive for temporary bonding which produces one type of an adhesive layer, that is, a cycloolefin- or elastomer-

based adhesive layer, and is peeled off by a mechanical force applied at room temperature (for example, Patent Documents 3 and 4).

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0008]

Patent Document 1: Japanese Patent Laid-Open Publication No. 2010-254808 (Claims)

Patent Document 2: Japanese Patent Laid-Open Publication No. 2013-48215 (Claims)

Patent Document 3: Japanese Patent Laid-Open Publication No. 2013-241568 (Claims)

Patent Document 4: Japanese Patent Laid-Open Publication No. 2015-214675 (Claims)

SUMMARY

PROBLEMS TO BE SOLVED

[0009]

However, the adhesive for temporary bonding as in Patent Document 1, which can be peeled off only by heating, has problems that the solder bump is dissolved during the heating step for peeling, that an adhesive force during the electronic circuit forming step or the semiconductor circuit forming step is reduced and the adhesive is peeled

off during the step, or conversely an adhesive force is increased and the adhesive cannot be peeled off.

[0010]

The adhesive for temporary bonding as in Patent Document 2, which is peeled off by a mechanical force applied at room temperature, is free from the above-mentioned problems. However, two types of adhesive layers have to be formed, which imposes a considerable burden on the process. The adhesives for temporary bonding as in Patent Document 3 and 4 produce one type of an adhesive layer and are peeled off by a mechanical force applied at room temperature. However, they have problems that cycloolefin- and elastomer-based materials decompose during the electronic circuit forming step or the semiconductor circuit forming step at high temperatures.

[0011]

In view of such a situation, an object of the embodiments disclosed herein is to provide a resin composition that is capable of bonding an electronic circuit formation substrate or a semiconductor circuit formation substrate and a support substrate together, has excellent heat resistance during bonding of an electronic circuit formation substrate or semiconductor circuit formation substrate having a thickness of 1 μm or more and 100 μm or less, has steady adhesive force through the process of manufacturing an

electronic component, a semiconductor device or the like, and can be peeled off under mild conditions at room temperature after the manufacturing process, an adhesive, a resin layer, a laminated film, and a processed wafer containing the resin composition, as well as a method for manufacturing an electronic component or a semiconductor device using these. The resin composition of the present disclosure can be used as a permanent adhesive or an adhesive for temporary bonding, and, in particular, can be suitably used as an adhesive for temporary bonding.

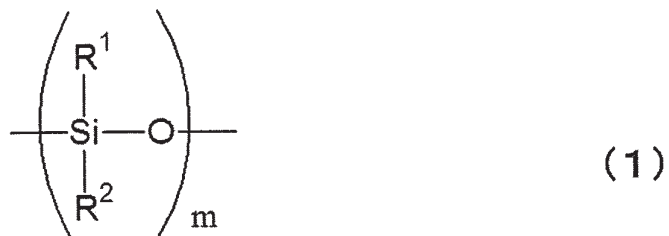
SOLUTIONS TO THE PROBLEMS

[0012]

The present disclosure provides a resin composition containing at least (a) a polyimide resin including a structure represented by the general formula (1) and (b) a crosslinker including a fluorene group:

[0013]

[Chemical Formula 1]



[0014]

wherein m is a natural number of 1 or more and 100 or

less, R^1 and R^2 may be same or different and each represent an alkyl group having 1 to 30 carbon atoms, a phenyl group, or a phenoxy group.

The present disclosure also provides a resin layer including a coating film of the resin composition of the present disclosure.

[0015]

The present disclosure also provides a permanent adhesive containing the resin composition of the present disclosure.

[0016]

The present disclosure also provides an adhesive for temporary bonding containing the resin composition of the present disclosure.

[0017]

The present disclosure also provides a method for manufacturing an electronic component or a semiconductor device using the resin composition of the present disclosure.

[0018]

The present disclosure also provides a laminated film including a heat-resistant insulating film and the resin composition of the present disclosure on at least one surface of the heat-resistant insulating film.

[0019]

The present disclosure also provides a method for manufacturing an electronic component or a semiconductor device using the laminated film of the present disclosure.

[0020]

The present disclosure also provides a processed wafer including an electronic circuit formation substrate or a semiconductor circuit formation substrate and a support substrate bonded together at least with the resin layer of the present disclosure or the laminated film of the present disclosure interposed between the electronic circuit formation substrate or the semiconductor circuit formation substrate and the support substrate.

[0021]

The present disclosure also provides a method for manufacturing an electronic component or a semiconductor device using the processed wafer of the present disclosure, including at least either of the steps of:

heat-treating the electronic circuit formation substrate or the semiconductor circuit formation substrate in the processed wafer;

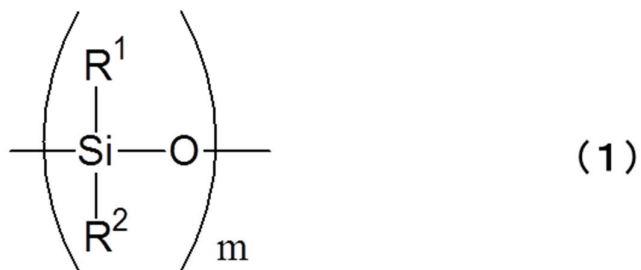
peeling the electronic circuit formation substrate or the semiconductor circuit formation substrate in the processed wafer from the support substrate; and

washing the resin layer attached to the electronic circuit formation substrate or the semiconductor circuit

formation substrate peeled from the processed wafer or the resin layer attached to the support substrate in the processed wafer with a solvent.

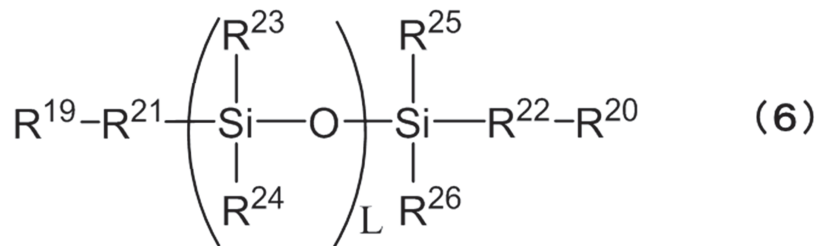
[0021a]

In an aspect, there is provided a resin composition comprising at least (a) a polyimide resin having a structure represented by the general formula (1) and (b) a crosslinker including a fluorene group:



wherein m is a natural number of 1 or more and 100 or less, R¹ and R² may be same or different and each represent an alkyl group having 1 to 30 carbon atoms, a phenyl group or a phenoxy group, and

wherein the composition further comprises (c) a siloxane polymer represented by the general formula (6):



wherein L is an integer of 10 or more and 100 or less, R^{19} and R^{20} may be same or different and each represent a monovalent organic group having 1 to 30 carbon atoms and 0 to 3 nitrogen atoms, R^{21} and R^{22} may be same or different and each represent an alkylene group having 1 to 30 carbon atoms or a phenylene group, R^{23} to R^{26} may be same or different and each represent an alkyl group having 1 to 30 carbon atoms, an alkoxy group, a phenyl group, or a phenoxy group, and an alkoxy group having 1 to 30 carbon atoms of R^{23} to R^{26} does not include a polyoxyalkylene structure.

[0021b]

In another aspect, there is provided a resin layer comprising a coating film of the resin composition as defined above.

[0021c]

In another aspect, there is provided a permanent adhesive comprising the resin composition as defined above.

[0021d]

In another aspect, there is provided an adhesive for temporary bonding comprising the resin composition as defined above.

[0021e]

In another aspect, there is provided a method for manufacturing an electronic component or a semiconductor device using the resin composition as defined above.

[0021f]

In another aspect, there is provided a laminated film comprising a heat-resistant insulating film and the resin composition as defined above laminated on at least one surface of the heat-resistant insulating film.

[0021g]

In another aspect, there is provided a method for manufacturing an electronic component or a semiconductor device using the laminated film as defined above.

[0021h]

In another aspect, there is provided a processed wafer comprising an electronic circuit formation substrate or a semiconductor circuit formation substrate and a support substrate bonded together with at least the resin layer as defined above or the laminated film as defined above interposed between the electronic circuit formation substrate or the semiconductor circuit formation substrate and the support substrate.

[0021i]

In another aspect, there is provided a method for manufacturing an electronic component or a semiconductor device using the processed wafer as defined above, the method comprising at least either of the steps of:

heat-treating the electronic circuit formation substrate or the semiconductor circuit formation substrate

in the processed wafer;

peeling the electronic circuit formation substrate or the semiconductor circuit formation substrate in the processed wafer from the support substrate; and

washing the resin layer attached to the electronic circuit formation substrate or the semiconductor circuit formation substrate peeled from the processed wafer or the resin layer attached to the support substrate in the processed wafer with a solvent.

EFFECTS

[0022]

According to the present disclosure, there can be provided a resin composition that is capable of bonding an electronic circuit formation substrate or a semiconductor circuit formation substrate and a support substrate together, has excellent heat resistance during bonding of an electronic circuit formation substrate or semiconductor circuit formation substrate having a thickness of 1 μm or more and 100 μm or less, has steady adhesive force through the process of manufacturing an electronic component, a semiconductor device or the like, and can be peeled off under mild conditions at room temperature after the manufacturing process, an adhesive, a resin layer, a laminated film, and a processed wafer containing the resin composition, as well as a method for manufacturing an

electronic component or a semiconductor device using these. The resin composition of the present disclosure can be used as a permanent adhesive or an adhesive for temporary bonding, and, in particular, can be suitably used as an adhesive for temporary bonding.

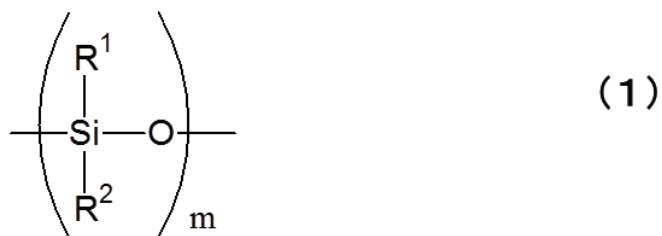
EMBODIMENTS OF THE INVENTION

[0023]

The present invention provides a resin composition containing at least (a) a polyimide resin including a structure represented by the general formula (1) and (b) a crosslinker including a fluorene group:

[0024]

[Chemical Formula 2]



[0025]

wherein m is a natural number of 1 or more and 100 or less, R¹ and R² may be same or different and each represent an alkyl group having 1 to 30 carbon atoms, a phenyl group, or a phenoxy group.

The polyimide resin (a) including the structure represented by the general formula (1) of the present invention will be described.

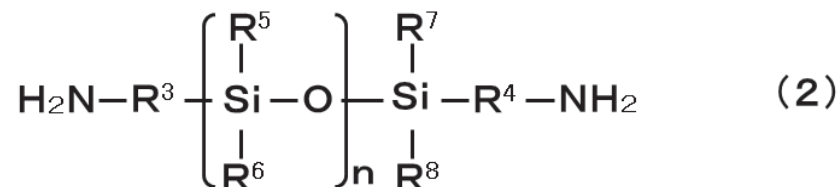
[0026]

The polyimide resin (a) includes the structure represented by the general formula (1). The structure represented by the general formula (1) may be included in

either a residue of an acid dianhydride or a residue of a diamine, but from the viewpoint of the solubility of the polyimide resin and from the viewpoint of cost, the structure represented by the general formula (1) is preferably included in the diamine residue as a residue of a polysiloxane diamine represented by the general formula (2):

[0027]

[Chemical Formula 3]



[0028]

wherein n is an integer from 1 to 100, R³ and R⁴ may be same or different and each represent an alkylene group having 1 to 30 carbon atoms or a phenylene group, and R⁵ to R⁸ may be same or different and each represent an alkyl group having 1 to 30 carbon atoms, a phenyl group, or a phenoxy group.

The average molecular weight of the polysiloxane diamine can be determined by calculation of the amino group equivalent through neutralization titration of amino groups of the polysiloxane diamine, and doubling of the amino group equivalent. For example, a predetermined amount of a

polysiloxane diamine serving as a sample is taken and put in a beaker, and dissolved in a predetermined amount of a 1 : 1 mixed solution of isopropyl alcohol (hereinafter referred to as IPA) and toluene. To the resulting solution, a 0.1 N aqueous hydrochloric acid solution is added dropwise with stirring, the amount of the 0.1 N aqueous hydrochloric acid solution added until the neutralization point is determined, and the amino group equivalent is calculated from the amount of the added aqueous solution. A value obtained by doubling of the amino group equivalent is the average molecular weight.

[0029]

Meanwhile, a relationship between the value of n and the molecular weight of the polysiloxane diamine can be obtained as a relational expression of a linear function by calculation of the molecular weights of the polysiloxane diamine in the cases where $n = 1$ and $n = 10$ from the chemical structural formula. The average value of n can be determined by application of the average molecular weights to the relational expression.

[0030]

Since the polysiloxane diamine represented by the general formula (2) is sometimes a mixture in which n is not a single value but has a plurality of values, n represents an average value in the present invention.

[0031]

Specific examples of the polysiloxane diamine represented by the general formula (2) include α,ω -bis(3-aminopropyl)polydimethylsiloxane, α,ω -bis(3-aminopropyl)polydiethylsiloxane, α,ω -bis(3-aminopropyl)polydipropylsiloxane, α,ω -bis(3-aminopropyl)polydibutylsiloxane, α,ω -bis(3-aminopropyl)polydiphenoxysiloxane, α,ω -bis(2-aminoethyl)polydimethylsiloxane, α,ω -bis(2-aminoethyl)polydiphenoxysiloxane, α,ω -bis(4-aminobutyl)polydimethylsiloxane, α,ω -bis(4-aminobutyl)polydiphenoxysiloxane, α,ω -bis(5-aminopentyl)polydimethylsiloxane, α,ω -bis(5-aminopentyl)polydiphenoxysiloxane, α,ω -bis(4-aminophenyl)polydimethylsiloxane, and α,ω -bis(4-aminophenyl)polydiphenoxysiloxane. These polysiloxane diamines may be used singly, or two or more of them may be used. Among them, a polysiloxane diamine in which n is 2 or more is preferred, because the glass transition temperature of the polyimide resin can be lowered, and good adhesiveness can be exhibited when thermocompression bonding is performed.

[0032]

The content of the residue of the polysiloxane diamine represented by the general formula (2) is preferably 30

mol% or more and 90 mol% or less, more preferably 40 mol% or more and 90 mol% or less in the total diamine residues. Within this range, the glass transition temperature of the polyimide resin is greatly lowered, and good adhesiveness can be obtained.

[0033]

The polyimide resin may have a residue of an aromatic diamine or a residue of an alicyclic diamine. The content of the residue of the aromatic diamine or the residue of the alicyclic diamine is preferably 0.1 mol% or more and 70 mol% or less, more preferably 0.1 mol% or more and 60 mol% or less in the total diamine residues. Within this range, a polyimide resin having good adhesiveness and heat resistance can be obtained.

[0034]

Specific examples of the aromatic diamine or the alicyclic diamine include 2,5-diaminophenol, 3,5-diaminophenol, 3,3'-dihydroxybenzidine, 4,4'-dihydroxy-3,3'-diaminophenyl propane, 4,4'-dihydroxy-3,3'-diaminophenyl hexafluoropropane, 4,4'-dihydroxy-3,3'-diaminophenyl sulfone, 4,4'-dihydroxy-3,3'-diaminophenyl ether, 3,3'-dihydroxy-4,4'-diaminophenyl ether, 4,4'-dihydroxy-3,3'-diaminophenyl propane methane, 4,4'-dihydroxy-3,3'-diaminobenzophenone, 1,3-bis(4-amino-3-hydroxy phenyl)benzene, 1,3-bis(3-amino-4-hydroxy

phenyl)benzene, bis(4-(4-amino-3-hydroxyphenoxy)benzene)propane, bis(4-(3-amino-4-hydroxyphenoxy)benzene)sulfone, bis(4-(3-amino-4-hydroxyphenoxy))biphenyl, p-phenylene diamine, m-phenylene diamine, 2,5-diaminotoluene, 2,4-diaminotoluene, 3,5-diaminobenzoic acid, 2,6-diaminobenzoic acid, 2-methoxy-1,4-phenylene diamine, 4,4'-diaminobenzanilide, 3,4'-diaminobenzanilide, 3,3'-diaminobenzanilide, 3,3'-dimethyl-4,4'-diaminobenzanilide, 9,9-bis(4-aminophenyl)fluorene, 9,9-bis(3-aminophenyl)fluorene, 9,9-bis(3-methyl-4-aminophenyl)fluorene, 9,9-bis(3,5-dimethyl-4-aminophenyl)fluorene, 9,9-bis(3-methoxy-4-aminophenyl)fluorene, 9,9-bis(4-aminophenyl)fluorene-4-carboxylic acid, 9,9-bis(4-aminophenyl)fluorene-4-methyl, 9,9-bis(4-aminophenyl)fluorene-4-methoxy, 9,9-bis(4-aminophenyl)fluorene-4-ethyl, 9,9-bis(4-aminophenyl)fluorene-4-sulfone, 9,9-bis(4-aminophenyl)fluorene-3-carboxylic acid, 9,9-bis(4-aminophenyl)fluorene-3-methyl, 1,3-diaminocyclohexane, 2,2'-dimethyl benzidine, 3,3'-dimethyl benzidine, 3,3'-dimethoxy benzidine, 2,4-diaminopyridine, 2,6-diaminopyridine, 1,5-diaminonaphthalene, 2,7-diaminofluorene, p-amino benzylamine, m-amino benzylamine, 4,4'-bis(4-aminophenoxy)biphenyl, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 3,4'-diaminodiphenyl

ether, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl methane, 4,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl sulfide, 3,3'-diamino benzophenone, 3,4'-diamino benzophenone, 4,4'-diamino benzophenone, 3,3'-dimethyl-4,4'-diaminodiphenyl methane, 1,3-bis(4-aminophenoxy)benzene, 1,3-bis(3-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, 1,4-bis(3-aminophenoxy)benzene, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(3-aminophenoxy)phenyl]propane, bis[4-(4-aminophenoxy)phenyl]methane, bis[4-(3-aminophenoxy)phenyl]methane, bis[4-(4-aminophenoxy)phenyl]ether, bis[4-(3-aminophenoxy)phenyl]ether, bis[4-(4-aminophenoxy)phenyl]sulfone, bis[4-(3-aminophenoxy)phenyl]sulfone, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, 1,4-diamino cyclohexane, 4,4'-methylene bis(cyclohexyl amine), 3,3'-methylene bis(cyclohexyl amine), 4,4'-diamino-3,3'-dimethyl dicyclohexyl methane, 4,4'-diamino-3,3'-dimethyl dicyclohexyl, and benzidine. These aromatic diamines or alicyclic diamines may be used singly, or two or more of them may be used.

[0035]

Among these aromatic diamines and alicyclic diamines,

aromatic diamines having a structure with high bendability are preferred from the viewpoint of adhesiveness.

Specifically, 1,3-bis(3-aminophenoxy)benzene, 3,3'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, and 3,3'-diamino benzophenone are particularly preferred.

[0036]

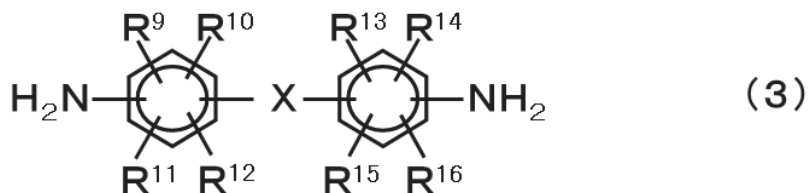
Among aromatic diamines and alicyclic diamines, the polyimide resin preferably contains an aromatic diamine having a hydroxyl group. If the polyimide resin contains an aromatic diamine having a hydroxyl group, fluidity in a high temperature range can be suppressed, and thus the protrusion of the resin composition in the bonding step by thermocompression bonding can be suppressed.

[0037]

The aromatic diamine having a hydroxyl group is more preferably an aromatic diamine represented by the general formula (3):

[0038]

[Chemical Formula 4]

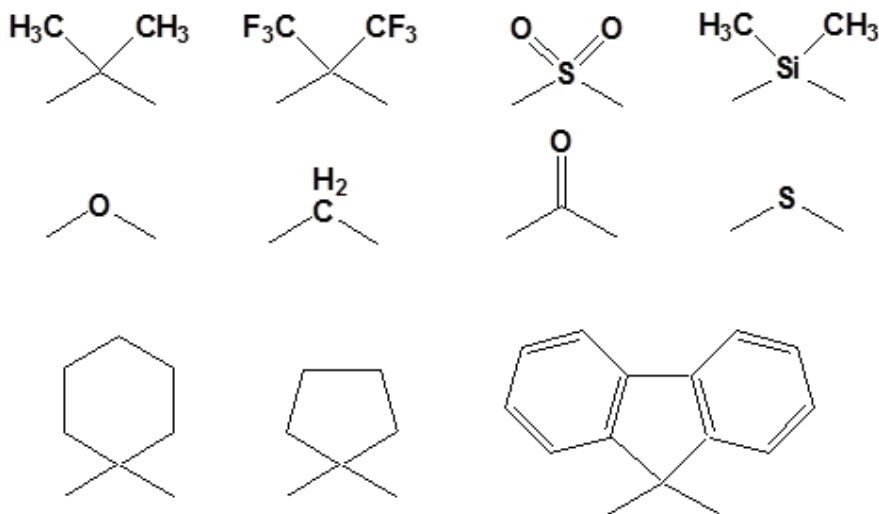


[0039]

wherein at least one of R^9 to R^{16} is a hydroxyl group, the others may be same or different, and each represent a group selected from a hydrogen atom, an alkyl group having 1 to 30 carbon atoms, an alkoxy group having 1 to 30 carbon atoms, a fluoroalkyl group having 1 to 30 carbon atoms, a halogen, a carboxyl group, a carboxylate ester group, a phenyl group, a sulfone group, a nitro group and a cyano group, as used herein, the halogen refers to fluorine, chlorine, bromine, or iodine, and X represents a direct bond or the following bonding structures.

[0040]

[Chemical Formula 5]



[0041]

Specific examples of the aromatic diamine having a hydroxyl group represented by the general formula (3) include 4,4'-dihydroxy-3,3'-diaminophenylpropane, 4,4'-dihydroxy-3,3'-diaminophenylhexafluoropropane, 4,4'-

dihydroxy-3,3'-diaminophenylsulfone, 4,4'-dihydroxy-3,3'-diaminophenyl ether, 3,3'-dihydroxy-4,4'-diaminophenyl ether, 4,4'-dihydroxy-3,3'-diaminophenylpropane methane, 4,4'-dihydroxy-3,3'-diaminobenzophenone, and 9,9-bis(3-amino-4-hydroxyphenyl)fluorene. These aromatic diamines having a hydroxyl group may be used singly, or two or more of them may be used.

[0042]

The content of the aromatic diamine having a hydroxyl group is preferably 0.1 mol% or more and 40 mol% or less, more preferably 0.1 mol% or more and 30 mol% or less in the total diamine residues. Within this range, the protrusion of the resin composition in the bonding step by thermocompression bonding can be suppressed without impairing good adhesiveness.

[0043]

The polyimide resin preferably contains a residue of an aromatic tetracarboxylic dianhydride as the acid dianhydride residue. If the polyimide resin contains the residue of the aromatic tetracarboxylic dianhydride, heat resistance is improved, and voids are not generated in the resin layer during the element processing step, and good heat resistance can be exhibited. The content of the residue of the aromatic tetracarboxylic dianhydride is preferably 90 mol% or more and 100 mol% or less in the

total acid dianhydride residues.

[0044]

Specific examples of the aromatic tetracarboxylic dianhydride include pyromellitic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 2,2'-dimethyl-3,3',4,4'-biphenyltetracarboxylic dianhydride, 5,5'-dimethyl-3,3',4,4'-biphenyltetracarboxylic dianhydride, 2,3,3',4'-biphenyltetracarboxylic dianhydride, 2,2',3,3'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-diphenyl ether tetracarboxylic dianhydride, 2,3,3',4'-diphenyl ether tetracarboxylic dianhydride, 2,2',3,3'-diphenyl ether tetracarboxylic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 2,2',3,3'-benzophenone tetracarboxylic dianhydride, 2,3,3',4'-benzophenone tetracarboxylic dianhydride, 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride, 2,3,3',4'-diphenylsulfone tetracarboxylic dianhydride, 3,3',4,4'-diphenylsulfoxide tetracarboxylic dianhydride, 3,3',4,4'-diphenylsulfide tetracarboxylic dianhydride, 3,3',4,4'-diphenylmethylenetetracarboxylic dianhydride, 4,4'-isopropylidenediphthalic dianhydride, 4,4'-(hexafluoroisopropylidene)diphthalic dianhydride, 3,4,9,10-perylenetetracarboxylic dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 3,3'',4,4''-p-

terphenyltetracarboxylic dianhydride, 3,3'',4,4''-m-terphenyltetracarboxylic dianhydride, 2,3,6,7-anthracenetetracarboxylic dianhydride, and 1,2,7,8-phenanethrenetetracarboxylic dianhydride. These aromatic tetracarboxylic dianhydrides may be used singly, or two or more of them may be used.

[0045]

The polyimide resin may contain a tetracarboxylic dianhydride having an aliphatic ring to such an extent that the heat resistance of the polyimide resin is not impaired. Specific examples of the tetracarboxylic dianhydride having an aliphatic ring include 2,3,5-tricarboxycyclopentyl acetic dianhydride, 1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,2,3,4-cyclopentanetetracarboxylic dianhydride, 1,2,3,5-cyclopentanetetracarboxylic dianhydride, 1,2,4,5-bicyclohexenetetracarboxylic dianhydride, 1,2,4,5-cyclohexanetetracarboxylic dianhydride, and 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-C]furane-1,3-dione. These tetracarboxylic dianhydrides may be used singly, or two or more of them may be used.

[0046]

The molecular weight of the polyimide resin can be adjusted by using equimolar amounts of a tetracarboxylic acid component and a diamine component for the synthesis,

or by using either of these components in excess. It is also possible to use either of the tetracarboxylic acid component and the diamine component in excess and block the terminal of the polymer chain with a terminal blocking agent such as an acid component or an amine component. As the terminal blocking agent of the acid component, a dicarboxylic acid or an anhydride thereof is preferably used. As the terminal blocking agent of the amine component, a monoamine is preferably used. In the adjustment, it is preferred to adjust the acid equivalent of the tetracarboxylic acid component and the amine equivalent of the diamine component to be equimolar including those of the terminal blocking agent of the acid component or the amine component.

[0047]

When the molar ratio is adjusted so that the tetracarboxylic acid component is in excess or the diamine component is in excess, dicarboxylic acids such as benzoic acid, phthalic anhydride, tetrachlorophthalic anhydride, and aniline, or anhydrides thereof, or monoamines may be added as a terminal blocking agent.

[0048]

The molar ratio of the tetracarboxylic acid component to the diamine component in the polyimide resin can be appropriately adjusted so that the viscosity of the resin

composition falls within a range in which the resin composition is easy to use in coating or the like. The molar ratio of the tetracarboxylic acid component to the diamine component is generally adjusted in the range of 100/100 to 100/95 or 100/100 to 95/100. If the molar balance is disrupted, the molecular weight of the resin decreases, mechanical strength of the film formed from the resin decreases, and the adhesive force of the film tends to be low. Therefore, it is preferred to adjust the molar ratio in the range in which the adhesive force is not reduced.

[0049]

The method of obtaining the polyimide resin by polymerization is not particularly limited. For example, when polyamic acid as a polyimide precursor is obtained by polymerization, a tetracarboxylic dianhydride and a diamine in an organic solvent are stirred at 0 to 100°C for 1 to 100 hours to give a polyamic acid resin solution. When the polyimide resin is soluble in the organic solvent, after the polyamic acid is obtained by polymerization, the temperature is raised to 120 to 300°C, and the polyamic acid resin solution is stirred as it is for 1 to 100 hours to convert the polyamic acid into a polyimide. In this way, a polyimide resin solution is obtained. In this step, toluene, o-xylene, m-xylene, or p-xylene may be added to

the reaction solution to remove water produced in the imidization reaction by azeotropy of the solvent and water.

[0050]

The polyimide resin may be either of a polyimide or polyamic acid, a precursor of the polyimide. The polyimide resin may be a partially ring-closed and imidized polyimide precursor.

[0051]

The resin composition of the present invention contains (b) a crosslinker including a fluorene group. The crosslinker is a compound that crosslinks the polyimide resin and is incorporated into the polyimide resin when it is heat cured, or a compound that forms a network structure by self reaction of the crosslinker and forms an interpenetrating polymer network structure with the polyimide resin when it is heat cured. Examples of the crosslinker include a compound having at least two crosslinkable functional groups selected from the group consisting of an epoxy group, an oxetane group, a maleimide group, an amino group, an isocyanate group, a methylol group, an acrylic group, a methacrylic group, and an episulfide group.

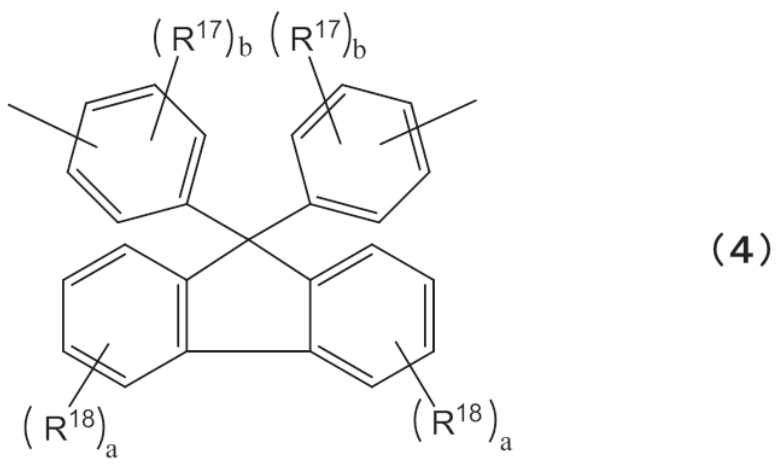
[0052]

In the present invention, from the viewpoint of heat resistance, the crosslinker (b) including a fluorene group

is more preferably a crosslinker including a structure represented by the general formula (4) or (5):

[0053]

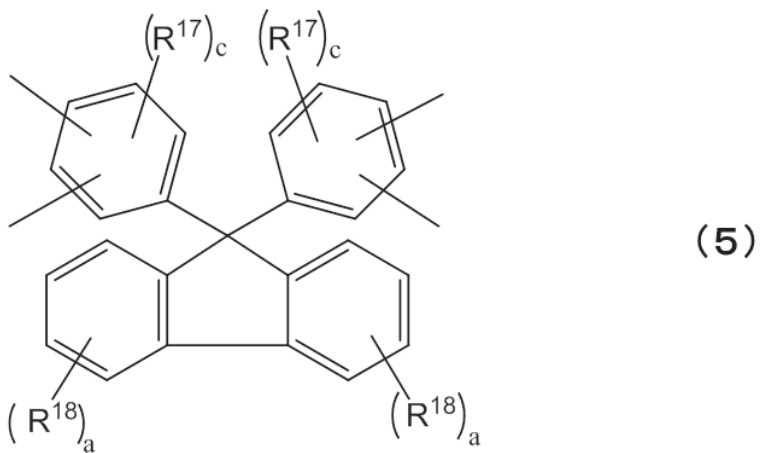
[Chemical Formula 6]



or

[0054]

[Chemical Formula 7]



[0055]

wherein R^{17} and R^{18} may be same or different, and each represent a group selected from an alkyl group having 1 to 30 carbon atoms, an alkoxy group having 1 to 30 carbon

atoms, a fluoroalkyl group having 1 to 30 carbon atoms, a hydroxyl group, a halogen, a carboxyl group, a carboxylate ester group, a phenyl group, a sulfone group, a nitro group, and a cyano group, a and b each represent an integer of 0 to 4, c represents an integer of 0 to 3, and the halogen in R¹⁷ and R¹⁸ refers to fluorine, chlorine, bromine or iodine.

From the viewpoint of versatility, the crosslinker (b) including a fluorene group of the present invention is preferably a fluorene compound having an epoxy group, an acrylic group, or an episulfide group as a crosslinkable functional group, and is more preferably a fluorene compound having an epoxy group that is excellent in heat resistance and cost effectiveness.

[0056]

Specific examples of the crosslinker including a fluorene group include "OGSOL" (registered trademark) PG 100, EG 200, CG 500, EG 280, and CG 400 (trade names, manufactured by Osaka Gas Chemicals Co., Ltd.) as an epoxy resin including a fluorene group, "OGSOL" (registered trademark) EA0200, EA0300, and GA5060P (trade names, manufactured by Osaka Gas Chemicals Co., Ltd.) as an acrylic resin including a fluorene group, and "OGSOL" (registered trademark) CS 500 (trade name, manufactured by Osaka Gas Chemicals Co., Ltd.) as an episulfide resin

including a fluorene group. Among these, an epoxy resin including a fluorene group is preferred from the viewpoint of heat resistance and cost effectiveness.

[0057]

If the resin composition of the present invention contains the crosslinker (b) including a fluorene group, the heat resistance of the resin composition is improved. In particular, the heat resistance during bonding of an electronic circuit formation substrate or semiconductor circuit formation substrate having a thickness of 1 μm or more and 100 μm or less is significantly improved.

[0058]

The crosslinker (b) including a fluorene group preferably has a 5% weight loss temperature of 250°C or more and 400°C or less, more preferably has a 5% weight loss temperature of 300°C or more and 400°C or less. When the 5% weight loss temperature of the epoxy resin is 250°C or more, the resin exhibits improved heat resistance, and when the 5% weight loss temperature of the epoxy resin is 400°C or less, the resin exhibits good reactivity. Thus, poor appearance such as a blister does not occur in an electronic circuit formation substrate or semiconductor circuit formation substrate having a thickness of 1 μm or more and 100 μm or less in the heat treatment during bonding of the electronic circuit formation substrate or

the semiconductor circuit formation substrate, and the epoxy resin can exhibit improved heat resistance.

[0059]

The 5% weight loss temperature of the crosslinker (b) including a fluorene group can be measured using a thermogravimetric analyzer (TGA). The measuring method will be specifically described. A predetermined amount of a resin is put in the TGA, and held at 60°C for 30 minutes to remove the moisture absorbed by the resin. Then, the resin is heated to 500°C at a rate of 5°C/min. The temperature at which 5% of the weight has been lost in the obtained weight loss curve is taken as the 5% weight loss temperature.

[0060]

The content of the crosslinker (b) including a fluorene group is preferably 0.1% by mass or more and 40% by mass or less relative to 100% by mass of the polyimide resin (a). The content of the crosslinker (b) including a fluorene group is more preferably 0.1% by mass or more and 20% by mass or less. When the content is less than 0.1% by mass, poor appearance such as a blister may occur depending on the thickness of the electronic circuit formation substrate or the semiconductor circuit formation substrate in the heat treatment during bonding of the electronic circuit formation substrate or semiconductor circuit

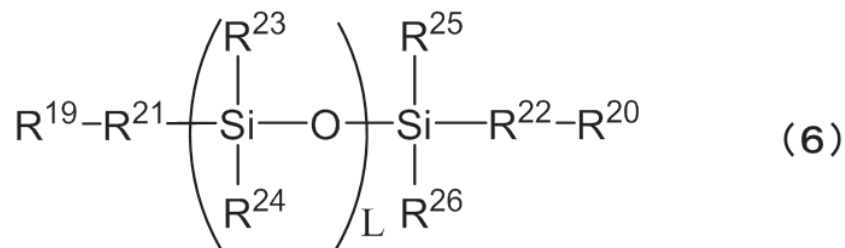
formation substrate having a thickness of 1 μm or more and 100 μm or less. When the content is more than 40% by mass, crosslinking of films proceeds and solubility in a rework solvent is lowered, and thus residues may be generated after washing or a long time may be necessary for rework.

[0061]

The resin composition of the present invention preferably contains (c) a siloxane polymer represented by the general formula (6):

[0062]

[Chemical Formula 8]



[0063]

wherein L is an integer of 10 or more and 100 or less, R^{19} and R^{20} may be same or different and each represent a monovalent organic group having 1 to 30 carbon atoms and 0 to 3 nitrogen atoms, R^{21} and R^{22} may be same or different and each represent an alkylene group having 1 to 30 carbon atoms or a phenylene group, R^{23} to R^{26} may be same or different and each represent an alkyl group having 1 to 30 carbon atoms, an alkoxy group, a phenyl group, or a phenoxy group, and an alkoxy group having 1 to 30 carbon atoms of

R^{23} to R^{26} does not include a polyoxyalkylene structure.

R^{19} and R^{20} may be same or different and each represent a monovalent organic group having 1 to 30 carbon atoms and 0 to 3 nitrogen atoms. For example, structures having an alkyl group, an alkylene group, an alkoxy group, a phenyl group, a phenoxy group, an amino group, a carboxyl group, a hydroxyl group, an epoxy group, an oxetane group, an ether group, an aralkyl group, an amide group, an imide group, a nitro group, or an ester group can be used.

[0064]

From the viewpoint of heat resistance, R^{19} and R^{20} of the siloxane polymer represented by the general formula (6) are preferably amino groups. When R^{19} and R^{20} are amino groups, they react with the acid anhydride residue of the polyimide resin (a) during the heat treatment step and can improve heat resistance.

[0065]

In the general formula (6), L is an integer of 10 or more and 100 or less. When the resin composition contains a siloxane polymer in which L is 10 or more and 100 or less, the adhesiveness of the surface of the resin layer obtained by applying the resin to a wafer and drying the resin can be lowered. Thus, the resin composition can bond the electronic circuit formation substrate or the semiconductor circuit formation substrate and the support

substrate together, and then be peeled off by a mechanical force applied at room temperature under mild conditions. The resin composition can also be dissolved with the rework solvent described below or the like under mild conditions at room temperature to be peeled off.

[0066]

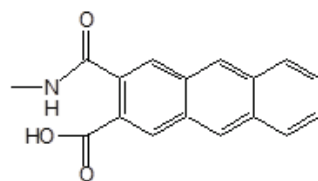
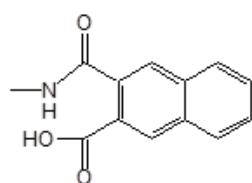
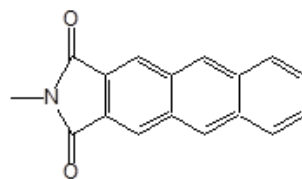
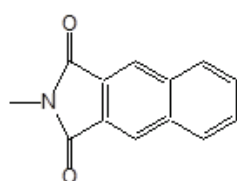
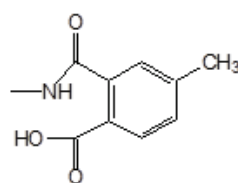
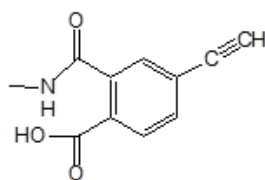
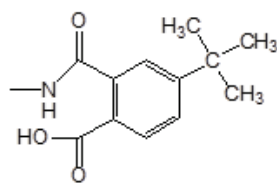
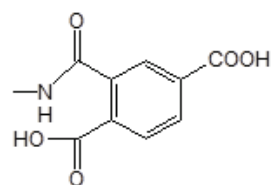
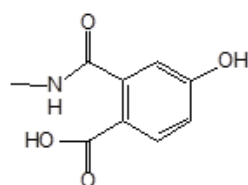
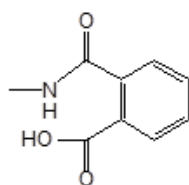
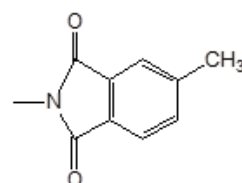
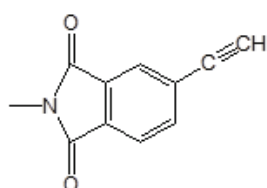
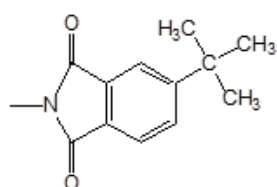
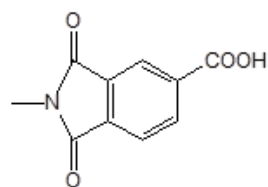
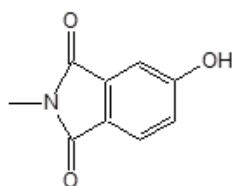
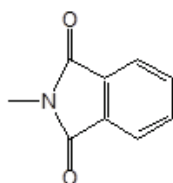
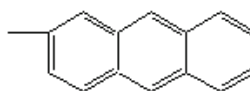
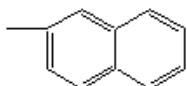
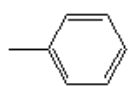
An adhesive containing a resin composition not containing the siloxane polymer (c) represented by the general formula (6) has strong adhesiveness of the surface of the resin layer and is difficult to be peeled off by application of a mechanical force. Therefore, the adhesive can be suitably used as a permanent adhesive. Meanwhile, the adhesive can be dissolved with the rework solvent described below or the like under mild conditions at room temperature to be peeled off.

[0067]

From the viewpoint of heat resistance, R^{19} and R^{20} in the general formula (6) preferably have a structure having an aromatic ring or an aromatic heterocyclic structure. Specific examples of R^{19} and R^{20} include, but are not limited to, the following structures.

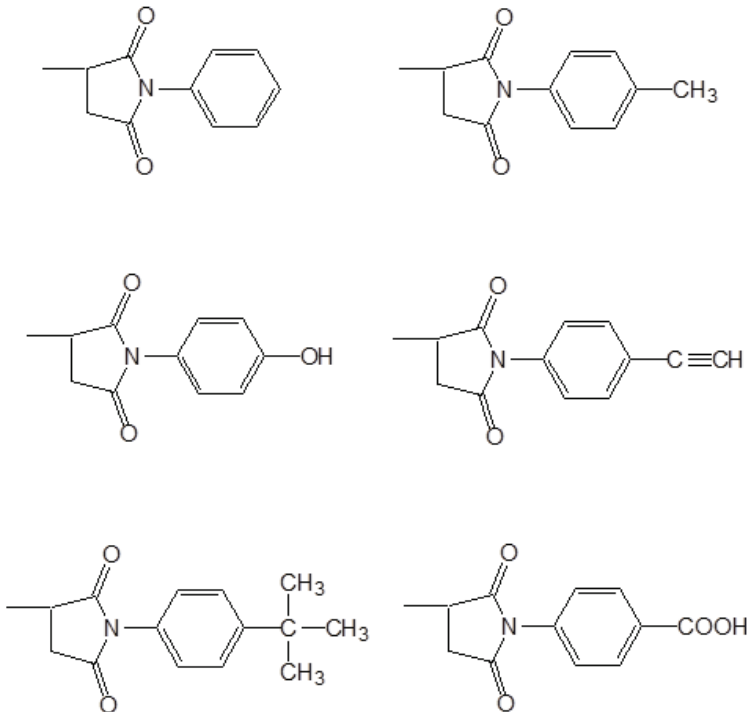
[0068]

[Chemical Formula 9]



[0069]

[Chemical Formula 10]



[0070]

The content of the siloxane polymer (c) represented by the general formula (6) is preferably 0.01% by mass or more and 30% by mass or less relative to 100% by mass of the polyimide resin (a). The content of the siloxane polymer (c) represented by the general formula (6) is further preferably 0.1% by mass or more and 15% by mass or less. When the content is 0.01% by mass or more, the peeling property is improved, and when the content is 30% by mass or less, the adhesiveness between the resin layer and the support substrate can be maintained.

[0071]

The siloxane polymer (c) represented by the general formula (6) may be added during or after the polymerization of the polyimide resin (a).

[0072]

The resin composition of the present invention preferably contains (d) a silane coupling agent. If the resin composition contains the silane coupling agent (d) (d), the adhesiveness of the resin composition is improved and peeling of the wafer during polishing of the backside can be suppressed.

[0073]

Examples of the silane coupling agent (d) include, but are not limited to, vinyltrimethoxysilane, vinyltriethoxysilane, epoxycyclohexylethyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, p-styryltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, and N-phenyl-3-aminopropyltrimethoxysilane. The resin composition may contain two or more of them. In the present invention, from the viewpoint of heat resistance, a compound represented by the general formula (7) is preferred:

[0074]

[Chemical Formula 11]



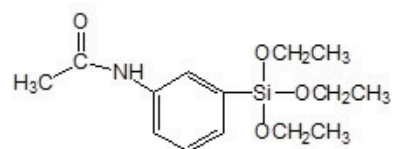
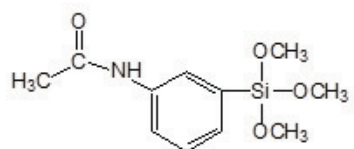
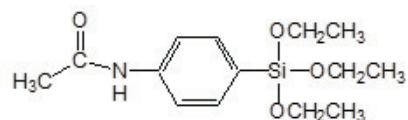
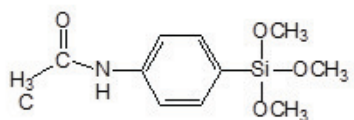
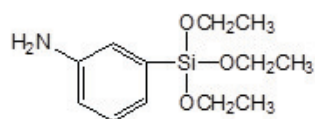
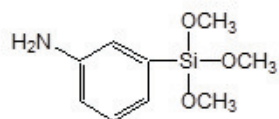
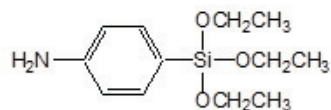
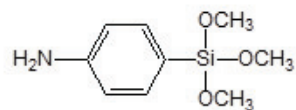
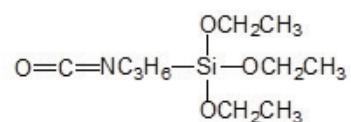
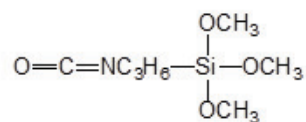
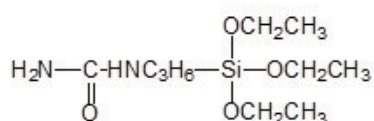
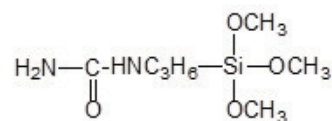
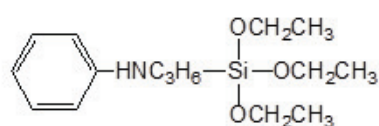
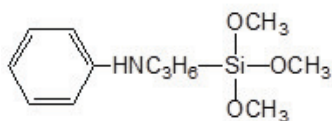
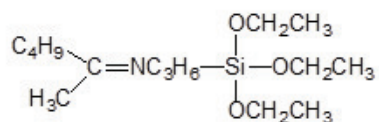
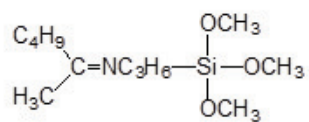
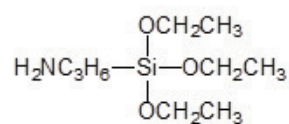
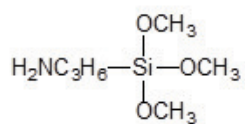
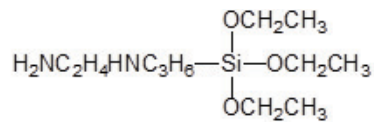
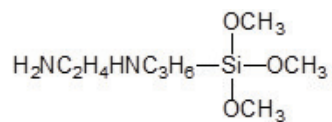
[0075]

wherein R^{27} represents a monovalent organic group having 2 to 20 carbon atoms and 1 to 3 nitrogen atoms, R^{28} represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, or an aromatic group, and d represents an integer of 0 to 4.

R^{27} represents a monovalent organic group having 2 to 20 carbon atoms and 1 to 3 nitrogen atoms. For example, a structure having an amino group, an isocyanate group, or a ureido group can be used. Specific examples of the compound represented by the general formula (7) include, but are not limited to, the following structures.

[0076]

[Chemical Formula 12]

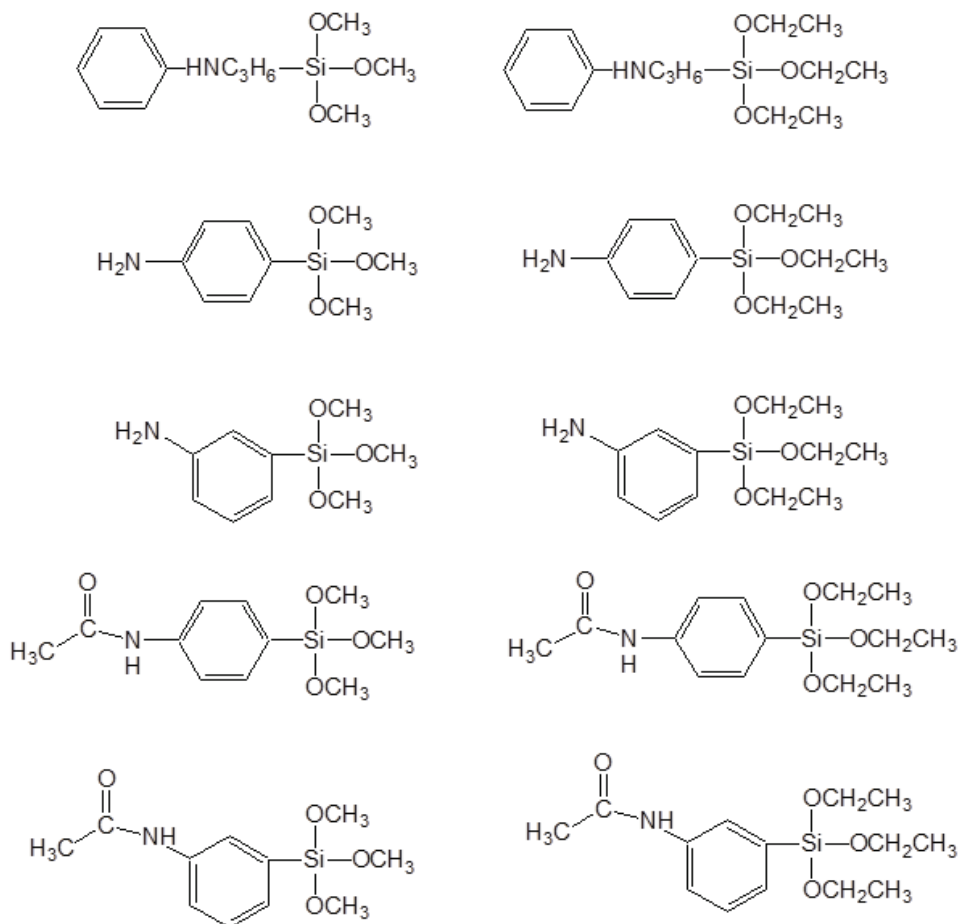


[0077]

From the viewpoint of heat resistance, R^{27} is preferably a structure having an aromatic ring or an aromatic heterocyclic structure. Preferred specific examples of the compound represented by the general formula (7) include, but are not limited to, the following structures.

[0078]

[Chemical Formula 13]



[0079]

The content of the silane coupling agent (d) is

preferably 0.01% by mass or more and 30% by mass or less relative to 100% by mass of the polyimide resin (a). The content of the silane coupling agent (d) is further preferably 0.1% by mass or more and 15% by mass or less. When the content is 0.01% by mass, an effect of improving the adhesiveness of the resin composition is exerted, and when the content is 30% by mass or less, the amount of the silane coupling agent remaining in the resin layer after the heat treatment can be minimized and generation of volatile components can be suppressed.

[0080]

The silane coupling agent may be added during or after the polymerization of the polyimide resin (a).

[0081]

The resin composition of the present invention preferably contains (e) inorganic fine particles. If the resin composition contains the inorganic fine particles, the heat resistance to the heat treatment after the bonding step of the resin composition can be improved. Specific examples of the inorganic fine particles include silica, alumina, titanium oxide, quartz powder, magnesium carbonate, potassium carbonate, barium sulfate, mica, and talc.

[0082]

The inorganic fine particles (e) may be added during

or after the polymerization of the polyimide resin (a).

[0083]

The number average particle diameter of the inorganic fine particles (e) is preferably 2 nm or more and 5 μm or less, more preferably 5 nm or more and 3 μm or less. Within this range, the filterability of the resin composition is good, and the heat resistance to the heat treatment after the bonding step can be improved.

[0084]

When a value as converted according to the specific surface area method is used, the number average particle diameter of the inorganic fine particles (e) of the present invention is obtained by drying followed by burning of the inorganic fine particles, measurement of the specific surface area of the resulting particles, and calculation of the particle size from the specific surface area to obtain the average particle diameter as a number average on the assumption that the particles are spheres. The instrument used is not particularly limited, and ASAP 2020 (trade name, manufactured by Micromeritics) or the like can be used.

[0085]

The content of the inorganic fine particles (e) is preferably 0.1% by mass or more and 40% by mass or less relative to 100% by mass of the polyimide resin (a). The

content of the inorganic fine particles (e) is further preferably 0.1% by mass or more and 20% by mass or less. Within this range, the filterability of the resin composition is good, and the heat resistance to the heat treatment after the bonding step can be improved.

[0086]

The resin composition of the present invention may contain a solvent. If the resin composition contains a solvent, the viscosity of the resin composition can be adjusted to a viscosity suitable for coating methods described below. The content of the solvent is preferably 5% by mass or more and 100,000% by mass or less relative to 100% by mass of the polyimide resin (a).

[0087]

Examples of the solvent to be used in the resin composition of the present invention include polar aprotic solvents such as N-methyl-2-pyrrolidone, γ -butyrolactone, N,N-dimethylformamide, N,N-dimethylacetamide, and dimethyl sulfoxide, ethers such as tetrahydrofuran, dioxane, and propylene glycol monomethyl ether, ketones such as acetone, methyl ethyl ketone, and diisobutyl ketone, esters such as ethyl acetate, propylene glycol monomethyl ether acetate, and ethyl lactate, and aromatic hydrocarbons such as toluene and xylene, and these solvents may be used singly, or two or more of them may be used.

[0088]

The SP value of the solvent contained in the resin composition of the present invention is preferably 7.5 or more and 9.0 or less. The SP value is more preferably 7.5 or more and 8.0 or less. Because the polyimide resin (a) of the present invention contains a polysiloxane structure with low polarity and a residue with high polarity including an imide group and an aromatic group, layers of the resin composition may separate and thus the storage stability tends to be poor. However, if the resin composition contains a solvent having an SP value of 7.5 or more and 9.0 or less, layers do not separate and thus good storage stability can be exhibited.

[0089]

Examples of the solvents having an SP value of 7.5 or more and 9.0 or less include methyl acetate (SP value: 8.8), ethyl acetate (SP value: 8.7), 3-methoxybutyl acetate (SP value: 8.7), diethylene glycol methyl ethyl ether (SP value: 8.2), diethylene glycol dimethyl ether (SP value: 8.1), dipropylene glycol methyl ether acetate (SP value: 8.7), methyl ethyl ketone (SP value: 9.0), dipropylene glycol dimethyl ether (SP value: 7.8), and dipropylene glycol methyl n-propyl ether (SP value: 8.0). These solvents may be used singly, or two or more of them may be used.

[0090]

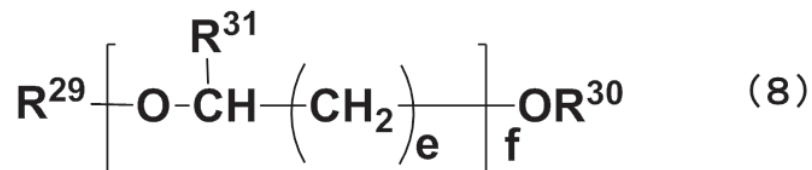
There are various methods for determining the SP value of a solvent. In the present invention, the SP value calculated from the estimation method proposed by Fedors is used. In the method of Fedors, the total cohesive energy and the total molar molecular capacity of the entire substance are calculated from the cohesive energy and the molar molecular volume of the structural unit of the substance, and the square root of the value obtained by dividing the total cohesive energy by the total molar molecular capacity is taken as SP value.

[0091]

From the viewpoint of solubility of the polyimide resin (a), a solvent represented by the general formula (8) is preferred:

[0092]

[Chemical Formula 14]



[0093]

wherein R^{29} and R^{30} each independently represent a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, an acetyl group, or an aromatic group, R^{31} represents a hydrogen atom or a methyl group, e is 0, 1 or 2, and f is

an integer of 1 to 3.

Specific examples of the solvent represented by the general formula (8) include, but are not limited to, propylene glycol mono-t-butyl ether, ethylene glycol mono-t-butyl ether, propylene glycol mono-n-butyl ether, propylene glycol monopropyl ether, propylene glycol monoethyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol monopropyl ether, dipropylene glycol dimethyl ether, dipropylene glycol diethyl ether, dipropylene glycol dipropyl ether, dipropylene glycol di-n-butyl ether, dipropylene glycol di-t-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monopropyl ether, dipropyl glycol mono-n-butyl ether, tripropylene glycol monomethyl ether, tripropylene glycol monoethyl ether, tripropylene glycol monopropyl ether, diethylene glycol methyl ethyl ether, and diethylene glycol dimethyl ether.

[0094]

The solvent contained in the resin composition of the present invention more preferably has an SP value of 7.5 or more and 9.0 or less and is represented by the general formula (8). Examples of the solvent include dipropylene glycol dimethyl ether (SP value: 7.8), dipropylene glycol methyl-n-propyl ether (SP value: 8.0), diethylene glycol methyl ethyl ether (SP value: 8.2), and diethylene glycol

dimethyl ether (SP value: 8.1). Dipropylene glycol dimethyl ether (SP value: 7.8) and dipropylene glycol methyl-n-propyl ether (SP value: 8.0) having an SP value of 7.5 or more and 8.0 or less are more preferred.

[0095]

Other solvents can be added to such an extent that they do not impair the effect of the storage stability and solubility of the polyimide resin (a). Examples of the other solvents include, but are not limited to, amide polar solvents such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, and 1,3-dimethyl-2-imidazoline, lactone polar solvents such as β -propiolactone, γ -butyrolactone, γ -valerolactone, δ -valerolactone, γ -caprolactone, and ϵ -caprolactone, and ethyl lactate.

[0096]

The organic solvent used as the polymerization solvent in the method in which the polyimide resin (a) is obtained by polymerization can be used as the solvent contained in the resin composition without being removed from the polymerization solution.

[0097]

Other resins can be added to the resin composition of the present invention to such an extent that they do not impair the effect of the present invention. A surfactant

may be added to improve characteristics such as tackiness, heat resistance, coating property, and storage stability. Other resins and a surfactant may be added during or after the polymerization of the polyimide resin (a).

[0098]

The resin composition of the present invention preferably has a glass transition temperature after curing of 30°C or more and 150°C or less. The resin composition of the present invention further preferably has a glass transition temperature after curing of 40°C or more and 120°C or less. When the glass transition temperature after curing is 30°C or more, the resin composition is not softened by the heat applied in the backside polishing step, and breakage of the wafer in the backside polishing step can be prevented. When the glass transition temperature after curing is 150°C or less, the resin composition can exhibit good adhesiveness in thermocompression bonding.

[0099]

The glass transition temperature of the resin composition of the present invention after curing can be measured using a differential scanning calorimeter (DSC). The measuring method will be specifically described. The resin composition of the present invention was applied in a thickness of 20 μm to a gloss surface of an 18 μm -thick

electrolytic copper foil piece with a bar coater, and then dried at 80°C for 10 minutes and at 150°C for 10 minutes, and in addition, heated at 250°C for 10 minutes in a nitrogen atmosphere to be completely cured, whereby a resin composition-laminated copper foil piece was obtained. Then, the whole surface of the copper foil of the obtained polyimide-laminated copper foil piece was etched with a ferric chloride solution to give a single film of the resin composition. About 10 mg of the obtained single film of the resin composition was placed in an aluminum standard container and measured with a differential scanning calorimeter DSC-50 (manufactured by Shimadzu Corporation). The glass transition temperature can be calculated from the inflection point of the obtained DSC curve.

[0100]

The resin composition of the present invention can be suitably used in a resin layer including a coating film, a permanent adhesive, an adhesive for temporary bonding, and a laminated film.

[0101]

The laminated film of the present invention can be obtained by laminating the resin composition of the present invention on one surface or both surfaces of a heat-resistant insulating film. The laminated film of the present invention can also be used as it is as an adhesive

film. The laminated film can also be used as a transfer film. That is, the resin layer of the laminated film is pressure-bonded to a glass substrate or the like, and then only the heat-resistant insulating film is peeled off to transfer the resin layer to a glass substrate or the like.

[0102]

Examples of the heat-resistant insulating film of the present invention include, but are not limited to, the following plastic films: a polypropylene film, a polyethylene film, a polystyrene film, a polyethylene terephthalate (PET) film, a polyphenylene sulfide (PPS) film, a polyimide film, a polyamide film, a polyamideimide film, a polyester film, an aromatic polyester film, a polyethersulfone film, fluorine-containing polymer films such as a polytetrafluoroethylene film (PTFE), a polyether ether ketone film, a polystyrene film, a polyphenylene ether film, a polyarylate film, and a polysulfone film. Specific examples of the plastic films include, but are not limited to, "Lumirror" (registered trademark), "Torelina" (registered trademark), and "Torayfan" (registered trademark) (manufactured by Toray Industries, Inc.), "Kapton" (registered trademark) (manufactured by DU PONT-TORAY CO., LTD.), "Upilex" (registered trademark) (manufactured by Ube Industries, Ltd.), and "Apical" (registered trademark) (manufactured by KANEKA CORPORATION)

(all trade names).

[0103]

The thickness of the heat-resistant insulating film is, without particular limitation, preferably 3 μm or more, more preferably 5 μm or more, still more preferably 10 μm or more from the viewpoint of strength as a support. The thickness of the heat-resistant insulating film is preferably 150 μm or less, more preferably 75 μm or less, still more preferably 50 μm or less from the viewpoint of flexibility.

[0104]

Examples of the method of applying the resin composition of the present invention to the heat-resistant insulating film include a method in which a bar coater, a roll coater, a knife coater, a comma coater, a reverse coater, a doctor blade float coater, a gravure coater, a slit die coater or the like is used. A resin layer having good adhesiveness and heat resistance can be obtained by continuous or intermittent heat treatment of the resin composition at 50°C or more and 500°C or less, preferably at 70°C or more and 450°C or less for 1 minute or more and 3 hours or less after the application to remove the organic solvent in the resin composition and cure the resin composition.

[0105]

When the laminated film of the present invention is used as a transfer film, from the viewpoint of transferability, the resin composition is applied to a heat-resistant insulating film, and then heat-treated continuously or intermittently at 50°C or more and 200°C or less, preferably at 70°C or more and 150°C or less for 1 minute or more and 3 hours or less to remove the organic solvent. A resin layer having good adhesiveness and heat resistance can be obtained by transfer to a substrate such as a glass substrate followed by additional continuous or intermittent heat treatment of the resin composition at 50°C or more and 500°C or less, preferably at 70°C or more and 450°C or less for 1 minute or more and 3 hours or less to cure the resin composition.

[0106]

When the resin composition is laminated on both surfaces of the heat-resistant insulating film, the resin composition may be applied to one surface at a time and dried, or may be applied to both surfaces at once and dried. A release-treated film may be laminated on the surface of the applied resin composition as needed.

[0107]

The thickness of the resin composition to be laminated can be appropriately selected, and is 0.1 μm or more and 500 μm or less, preferably 1 μm or more and 100 μm or less.

[0108]

When the laminated film of the present invention is used as an adhesive film, one surface or both surfaces of the heat-resistant insulating film may be subjected to adhesiveness improvement treatment according to the purpose. As the adhesiveness improvement treatment, discharge treatment such as normal pressure plasma treatment, corona discharge treatment, or low temperature plasma treatment is preferred.

[0109]

A press, a roll laminator or the like can be used to pressure-bond other substrates to the adhesive film, and the pressure bonding can be performed with heating as needed. In such a case, the temperature is 20°C or more and 300°C or less, preferably 250°C or less. The pressure of the pressure bonding is 0.1 MPa or more and 2.0 MPa or less, more preferably 0.2 MPa or more and 1.5 MPa or less. The pressure bonding may be performed in air or in nitrogen. The pressure bonding is preferably performed in vacuum.

[0110]

When the laminated film of the present invention is used as a transfer film, one surface or both surfaces of the heat-resistant insulating film may be subjected to release treatment according to the purpose. The release

treatment is preferably application of a silicone resin, a fluororesin or the like.

[0111]

When the resin composition is transferred, the resin layer of the laminated film is attached to a substrate such as a glass substrate and pressure-bonded to the substrate. A press, a roll laminator or the like can be used for the pressure bonding, and the pressure bonding can be performed with heating as needed. In such a case, the temperature is 20°C or more and 200°C or less, preferably 180°C or less. The pressure of the pressure bonding is 0.05 MPa or more and 2.0 MPa or less, more preferably 0.1 MPa or more and 1.5 MPa or less. The pressure bonding may be performed in air or in nitrogen. The pressure bonding is preferably performed in vacuum.

[0112]

When other substrates are pressure-bonded to the transferred resin layer, the substrates are pressure-bonded with a press, a roll laminator or the like after peeling of the heat-resistant insulating film. The pressure bonding can be performed with heating as needed. In such a case, the temperature is 20°C or more and 300°C or less, preferably 250°C or less. The pressure of the pressure bonding is 0.1 MPa or more and 2.0 MPa or less, more preferably 0.2 MPa or more and 1.5 MPa or less. The

pressure bonding may be performed in air or in nitrogen.

The pressure bonding is preferably performed in vacuum.

[0113]

The resin composition of the present invention can be used in manufacture of an electronic component and a semiconductor device. More specifically, the resin composition can be suitably used in manufacture of an electronic component and a semiconductor device in which the electronic circuit formation substrate or semiconductor circuit formation substrate having a thickness of 1 μm or more and 100 μm or less is heat-treated in circuit formation processing. For example, the resin composition of the present invention is used in the manufacture of a thin capacitor and the manufacture of a semiconductor device in which semiconductor chips are laminated with the semiconductor chips connected with a through-silicon via (TSV) in order to achieve higher levels of integration and higher packaging density of semiconductor devices.

[0114]

Because an electronic circuit formation substrate or semiconductor circuit formation substrate having a thickness of 1 μm or more and 100 μm or less warps largely, is difficult to form a circuit, and cracks and breaks easily, the electronic circuit formation substrate or the semiconductor circuit formation substrate is fixed to a

support substrate such as a silicon substrate, a glass substrate, and a film, with an adhesive for temporary bonding, to form a processed wafer. The resin composition of the present invention can be suitably used as an adhesive for temporary bonding to bond the electronic circuit formation substrate or the semiconductor circuit formation substrate and the support substrate together. In particular, the resin composition has excellent heat resistance during bonding of the electronic circuit formation substrate or semiconductor circuit formation substrate having a thickness of 1 μm or more and 100 μm or less.

[0115]

In the present invention, an electronic circuit formation substrate or semiconductor circuit formation substrate having a thickness of 1 μm or more and 100 μm or less can be bonded to a support substrate, or a thick electronic circuit formation substrate or semiconductor circuit formation substrate can be bonded to a support substrate and then thinned. As the thinning step, a polishing step, an etching step or the like can be employed.

[0116]

For example, in the manufacture of an electronic component, a ceramic substrate, which is an electronic

circuit formation substrate having a thickness of 1 μm or more and 100 μm or less, is bonded to a support substrate such as a silicon substrate, a glass substrate, and a film using an adhesive for temporary bonding to form a processed wafer. Then, the electronic circuit formation substrate is heat-treated at a temperature of 230°C or more and 450°C or less in circuit formation processing or the like. Then, the electronic circuit formation substrate is peeled from the support substrate. The resin composition of the present invention can be suitably used as the adhesive for temporary bonding for manufacturing electronic components.

[0117]

For example, in the manufacture of a semiconductor device, a silicon substrate, which is a semiconductor circuit formation substrate, is bonded to a support substrate such as a silicon substrate, a glass substrate, and a film using an adhesive for temporary bonding to form a processed wafer. Then, the surface not having a circuit (the backside) is polished to form a semiconductor circuit formation substrate having a thickness of 1 μm or more and 100 μm or less. Then, the semiconductor circuit formation substrate is heat-treated at a temperature of 230°C or more and 450°C or less in circuit formation processing or the like. Then, the semiconductor circuit formation substrate is peeled from the support substrate. The resin

composition of the present invention can be suitably used as the adhesive for temporary bonding for manufacturing semiconductor devices.

[0118]

Examples of a method for applying the resin composition to a support substrate such as a silicon substrate, a glass substrate, and a film include a spin coater, a roll coater, screen printing, and a slit die coater. A resin layer may also be transferred and laminated on a support substrate using the above-mentioned transfer film. A resin layer having good adhesiveness and heat resistance can be obtained by continuous or intermittent heat treatment of the resin composition at 50°C or more and 500°C or less, preferably at 70°C or more and 450°C or less for 1 minute or more and 3 hours or less to remove the organic solvent in the resin composition and cure the resin composition after the application or transfer of the resin composition. The thickness of the resin layer can be appropriately selected, and is 0.1 μm or more and 500 μm or less, preferably 1 μm or more and 100 μm or less.

[0119]

In the present invention, the resin composition may be applied and laminated on a support substrate, and in addition, the resin composition may be applied and

laminated on an electronic circuit formation substrate or a semiconductor circuit formation substrate, or the resin layer of the resin composition may be transferred and laminated on an electronic circuit formation substrate or a semiconductor circuit formation substrate using the transfer film. A layer including other resin compositions can also be present on the side of the support substrate, or the electronic circuit formation substrate or the semiconductor circuit formation substrate. That is, the resin composition of the present invention can be used in combination with other adhesives. However, the electronic circuit formation substrate or the semiconductor circuit formation substrate and the support substrate are preferably bonded together only with the resin composition of the present invention, because the resin composition of the present invention is a resin composition that has excellent heat resistance during bonding of an electronic circuit formation substrate or a semiconductor circuit formation and has steady adhesive force through the process of manufacturing a semiconductor device or the like, and can be peeled off under mild conditions at room temperature after the manufacturing process. That is, in the processed wafer of the present invention, the electronic circuit formation substrate or the semiconductor circuit formation substrate and the support substrate are preferably bonded

together only with the resin layer of the present invention or the laminated film of the present invention interposed between the electronic circuit formation substrate or the semiconductor circuit formation substrate and the support substrate. Due to bonding using one type of adhesive layer, only one adhesive layer is to be formed, and thus a burden on the process is reduced.

[0120]

A processed wafer can be produced by stacking and pressure-bonding the support substrate on which the resin layer of the present invention is laminated and the electronic circuit formation substrate or the semiconductor circuit formation substrate together. For the pressure bonding, a press, a roll laminator or the like can be used. The pressure bonding can be performed with heating as needed. In such a case, the temperature is 20°C or more and 300°C or less, preferably 250°C or less. The pressure of the pressure bonding is 0.1 MPa or more and 2.0 MPa or less, more preferably 0.2 MPa or more and 1.5 MPa or less. The pressure bonding may be performed in air or in nitrogen. The pressure bonding is preferably performed in vacuum.

[0121]

In the present invention, a laminated film including a heat-resistant insulating film and the resin composition of

the present invention on at least one surface of the heat-resistant insulating film, that is, the above-mentioned adhesive film can be used as the support substrate. A processed wafer can be produced by stacking and pressure-bonding the adhesive film on the electronic circuit formation substrate or the semiconductor circuit formation substrate. For pressure bonding, a press, a roll laminator or the like can be used. The pressure bonding can be performed with heating as needed. In such a case, the temperature is 20°C or more and 300°C or less, preferably 250°C or less. The pressure of the pressure bonding is 0.1 MPa or more and 2.0 MPa or less, more preferably 0.2 MPa or more and 1.5 MPa or less. The pressure bonding may be performed in air or in nitrogen. The pressure bonding is preferably performed in vacuum.

[0122]

Examples of a method for peeling the support substrate from the electronic circuit formation substrate or the semiconductor circuit formation substrate include a thermal slide peeling method, a laser irradiation peeling method, a mechanical peeling method at room temperature, and a solvent peeling method at room temperature. The resin composition of the present invention can be suitably used in the mechanical peeling method at room temperature or the solvent peeling method at room temperature. The mechanical

peeling method at room temperature refers to a method of gradually mechanically peeling off the electronic circuit formation substrate or the semiconductor circuit formation substrate gradually from an end of the substrate at room temperature. The solvent peeling method at room temperature is a method in which a hole for solvent passage is formed in the support substrate, and the resin layer is dissolved with a solvent to peel off the support substrate. In the present invention, as the solvent used in the solvent peeling method, a rework solvent described below is preferably used.

[0123]

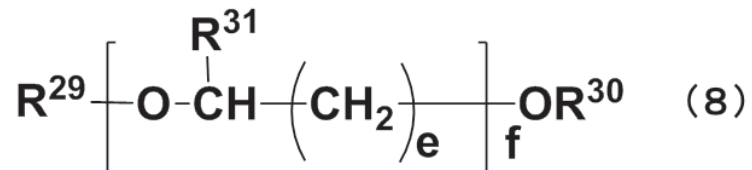
The method may include, after the step of peeling the electronic circuit formation substrate or the semiconductor circuit formation substrate from the support substrate, a step of reworking the resin layer remaining on the electronic circuit formation substrate or the semiconductor circuit formation substrate and the support substrate as well as the residue of the resin layer with an organic solvent or an alkaline aqueous solution.

[0124]

In the resin composition of the present invention, as the rework solvent, a rework solvent containing (A) an amine solvent and (B) a solvent represented by the general formula (8) is preferably used:

[0125]

[Chemical Formula 15]



[0126]

wherein R^{29} and R^{30} each independently represent a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, an acetyl group, or an aromatic group, R^{31} represents a hydrogen atom or a methyl group, e is 0, 1 or 2, and f is an integer of 1 to 3.

The amine solvent (A) has a ring opening effect on an imide group to make the resin composition easily soluble in the rework solvent, and thus, the washing time can be shortened. To open the ring of the imide group, an amine solvent including a primary amine and a secondary amine is preferred, and specific examples of the amine solvent include, but are not limited to, monomethanolamine, dimethanolamine, monoethanolamine, dimethanolamine, dimethylamine, monopropanolamine, isopropanolamine, isopropylamine, and diisopropylamine. An amine solvent including a primary amine is more preferred, and specific examples of the amine solvent include, but are not limited to, monomethanolamine, monoethanolamine, monopropanolamine, isopropanolamine, and isopropylamine.

[0127]

From the viewpoint of solubility of the polyimide resin (a), the rework solvent preferably contains the solvent (B) represented by the general formula (8), and specific examples of the solvent (B) represented by the general formula (8) include, but are not limited to, propylene glycol mono-t-butyl ether, ethylene glycol mono-t-butyl ether, propylene glycol mono-n-butyl ether, propylene glycol monopropyl ether, propylene glycol monoethyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol monopropyl ether, dipropylene glycol dimethyl ether, dipropylene glycol diethyl ether, dipropylene glycol dipropyl ether, dipropylene glycol di-n-butyl ether, dipropylene glycol di-t-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monopropyl ether, dipropyl glycol mono-n-butyl ether, tripropylene glycol monomethyl ether, tripropylene glycol monoethyl ether, tripropylene glycol monopropyl ether, diethylene glycol methyl ethyl ether, and diethylene glycol dimethyl ether.

[0128]

A solvent represented by the general formula (8) and having an SP value of 7.5 or more and 9.0 or less is more preferred. Examples of the solvent include dipropylene glycol dimethyl ether (SP value: 7.8), dipropylene glycol

methyl-n-propyl ether (SP value: 8.0), diethylene glycol methyl ethyl ether (SP value: 8.2), and diethylene glycol dimethyl ether (SP value: 8.1). Dipropylene glycol dimethyl ether (SP value: 7.8) and dipropylene glycol methyl-n-propyl ether (SP value: 8.0) having an SP value of 7.5 or more and 8.0 or less are more preferred.

[0129]

The rework solvent used in the present invention preferably contains an amide polar solvent in addition to (A) and (B). The amide polar solvent has the effect of compatibilizing (A) and (B) and improving the storage stability of the rework solvent. As the amide polar solvent, a polar solvent including a tertiary amide excellent in storage stability is preferred. Specific examples of the amide polar solvent include, but are not limited to, N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, and 1,3-dimethyl-2-imidazoline.

[0130]

The rework solvent can contain an aqueous solution of sodium hydroxide, sodium hydrogencarbonate, potassium hydroxide, or tetramethylammonium hydroxide, or an organic solvent of dimethyl sulfoxide or the like as needed.

[0131]

The rework solvent can be suitably used as a solvent used in a solvent peeling method at room temperature.

EXAMPLES

[0132]

The present invention will be described below by way of examples. The present invention is not limited to these examples. Methods for measurement of glass transition temperature, measurement of 5% weight loss temperature, adhesiveness evaluation, protrusion evaluation, heat resistance evaluation after adhesiveness evaluation, back grinding evaluation, heat resistance evaluation after back grinding evaluation, peeling evaluation and rework evaluation will be described.

[0133]

(1) Measurement of glass transition temperature

Each resin composition of the following Manufacturing Examples 1 to 32 (AH1 to 32) was applied in a thickness of 20 μm to a gloss surface of an 18 μm -thick electrolytic copper foil piece with a bar coater, and then dried at 80°C for 10 minutes and at 150°C for 10 minutes, and then heat-treated at 250°C for 10 minutes in a nitrogen atmosphere to be cured, whereby a resin composition-laminated copper foil piece was obtained. Then, the whole surface of the copper foil of the obtained resin composition-laminated copper foil piece was etched with a ferric chloride solution to give a single film of the resin composition.

[0134]

About 10 mg of the obtained single film of the resin composition was placed in an aluminum standard container and measured with a differential scanning calorimeter DSC-50 (manufactured by Shimadzu Corporation) (DSC method). The glass transition temperature was calculated from the inflection point of the obtained DSC curve. The single film was predried at 80°C for 1 hour, and then measured at a heating rate of 20°C/min.

[0135]

(2) Measurement of 5% weight loss temperature

About 15 mg of (b) a crosslinker including a fluorene group was placed in an aluminum standard container and measured using a thermogravimetric analyzer TGA-50 (manufactured by Shimadzu Corporation). The measurement conditions were as follows: the temperature was kept at 60°C for 30 minutes and then was raised to 500°C at a heating rate of 5°C/min.

[0136]

The temperature at which 5% of the weight had been lost in the obtained weight loss curve was read and taken as the 5% weight loss temperature.

[0137]

(3) Adhesiveness evaluation

To an 8-inch silicon wafer (manufactured by Shin-Etsu

Chemical Co., Ltd.) having a thickness of 750 μm , each resin composition obtained in the following Manufacturing Examples 1 to 32 was applied using a spin coater with adjusting the rotation speed so that the thickness after drying was 20 μm , heat-treated at 120°C for 10 minutes to be dried, and then heat-treated at 200°C for 3 minutes to be cured, whereby a resin composition layer-laminated silicon substrate was obtained.

[0138]

Each laminated film S1 to S32 produced in the following Manufacturing Examples 33 to 64 was laminated on an 8-inch silicon substrate (manufactured by Shin-Etsu Chemical Co., Ltd.) using a vacuum laminator VTM-200M (manufactured by Takatori Corporation) so that the resin layer of each laminated film would come into contact with the silicon substrate. The lamination conditions were as follows: a heater temperature of 100°C, a roll temperature of 100°C, a lamination speed of 5 mm/sec, a lamination roll pressure of 0.2 MPa, and a chamber pressure of 150 Pa. The support film layer of the obtained laminate was peeled off to give a resin composition-laminated substrate.

[0139]

An 8-inch alkali-free glass substrate (manufactured by Corning Incorporated) having a thickness of 0.7 mm was placed over the resin composition-laminated silicon

substrate produced by the above method, and the substrates were pressure-bonded at a pressure of 0.5 MPa for 5 minutes using a hot press with the upper plate and the lower plate each set at 180°C to give a glass substrate-laminated silicon substrate.

[0140]

Each laminated film produced in the following Manufacturing Examples 65 to 96 was laminated on an 8-inch silicon substrate (manufactured by Shin-Etsu Chemical Co., Ltd.) using a vacuum laminator VTM-200M (manufactured by Takatori Corporation) so that the resin layer of each laminated film would come into contact with the silicon substrate. The lamination conditions were as follows: a heater temperature of 100°C, a roll temperature of 100°C, a lamination speed of 5 mm/sec, a lamination roll pressure of 0.2 MPa, and a chamber pressure of 150 Pa. The obtained laminated substrate was pressure-bonded for 5 minutes at 0.5 MPa using a hot press with the upper plate and the lower plate each set at 180°C to give a film-laminated silicon substrate.

[0141]

If the glass substrate or the film was successfully laminated on the silicon substrate, the adhesiveness was evaluated as "A", and if the glass substrate or the film was not successfully laminated on the silicon substrate,

the adhesiveness was evaluated as "D".

[0142]

The obtained glass substrate-laminated silicon substrate or film-laminated silicon substrate was observed with the naked eye from the glass side or film side to evaluate the presence or absence of voids. The evaluation criteria are as follows.

A: No void

B: Voids of 1 cm or less

C: Voids of 1 cm or more

[0143]

(4) Protrusion evaluation

The glass substrate-laminated silicon substrate or the film-laminated silicon substrate evaluated as described above for adhesiveness was visually observed from the edge of the silicon substrate for protrusions of the resin composition. The evaluation criteria are as follows.

A: No protrusion

B: Protrusion

[0144]

(5) Heat resistance evaluation after adhesiveness evaluation

The glass substrate-laminated silicon substrate or the film-laminated silicon substrate evaluated as described above for protrusions was heat-treated at 250°C for 10

minutes and then observed with the naked eye from the glass or film side to evaluate the presence or absence of voids. The evaluation criteria are as follows.

A: No void

B: Voids of 1 cm or less

C: Voids of 1 cm or more

[0145]

(6) Back grinding evaluation of silicon substrate

The glass substrate-laminated silicon substrate or the film-laminated silicon substrate evaluated as described above for heat resistance after the adhesiveness evaluation was set in a grinder DAG810 (manufactured by DISCO Corporation), and the silicon substrate was polished to a thickness of 30 μm or 100 μm . The silicon substrate after grinding was observed with the naked eye, and the presence or absence of fractures or cracks was evaluated. The evaluation criteria are as follows.

A: No fracture or crack in both 30 μm and 100 μm substrates

B: Fracture and/or crack in only 30 μm substrate

C: Fracture and/or crack in only 100 μm substrate

D: Fracture and/or crack in both 30 μm and 100 μm substrates

[0146]

(7) Heat resistance evaluation after back grinding

evaluation

The glass substrate-laminated silicon substrate or the film-laminated silicon substrate evaluated as described above for back grinding was heat-treated at 270°C for 10 minutes and then observed with the naked eye from the thin silicon substrate side to evaluate the presence or absence of a blister in the thin silicon substrate. The evaluation criteria are as follows.

A: No blister in both 30 μm and 100 μm substrates

B: Blister only in 30 μm substrate

C: Blister only in 100 μm substrate

D: Blister in both 30 μm and 100 μm substrates

[0147]

(8) Evaluation of peeling

1. Mechanical peeling method at room temperature

A dicing tape was attached to the silicon substrate of the glass substrate-laminated silicon substrate or the film-laminated silicon substrate back ground as described above using a dicing frame, the dicing tape surface was set on a suction pad by vacuum suction, and then one point of the glass substrate or the film was lifted with a pincette at room temperature to peel off the glass substrate.

[0148]

2. Solvent peeling method at room temperature

A glass substrate-laminated silicon substrate was

produced using the above 8-inch alkali-free glass substrate provided with holes for solvent passage. Then, the substrate was immersed in the rework solvent obtained in Manufacturing Example 97 under the condition of 23°C for 10 minutes, and then the substrate was peeled off with bare hands. The film-laminated silicon substrate was not subjected to solvent peeling at room temperature.

[0149]

The evaluation criteria for peeling evaluation are as follows.

Glass substrate-laminated silicon substrate

A: Successfully peeled off in both 1. and 2.

B1: Successfully peeled off only in 1. Mechanical peeling method at room temperature.

B2: Successfully peeled off only in 2. Solvent peeling method at room temperature.

C: Not successfully peeled off in both 1. and 2.

Film laminated-silicon substrate

a: Successfully peeled off in Mechanical peeling method at room temperature.

c: Not successfully peeled off.

[0150]

(9) Rework evaluation

The resin layer attached to the silicon substrate peeled off as described above was reworked under the

conditions of 23°C for 10 minutes with the rework solvent obtained in Manufacturing Example 97, and the solubility was observed with the naked eye. The evaluation criteria are as follows.

A: No residue

B: Dissolved, but a residue remained on the substrate.

C: Not dissolved.

[0151]

(10) Measurement of average molecular weight of polysiloxane diamine and calculation of numerical value of n

Polysiloxane diamine (5 g) as a sample was taken in a beaker, and 50 mL of a 1 : 1 mixed solution of IPA and toluene was added to the beaker to dissolve the polysiloxane diamine. Then, using an automatic potentiometric titrator AT-610 manufactured by Kyoto Electronics Manufacturing Co., Ltd., a 0.1 N aqueous hydrochloric acid solution was added dropwise with stirring to the resulting solution, and the amount of the aqueous solution added until the neutralization point was determined. The average molecular weight was calculated from the amount of the added 0.1 N aqueous hydrochloric acid solution according to the following formula (9).

$$2 \times [10 \times 36.5 \times (\text{amount of added aqueous solution (g)})] / 5 = \text{average molecular weight (9)}$$

Then, the molecular weights of the polysiloxane diamine used were calculated from its chemical structural formula for the cases of $n = 1$ and $n = 10$, and a relationship between the value of n and the molecular weight was obtained as a relational expression of a linear function. The average value of n was determined by applying the average molecular weights to the relational expression.

[0152]

Names of abbreviations of acid dianhydrides, diamines, fillers, and solvents shown in the following manufacturing examples are as follows.

ODPA: 3,3',4,4'-diphenyl ether tetracarboxylic dianhydride

APPS1: α,ω -bis(3-aminopropyl)polydimethylsiloxane
(average molecular weight: 860, $n = 9$ in formula (1))

APPS2: α,ω -bis(3-aminopropyl)polydimethylsiloxane
(average molecular weight: 1600, $n = 19$ in formula (1))

APPS3: α,ω -bis(3-aminopropyl)polydimethylsiloxane
(average molecular weight: 4400, $n = 57$ in formula (1))

APB: 1,3-bis(3-aminophenoxy)benzene

FDA: 9,9-bis(3-amino-4-hydroxyphenyl)fluorene

BAFL: 9,9-bis(4-aminophenyl)fluorene

PG-100: fluorene group-containing epoxy resin
(manufactured by Osaka Gas Chemicals Co., Ltd.)

CG-500: fluorene group-containing epoxy resin
(manufactured by Osaka Gas Chemicals Co., Ltd.)

EG-200: fluorene group-containing epoxy resin
(manufactured by Osaka Gas Chemicals Co., Ltd.)

EG-280: fluorene group-containing epoxy resin
(manufactured by Osaka Gas Chemicals Co., Ltd.)

CG-400: fluorene group-containing epoxy resin
(manufactured by Osaka Gas Chemicals Co., Ltd.)

CS-500: fluorene group-containing episulfide resin
(manufactured by Osaka Gas Chemicals Co., Ltd.)

EA-0300: fluorene group-containing acrylic resin
(manufactured by Osaka Gas Chemicals Co., Ltd.)

JER828: 2,2-bis(4-glycidyoxyphenyl)propane
(manufactured by Mitsubishi Chemical Corporation)

MEK-ST-40: Organic solvent-dispersed silica (solvent:
MEK, silica: 40 wt%) (manufactured by Nissan Chemical
Industries, Ltd.)

DMM: dipropylene glycol dimethyl ether
[0153]

Synthesis Example 1 (Polymerization of polyamic acid)

Into a reaction kettle equipped with a thermometer, a
dry nitrogen inlet, a heating/cooling unit that operates
with warm water/cooling water, and a stirrer, 602.0 g (0.7
mol) of APPS1, 43.8 g (0.15 mol) of APB, and 57.1g (0.15
mol) of FDA were charged together with 1013.1 g of DMM, and

dissolved. Then, to the resulting solution, 310.2 g (1 mol) of ODPA was added, and the resulting mixture was reacted at room temperature for 1 hour and then at 60°C for 5 hours to give a 50% by mass polyamic acid solution PA1.
[0154]

Synthesis Examples 2 to 6 (Polymerization of polyamic acid)

A 50% by mass polyamic acid solution (PA2 to PA5) was obtained in the same manner as in Manufacturing Example 1 except that the type and the charged amount of acid dianhydride and diamine were changed as shown in Table 1.

[0155]

[Table 1]

Upper row: ratio (mol%)/lower row: content (g) Resin concentration: 50 wt%

		Acid dianhydride	Diamine					Solvent (g)
			Siloxane		Aromatic			
		ODPA	APPS1	APPS2	APB	FDA	BAFL	DMM (SP value: 7.8)
Synthesis Example 1	PA1	100	70		15	15		
		310.2	602.0		43.8	57.1		
Synthesis Example 2	PA2	100	80		10	10		1065.4
		310.2	688.0		29.2	38.0		
Synthesis Example 3	PA3	100		80	10	10		1657.4
		310.2		1280.0	29.2	38.0		
Synthesis Example 4	PA4	100	60		25	15		956.3
		310.2	516.0		73.0	57.1		
Synthesis Example 5	PA5	100	50		35	15		899.6
		310.2	430.0		102.3	57.1		
Synthesis Example 6	PA6	100	70		15		15	1008.3
		310.2	602.0		43.8		52.3	

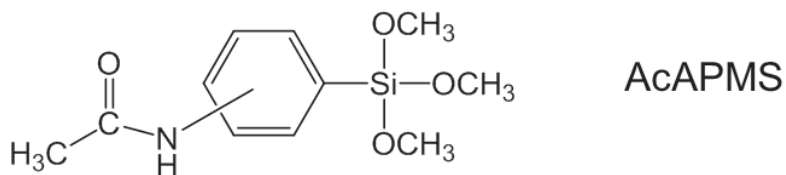
[0156]

Synthesis Example 7

Into a 500-ml flask, 500 g of hexane was charged, and 21.33 g (0.1 mol) of aminophenyltrimethoxysilane (a mixture of 3-aminophenyltrimethoxysilane and 4-aminophenyltrimethoxysilane at a weight ratio of 6 : 4) was added to the flask. Then, 10.21 g (0.1 mol) of acetic anhydride was added dropwise slowly, and the resulting mixture was reacted at room temperature for 3 hours. The precipitate was filtered off and dried, and the resulting compound was designated as AcAPMS. The structure of AcAPMS is shown below.

[0157]

[Chemical Formula 16]



[0158]

Manufacturing Example 1 (Adjustment of resin composition)

To a reaction kettle equipped with a stirrer, 200.0 g of the polyamic acid solution (PA1) obtained in Synthesis Example 1, 10.0 g of CG500, an epoxy resin, and 12.0 g of MEK-ST-40, a filler solution were charged together and stirred for 2 hours at room temperature to give a resin

composition (AH1).

[0159]

Manufacturing Examples 2 to 32 (Adjustment of
resin composition)

Resin compositions (AH2 to AH32) were obtained in the same manner as in Manufacturing Example 1 except that the type and the charged amount of the polyimide resin (a), the epoxy resin (b), the siloxane polymer (c), the silane coupling agent (d), and the filler (e) were changed as shown in Table 2.

[0160]

[Table 2-1]

		(a) Polyimide resin Concentration: 50 wt%		(b) Crosslinker including fluorene group			(c) Siloxane polymer		(d) Silane coupling agent		(e) Inorganic particles Concentration: 40 wt%		Glass transition temperature (°C)
		Type	Charged amount (g)	Type	5% Weight loss temperature (°C)	Charged amount (g)	Type	Charged amount (g)	Type	Charged amount (g)	Type	Charged amount (g)	
Manufacturing Example 1	AH1	PA1	200.0	CG500	400	0.1					MEK-ST-40	20.0	60
Manufacturing Example 2	AH2	PA1	200.0	CG500	400	1.0					MEK-ST-40	20.0	75
Manufacturing Example 3	AH3	PA1	200.0	CG500	400	10.0					MEK-ST-40	20.0	81
Manufacturing Example 4	AH4	PA1	200.0	CG500	400	20.0					MEK-ST-40	20.0	85
Manufacturing Example 5	AH5	PA1	200.0	CG500	400	40.0					MEK-ST-40	20.0	87
Manufacturing Example 6	AH6	PA2	200.0	CG500	400	10.0					MEK-ST-40	20.0	54
Manufacturing Example 7	AH7	PA3	200.0	CG500	400	10.0							33
Manufacturing Example 8	AH8	PA3	200.0	CG500	400	10.0					MEK-ST-40	1.0	34
Manufacturing Example 9	AH9	PA3	200.0	CG500	400	10.0					MEK-ST-40	10.0	34
Manufacturing Example 10	AH10	PA3	200.0	CG500	400	10.0					MEK-ST-40	20.0	36
Manufacturing Example 11	AH11	PA4	200.0	CG500	400	10.0					MEK-ST-40	20.0	109
Manufacturing Example 12	AH12	PA5	200.0	CG500	400	10.0					MEK-ST-40	20.0	122
Manufacturing Example 13	AH13	PA6	200.0	CG500	400	10.0					MEK-ST-40	20.0	85
Manufacturing Example 14	AH14	PA1	200.0	EG200	386	10.0					MEK-ST-40	20.0	78
Manufacturing Example 15	AH15	PA1	200.0	EG280	368	10.0					MEK-ST-40	20.0	76
Manufacturing Example 16	AH16	PA1	200.0	PG100	354	10.0					MEK-ST-40	20.0	75

[0161]
[Table 2-2]

	(a) Polyimide resin Concentration: 50 wt%		(b) Crosslinker including fluorene group			(c) Siloxane polymer		(d) Silane coupling agent		(e) Inorganic particles Concentration: 40 wt%		Glass transition temperature (°C)
	Type	Charged amount (g)	Type	5% Weight loss temperature (°C)	Charged amount (g)	Type	Charged amount (g)	Type	Charged amount (g)	Type	Charged amount (g)	
Manufacturing Example 17	AH17	PA1	CG400	326	10.0					MEK-ST-40	20.0	73
Manufacturing Example 18	AH18	PA1	CS500	282	10.0					MEK-ST-40	20.0	73
Manufacturing Example 19	AH19	PA1	EA0300	395	10.0					MEK-ST-40	20.0	70
Manufacturing Example 20	AH20	PA1	JER828	280	10.0					MEK-ST-40	20.0	69
Manufacturing Example 21	AH21	PA3	CG500	400	10.0					MEK-ST-40	20.0	34
Manufacturing Example 22	AH22	PA1	CG500	400	10.0	APPS3	0.001	AcAPMS	1.0	MEK-ST-40	20.0	78
Manufacturing Example 23	AH23	PA1	CG500	400	10.0	APPS3	0.01			MEK-ST-40	20.0	79
Manufacturing Example 24	AH24	PA1	CG500	400	10.0	APPS3	1.0			MEK-ST-40	20.0	79
Manufacturing Example 25	AH25	PA1	CG500	400	10.0	APPS3	15.0			MEK-ST-40	20.0	80
Manufacturing Example 26	AH26	PA1	CG500	400	10.0	APPS3	30.0			MEK-ST-40	20.0	81
Manufacturing Example 27	AH27	PA3	CG500	400	10.0	APPS3	1.0	AcAPMS	0.001	MEK-ST-40	20.0	33
Manufacturing Example 28	AH28	PA3	CG500	400	10.0	APPS3	1.0	AcAPMS	0.01	MEK-ST-40	20.0	33
Manufacturing Example 29	AH29	PA3	CG500	400	10.0	APPS3	1.0	AcAPMS	1.0	MEK-ST-40	20.0	33
Manufacturing Example 30	AH30	PA3	CG500	400	10.0	APPS3	1.0	AcAPMS	15.0	MEK-ST-40	20.0	31
Manufacturing Example 31	AH31	PA1								MEK-ST-40	20.0	55
Manufacturing Example 32	AH32	PA3								MEK-ST-40	20.0	21

[0162]

Manufacturing Example 33

The resin composition (AH1) obtained in Manufacturing Example 1 was applied to a support film layer SR7 (thickness: 75 μm , a polyester film, manufactured by OHTSUKI INDUSTRIAL CO., LTD.) with a bar coater, and dried at 100°C for 10 minutes. Then, SR7 (manufactured by OHTSUKI INDUSTRIAL CO., LTD.) was laminated thereon as a protective film layer to give a laminated film (S1) having a resin layer thickness of 20 μm .

[0163]

Manufacturing Examples 34 to 64

Laminated films (S2 to S32) were obtained in the same manner as in Manufacturing Example 33 except that the type of the resin composition was changed as shown in Table 3.

[0164]

[Table 3]

	Laminated film	Resin composition	Support film	Protective film
Manufacturing Example 33	S1	AH1	SR7 Polyester film	SR7 Polyester film
Manufacturing Example 34	S2	AH2		
Manufacturing Example 35	S3	AH3		
Manufacturing Example 36	S4	AH4		
Manufacturing Example 37	S5	AH5		
Manufacturing Example 38	S6	AH6		
Manufacturing Example 39	S7	AH7		
Manufacturing Example 40	S8	AH8		
Manufacturing Example 41	S9	AH9		
Manufacturing Example 42	S10	AH10		
Manufacturing Example 43	S11	AH11		
Manufacturing Example 44	S12	AH12		
Manufacturing Example 45	S13	AH13		
Manufacturing Example 46	S14	AH14		
Manufacturing Example 47	S15	AH15		
Manufacturing Example 48	S16	AH16		
Manufacturing Example 49	S17	AH17		
Manufacturing Example 50	S18	AH18		
Manufacturing Example 51	S19	AH19		
Manufacturing Example 52	S20	AH20		
Manufacturing Example 53	S21	AH21		
Manufacturing Example 54	S22	AH22		
Manufacturing Example 55	S23	AH23		
Manufacturing Example 56	S24	AH24		
Manufacturing Example 57	S25	AH25		
Manufacturing Example 58	S26	AH26		
Manufacturing Example 59	S27	AH27		
Manufacturing Example 60	S28	AH28		
Manufacturing Example 61	S29	AH29		
Manufacturing Example 62	S30	AH30		
Manufacturing Example 63	S31	AH31		
Manufacturing Example 64	S32	AH32		

[0165]

Manufacturing Example 65

The resin composition (AH1) obtained in Manufacturing Example 1 was applied to a support film layer 140EN-Y (thickness: 35 μm , 1% weight loss temperature: higher than 450°C, melting point: higher than 300°C, linear expansion coefficient: 5 ppm/°C, a polyimide film, manufactured by DUPONT-TORAY CO., LTD.) with a bar coater, and dried at 100°C for 10 minutes, and then heat-treated at 200°C for 3 minutes to be cured. SR7 (manufactured by OHTSUKI INDUSTRIAL CO., LTD.) was laminated thereon as a protective film layer to give a laminated film (S33) having a resin layer thickness of 20 μm .

Manufacturing Examples 66 to 96

Laminated films (S34 to S64) were obtained in the same manner as in Manufacturing Example 65 except that the type of the resin composition was changed as shown in Table 4.

[0166]

[Table 4]

	Laminated film	Resin composition	Support film	Protective film
Manufacturing Example 65	S33	AH1	140EN-Y Polyimide film	SR7 Polyester film
Manufacturing Example 66	S34	AH2		
Manufacturing Example 67	S35	AH3		
Manufacturing Example 68	S36	AH4		
Manufacturing Example 69	S37	AH5		
Manufacturing Example 70	S38	AH6		
Manufacturing Example 71	S39	AH7		
Manufacturing Example 72	S40	AH8		
Manufacturing Example 73	S41	AH9		
Manufacturing Example 74	S42	AH10		
Manufacturing Example 75	S43	AH11		
Manufacturing Example 76	S44	AH12		
Manufacturing Example 77	S45	AH13		
Manufacturing Example 78	S46	AH14		
Manufacturing Example 79	S47	AH15		
Manufacturing Example 80	S48	AH16		
Manufacturing Example 81	S49	AH17		
Manufacturing Example 82	S50	AH18		
Manufacturing Example 83	S51	AH19		
Manufacturing Example 84	S52	AH20		
Manufacturing Example 85	S53	AH21		
Manufacturing Example 86	S54	AH22		
Manufacturing Example 87	S55	AH23		
Manufacturing Example 88	S56	AH24		
Manufacturing Example 89	S57	AH25		
Manufacturing Example 90	S58	AH26		
Manufacturing Example 91	S59	AH27		
Manufacturing Example 92	S60	AH28		
Manufacturing Example 93	S61	AH29		
Manufacturing Example 94	S62	AH30		
Manufacturing Example 95	S63	AH31		
Manufacturing Example 96	S64	AH32		

[0167]

Manufacturing Example 97 (Adjustment of rework

solvent)

Into a reaction kettle equipped with a stirrer, 30 g of monoethanolamine, 30 g of DMM, and 30 g of N-methyl-2-pyrrolidone were charged, and stirred at room temperature for 1 hour to give a rework solvent.

[0168]

Example 1

To an 8-inch silicon substrate (manufactured by Shin-Etsu Chemical Co., Ltd.) having a thickness of 750 μm , the resin composition (AH1) obtained in Manufacturing Example 1 was applied using a spin coater with adjusting the rotation speed so that the thickness after drying was 20 μm , heat-treated at 120°C for 10 minutes to be dried, and then heat-treated at 200°C for 3 minutes to be cured, whereby a resin composition-laminated silicon substrate was obtained.

[0169]

An 8-inch alkali-free glass substrate (manufactured by Corning Incorporated) having a thickness of 0.7 mm was placed over the resin composition-laminated silicon substrate produced by the above method, and the substrates were pressure-bonded at a pressure of 0.5 MPa for 5 minutes using a hot press with the upper plate and the lower plate each set at 180°C to give a glass substrate-laminated silicon substrate. Using the obtained glass substrate-laminated silicon substrate, adhesiveness evaluation,

protrusion evaluation, heat resistance evaluation after adhesiveness evaluation, back grinding evaluation of the silicon substrate, heat resistance evaluation after back grinding evaluation, peeling evaluation, and rework evaluation were carried out, and the results are summarized in Table 5.

[0170]

Examples 2 to 30

A glass substrate-laminated silicon substrate was obtained in the same manner as in Example 1 except that the resin composition was changed as shown in Table 5.

[0171]

Using the obtained glass substrate-laminated silicon substrate, adhesiveness evaluation, protrusion evaluation, heat resistance evaluation after adhesiveness evaluation, back grinding evaluation of the silicon substrate, heat resistance evaluation after back grinding evaluation, peeling evaluation, and rework evaluation were carried out, and the results are summarized in Table 5.

[0172]

Comparative Examples 1 and 2

A glass substrate-laminated silicon substrate was obtained in the same manner as in Example 1 except that the resin composition was changed as shown in Table 5.

[0173]

Using the obtained glass substrate-laminated silicon substrate, adhesiveness evaluation, protrusion evaluation, heat resistance evaluation after adhesiveness evaluation, back grinding evaluation of the silicon substrate, heat resistance evaluation after back grinding evaluation, peeling evaluation, and rework evaluation were carried out, and the results are summarized in Table 5.

[0174]

[Table 5-1]

	Resin composition	Adhesiveness evaluation	Protrusion evaluation	Heat resistance evaluation after adhesiveness evaluation	Back grinding evaluation	Heat resistance evaluation after back grinding evaluation	Evaluation of peeling	Rework evaluation
Example 1	AH1	A	A	A	A	B	B2	A
Example 2	AH2	A	A	A	A	A	B2	A
Example 3	AH3	A	A	A	A	A	B2	A
Example 4	AH4	A	A	A	A	A	B2	A
Example 5	AH5	A	A	A	A	A	B2	B
Example 6	AH6	A	A	A	A	A	B2	A
Example 7	AH7	A	A	B	B	A	B2	A
Example 8	AH8	A	A	A	B	A	B2	A
Example 9	AH9	A	A	A	B	A	B2	A
Example 10	AH10	A	A	A	B	A	B2	A
Example 11	AH11	A	A	A	A	A	B2	A
Example 12	AH12	B	A	A	B	A	B2	A
Example 13	AH13	A	B	A	A	A	B2	A
Example 14	AH14	A	A	A	A	A	B2	A
Example 15	AH15	A	A	A	A	A	B2	A
Example 16	AH16	A	A	A	A	A	B2	A

[0175]

[Table 5-2]

	Resin composition	Adhesiveness evaluation	Protrusion evaluation	Heat resistance evaluation after adhesiveness evaluation	Back grinding evaluation	Heat resistance evaluation after back grinding evaluation	Evaluation of peeling	Rework evaluation
Example 17	AH17	A	A	A	A	A	B2	A
Example 18	AH18	A	A	A	A	A	B2	A
Example 19	AH19	A	A	A	A	A	B2	A
Example 20	AH20	A	A	A	A	B	B2	A
Example 21	AH21	A	A	A	A	A	B2	A
Example 22	AH22	A	A	A	A	A	B2	A
Example 23	AH23	A	A	A	A	A	A	A
Example 24	AH24	A	A	A	A	A	A	A
Example 25	AH25	A	A	A	A	A	A	A
Example 26	AH26	B	A	A	B	A	A	A
Example 27	AH27	A	A	A	B	A	A	A
Example 28	AH28	A	A	A	A	A	A	A
Example 29	AH29	A	A	A	A	A	A	A
Example 30	AH30	A	A	A	A	A	A	A
Comparative Example 1	AH31	A	A	A	A	D	B2	A
Comparative Example 2	AH32	A	A	A	D	D	B2	A

[0176]

Example 31

The protective film layer of the laminated film (S1) obtained in Manufacturing Example 33 was peeled off, and then the laminated film was laminated on an 8-inch silicon substrate (manufactured by Shin-Etsu Chemical Co., Ltd.) using a vacuum laminator VTM-200M (manufactured by Takatori Corporation) so that the resin layer would come into contact with the silicon substrate. The lamination conditions were as follows: a heater temperature of 100°C, a roll temperature of 100°C, a lamination speed of 5 mm/sec, a lamination roll pressure of 0.2 MPa, and a chamber pressure of 150 Pa. The support film layer of the obtained laminate was peeled off to give a resin composition-laminated silicon substrate. The resin composition-laminated silicon substrate was cured by heat treatment at 200°C for 3 minutes, and then the resin composition-laminated silicon substrate and another 8-inch alkali-free glass substrate (manufactured by Corning Incorporated) were stacked together so that the 8-inch alkali-free glass substrate was in contact with the resin layer, and the substrates were pressure-bonded at a pressure of 0.5 MPa for 5 minutes using a hot press with the upper plate and the lower plate each set at 180°C to give a glass substrate-laminated silicon substrate. Using

the obtained glass substrate-laminated silicon substrate, adhesiveness evaluation, protrusion evaluation, heat resistance evaluation after adhesiveness evaluation, back grinding evaluation of the silicon substrate, heat resistance evaluation after back grinding evaluation, peeling evaluation, and rework evaluation were carried out, and the results are summarized in Table 6.

[0177]

Examples 32 to 60

A glass substrate-laminated silicon substrate was obtained in the same manner as in Example 31 except that the laminated film was changed as shown in Table 6.

[0178]

Using the obtained glass substrate-laminated silicon substrate, adhesiveness evaluation, protrusion evaluation, heat resistance evaluation after adhesiveness evaluation, back grinding evaluation of the silicon substrate, heat resistance evaluation after back grinding evaluation, peeling evaluation, and rework evaluation were carried out, and the results are summarized in Table 6.

[0179]

Comparative Examples 3 and 4

A glass substrate-laminated silicon substrate was obtained in the same manner as in Example 31 except that the laminated film was changed as shown in Table 6.

[0180]

Using the obtained glass substrate-laminated silicon substrate, adhesiveness evaluation, protrusion evaluation, heat resistance evaluation after adhesiveness evaluation, back grinding evaluation of the silicon substrate, heat resistance evaluation after back grinding evaluation, peeling evaluation, and rework evaluation were carried out, and the results are summarized in Table 6.

[0181]

[Table 6-1]

	Laminated film	Resin composition	Adhesiveness evaluation	Protrusion evaluation	Heat resistance evaluation after adhesiveness evaluation	Back grinding evaluation	Heat resistance evaluation after back grinding evaluation	Evaluation of peeling	Rework evaluation
Example 31	S1	AH1	A	A	A	A	B	B2	A
Example 32	S2	AH2	A	A	A	A	A	B2	A
Example 33	S3	AH3	A	A	A	A	A	B2	A
Example 34	S4	AH4	A	A	A	A	A	B2	A
Example 35	S5	AH5	A	A	A	A	A	B2	B
Example 36	S6	AH6	A	A	A	A	A	B2	A
Example 37	S7	AH7	A	A	B	B	A	B2	A
Example 38	S8	AH8	A	A	A	B	A	B2	A
Example 39	S9	AH9	A	A	A	B	A	B2	A
Example 40	S10	AH10	A	A	A	B	A	B2	A
Example 41	S11	AH11	A	A	A	A	A	B2	A
Example 42	S12	AH12	B	A	A	B	A	B2	A
Example 43	S13	AH13	A	B	A	A	A	B2	A
Example 44	S14	AH14	A	A	A	A	A	B2	A
Example 45	S15	AH15	A	A	A	A	A	B2	A
Example 46	S16	AH16	A	A	A	A	A	B2	A

[0182]

[Table 6-2]

	Laminated film	Resin composition	Adhesiveness evaluation	Protrusion evaluation	Heat resistance evaluation after adhesiveness evaluation	Back grinding evaluation	Heat resistance evaluation after back grinding evaluation	Evaluation of peeling	Rework evaluation
Example 47	S17	AH17	A	A	A	A	A	B2	A
Example 48	S18	AH18	A	A	A	A	A	B2	A
Example 49	S19	AH19	A	A	A	A	A	B2	A
Example 50	S20	AH20	A	A	A	A	B	B2	A
Example 51	S21	AH21	A	A	A	A	A	B2	A
Example 52	S22	AH22	A	A	A	A	A	B2	A
Example 53	S23	AH23	A	A	A	A	A	A	A
Example 54	S24	AH24	A	A	A	A	A	A	A
Example 55	S25	AH25	A	A	A	A	A	A	A
Example 56	S26	AH26	B	A	A	B	A	A	A
Example 57	S27	AH27	A	A	A	B	A	A	A
Example 58	S28	AH28	A	A	A	A	A	A	A
Example 59	S29	AH29	A	A	A	A	A	A	A
Example 60	S30	AH30	A	A	A	A	A	A	A
Comparative Example 3	S31	AH31	A	A	A	A	D	B2	A
Comparative Example 4	S32	AH32	A	A	A	D	D	B2	A

[0183]

Example 61

The protective film layer of the laminated film (S33) obtained in Manufacturing Example 65 was peeled off, and then the laminated film was laminated on an 8-inch silicon substrate (manufactured by Shin-Etsu Chemical Co., Ltd.) using a vacuum laminator VTM-200M (manufactured by Takatori Corporation) so that the resin layer would come into contact with the silicon substrate. The lamination conditions were as follows: a heater temperature of 100°C, a roll temperature of 100°C, a lamination speed of 5 mm/sec, a lamination roll pressure of 0.2 MPa, and a chamber pressure of 150 Pa. The obtained laminated substrate was pressure-bonded for 5 minutes at 0.5 MPa using a hot press with the upper plate and the lower plate each set at 180°C to give a film-laminated silicon substrate. Using the obtained film-laminated silicon substrate, adhesiveness evaluation, protrusion evaluation, heat resistance evaluation after adhesiveness evaluation, back grinding evaluation of the silicon substrate, heat resistance evaluation after back grinding evaluation, peeling evaluation, and rework evaluation were carried out, and the results are summarized in Table 7.

[0184]

Examples 62 to 90

A film laminated-silicon substrate was obtained in the same manner as in Example 61 except that the laminated film was changed as shown in Table 7.

[0185]

Using the obtained film-laminated silicon substrate, adhesiveness evaluation, protrusion evaluation, heat resistance evaluation after adhesiveness evaluation, back grinding evaluation of the silicon substrate, heat resistance evaluation after back grinding evaluation, peeling evaluation, and rework evaluation were carried out, and the results are summarized in Table 7.

Comparative Examples 5 and 6

A film laminated-silicon substrate was obtained in the same manner as in Example 61 except that the laminated film was changed as shown in Table 7.

[0186]

Using the obtained film-laminated silicon substrate, adhesiveness evaluation, protrusion evaluation, heat resistance evaluation after adhesiveness evaluation, back grinding evaluation of the silicon substrate, heat resistance evaluation after back grinding evaluation, peeling evaluation, and rework evaluation were carried out, and the results are summarized in Table 7.

[0187]

[Table 7-1]

	Lamina ted film	Resin composi tion	Adhesive ness evalua tion	Protru sion evalua tion	Heat resistan ce evalua tion after adhesive ness evalua tion	Back grindi ng evalua tion	Heat resist ance evalua tion after back grindi ng evalua tion	Evalua tion of peelin g	Rework evalua tion
Examp le 61	S33	AH1	A	A	A	A	B	c	-
Examp le 62	S34	AH2	A	A	A	A	A	c	-
Examp le 63	S35	AH3	A	A	A	A	A	c	-
Examp le 64	S36	AH4	A	A	A	A	A	c	-
Examp le 65	S37	AH5	A	A	A	A	A	c	-
Examp le 66	S38	AH6	A	A	A	A	A	c	-
Examp le 67	S39	AH7	A	A	B	B	A	c	-
Examp le 68	S40	AH8	A	A	A	B	A	c	-
Examp le 69	S41	AH9	A	A	A	B	A	c	-
Examp le 70	S42	AH10	A	A	A	B	A	c	-
Examp le 71	S43	AH11	A	A	A	A	A	c	-
Examp le 72	S44	AH12	B	A	A	B	A	c	-
Examp le 73	S45	AH13	A	B	A	A	A	c	-
Examp le 74	S46	AH14	A	A	A	A	A	c	-
Examp le 75	S47	AH15	A	A	A	A	A	c	-
Examp le 76	S48	AH16	A	A	A	A	A	c	-

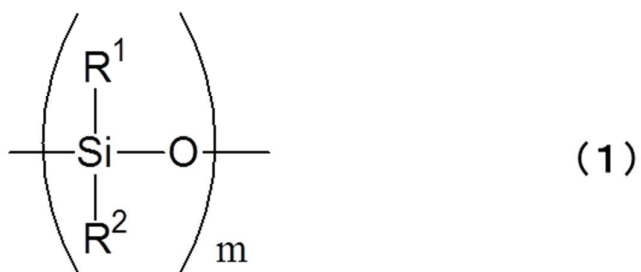
[0188]

[Table 7-2]

	Lamina ted film	Resin composi tion	Adhesive ness evalua tion	Protru sion evalua tion	Heat resistan ce evalua tion after adhesive ness evalua tion	Back grindi ng evalua tion	Heat resista nce evalua tion after back grindin g evalua tion	Evalua tion of peelin g	Rework evalua tion
Example 77	S49	AH17	A	A	A	A	A	c	-
Example 78	S50	AH18	A	A	A	A	A	c	-
Example 79	S51	AH19	A	A	A	A	A	c	-
Example 80	S52	AH20	A	A	A	A	B	c	-
Example 81	S53	AH21	A	A	A	A	A	c	-
Example 82	S54	AH22	A	A	A	A	A	c	-
Example 83	S55	AH23	A	A	A	A	A	a	A
Example 84	S56	AH24	A	A	A	A	A	a	A
Example 85	S57	AH25	A	A	A	A	A	a	A
Example 86	S58	AH26	B	A	A	B	A	a	A
Example 87	S59	AH27	A	A	A	B	A	a	A
Example 88	S60	AH28	A	A	A	A	A	a	A
Example 89	S61	AH29	A	A	A	A	A	a	A
Example 90	S62	AH30	A	A	A	A	A	a	A
Compara tive Example 5	S63	AH31	A	A	A	A	D	c	-
Compara tive Example 6	S64	AH32	A	A	A	D	D	c	-

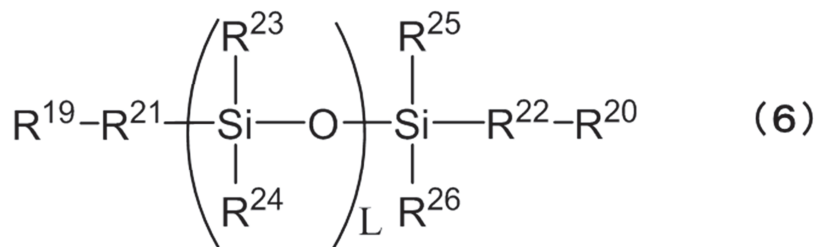
CLAIMS

1. A resin composition comprising at least (a) a polyimide resin having a structure represented by the general formula (1) and (b) a crosslinker including a fluorene group:



wherein m is a natural number of 1 or more and 100 or less, R¹ and R² may be same or different and each represent an alkyl group having 1 to 30 carbon atoms, a phenyl group or a phenoxy group, and

wherein the composition further comprises (c) a siloxane polymer represented by the general formula (6):



wherein L is an integer of 10 or more and 100 or less, R¹⁹ and R²⁰ may be same or different and each represent a monovalent organic group having 1 to 30 carbon atoms and 0 to 3 nitrogen atoms, R²¹ and R²² may be same or different and each represent an alkylene group having 1 to 30 carbon atoms or a phenylene group, R²³ to R²⁶ may be same or different and each

represent an alkyl group having 1 to 30 carbon atoms, an alkoxy group, a phenyl group, or a phenoxy group, and an alkoxy group having 1 to 30 carbon atoms of R^{23} to R^{26} does not include a polyoxyalkylene structure.

2. The resin composition according to claim 1, wherein the crosslinker (b) including a fluorene group is an epoxy resin including a fluorene group.

3. The resin composition according to claim 1 or 2, wherein the crosslinker (b) including a fluorene group has a 5% weight loss temperature of 250°C or more and 400°C or less.

4. The resin composition according to any of claims 1 to 3, having a content of the crosslinker (b) including a fluorene group of 0.1% by mass or more and 40% by mass or less relative to 100% by mass of the polyimide resin (a).

5. The resin composition according to any of claims 1 to 4, wherein R^{19} and R^{20} of the siloxane polymer (c) represented by the general formula (6) are amino groups.

6. The resin composition according to any of claims 1 to 5, having a content of the siloxane polymer (c) represented by the general formula (6) of 0.01% by mass or more and 30% by mass or less relative to 100% by mass of the polyimide resin

(a) having a structure represented by the general formula (1).

7. The resin composition according to any of claims 1 to 6, further comprising (d) a silane coupling agent.

8. The resin composition according to claim 7, having a content of the silane coupling agent (d) of 0.01% by mass or more and 30% by mass or less relative to 100% by mass of the polyimide resin (a) having a structure represented by the general formula (1).

9. The resin composition according to any of claims 1 to 8, further comprising (e) inorganic fine particles.

10. The resin composition according to claim 9, having a content of the inorganic fine particles (e) of 0.1% by mass or more and 40% by mass or less relative to 100% by mass of the polyimide resin (a).

11. The resin composition according to any of claims 1 to 10, having a glass transition temperature after curing of 30°C or more and 150°C or less.

12. A resin layer comprising a coating film of the resin composition according to any of claims 1 to 11.

13. A permanent adhesive comprising the resin composition according to any of claims 1 to 11.
14. An adhesive for temporary bonding comprising the resin composition according to any of claims 1 to 11.
15. The adhesive for temporary bonding according to claim 14, for bonding an electronic circuit formation substrate or a semiconductor circuit formation substrate and a support substrate together.
16. The adhesive for temporary bonding according to claim 15, wherein the support substrate is any of a silicon substrate, a glass substrate, and a film.
17. A method for manufacturing an electronic component or a semiconductor device using the resin composition according to any of claims 1 to 11.
18. A laminated film comprising a heat-resistant insulating film and the resin composition according to any of claims 1 to 11 laminated on at least one surface of the heat-resistant insulating film.
19. The laminated film according to claim 18, wherein the

heat-resistant insulating film has a release-treated surface.

20. The laminated film according to claim 18 or 19, further comprising a film having a release-treated surface laminated on a surface of the resin composition laminated on the heat-resistant insulating film.

21. A method for manufacturing an electronic component or a semiconductor device using the laminated film according to any of claims 18 to 20.

22. A processed wafer comprising an electronic circuit formation substrate or a semiconductor circuit formation substrate and a support substrate bonded together with at least the resin layer according to claim 12 or the laminated film according to any of claims 18 to 20 interposed between the electronic circuit formation substrate or the semiconductor circuit formation substrate and the support substrate.

23. The processed wafer according to claim 22, wherein the electronic circuit formation substrate or the semiconductor circuit formation substrate and the support substrate are bonded together with only the resin layer according to claim 12 or only the laminated film according to any of claims 18 to 20 interposed between the electronic circuit formation

substrate or the semiconductor circuit formation substrate and the support substrate.

24. The processed wafer according to claim 22 or 23, wherein the electronic circuit formation substrate or the semiconductor circuit formation substrate has a thickness of 1 μm or more and 100 μm or less.

25. A method for manufacturing an electronic component or a semiconductor device using the processed wafer according to any of claims 22 to 24, the method comprising at least either of the steps of:

heat-treating the electronic circuit formation substrate or the semiconductor circuit formation substrate in the processed wafer;

peeling the electronic circuit formation substrate or the semiconductor circuit formation substrate in the processed wafer from the support substrate; and

washing the resin layer attached to the electronic circuit formation substrate or the semiconductor circuit formation substrate peeled from the processed wafer or the resin layer attached to the support substrate in the processed wafer with a solvent.

26. The method for manufacturing an electronic component or a semiconductor device according to claim 25, comprising the

step of heat-treating the electronic circuit formation substrate or the semiconductor circuit formation substrate in the processed wafer at a temperature of 230°C or more and 450°C or less.