

KIT, DETERGENT COMPOSITION, AND METHOD FOR MANUFACTURING SEMICONDUCTOR ELEMENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to kit with a temporary bonding material including a silicone compound and a detergent composition for removing the temporary bonding material; a detergent composition; and a method for manufacturing a semiconductor element.

2. Description of the Related Art

[0002] A detergent composition for removing a temporary bonding material has hitherto been studied. For example, in JP2016-011361A, a peeling composition for removing a bonding material including a styrene-based hydrogenated elastomer, which includes at least one of a cyclic terpene-based solvent, a nonionic surfactant, or a silicon-based surfactant is disclosed.

SUMMARY OF THE INVENTION

[0004] As a result of the studies on the peeling composition described in JP2016-011361A, it was found that the peeling composition has an effect on the peeling of a bonding material including a styrene-based hydrogenated elastomer, but cannot remove a residue derived from a release agent sufficiently. Further, the present inventors have studied thereon, and thus, it was found that a residue derived from a silicone compound particularly easily remains.

The present invention is made to solve such problems, and thus, has an object to provide a kit including a temporary bonding material and a detergent composition, the kit being capable of suitably removing a residue derived from the temporary bonding material including a silicone compound; a detergent composition; and a method for manufacturing a semiconductor element.

[0005] With regard to the object, the present inventors have conducted extensive studies, and as a result, they have found that the object can be accomplished by removing a temporary bonding material including a silicone compound with a detergent composition including an acid or base and an organic solvent. Specifically, according to <1>, and preferably according to <2> to <30>, the object was accomplished.

<1> A kit comprising:

a detergent composition including an acid or base and an organic solvent; and
a temporary bonding material including a silicone compound,

in which a value represented by Formula (a) of the acid is 0 to 10 and a value

represented by Formula (b) of the base is -5 to 0;

Formula (a) ClogP-pKa

Formula (b) ClogP-pKb

in Formulae (a) and (b), ClogP represents a value represented by a base-10 logarithm logP of P which is a 1-octanol/water partition coefficient representing a ratio of an equilibrium concentration in 1-octanol and water, pKa represents an acid dissociation constant, and pKb represents a base dissociation constant.

<2> The kit as described in <1>,

in which the silicone compound is a silicone oil.

<3> The kit as described in <1> or <2>,

in which the silicone compound includes a polyether-modified silicone.

<4> The kit as described in <3>,

in which a ratio represented by Formula (A) of the polyether-modified silicone is 80% or more;

Formula (A) $\{(MO+EO)/AO\} \times 100$

in Formula (A), MO is % by mole of methylene oxide included in the polyether structure in the polyether-modified silicone, EO is % by mole of ethylene oxide included in the polyether structure in the polyether-modified silicone, and AO is % by mole of alkylene oxide included in the polyether structure in the polyether-modified silicone.

<5> The kit as described in any one of <1> to <4>,

in which a content of the silicone compound in the temporary bonding material is 0.001% to 1.0% by mass.

<6> The kit as described in any one of <1> to <5>,

in which the temporary bonding material includes an elastomer.

<7> The kit as described in <6>,

in which the elastomer is a polystyrene-based elastomer.

<8> The kit as described in <6> or <7>,

in which a solubility of the elastomer in the organic solvent at 25°C is 18% to 40% by mass.

<9> The kit as described in any one of <1> to <8>,

in which the organic solvent is at least one selected from an aromatic compound, a saturated alicyclic compound, a cyclic ketone, or a cyclic terpene.

<10> The kit as described in any one of <1> to <9>,

in which the detergent composition includes an acid and the acid is at least one selected from a phosphoric acid, a phosphonic acid, a phosphinic acid, a sulfonic acid, or a carboxylic acid.

<11> The kit as described in any one of <1> to <9>,

in which the detergent composition includes a base and the base is at least one selected from an aliphatic amine, an aromatic amine, or a heterocyclic amine.

<12> The kit as described in any one of <1> to <11>,

in which the mass ratio of the acid or base to the organic solvent is 0.0001:99.9999 to 50:50.

<13> A detergent composition for a temporary bonding material including a silicone compound, comprising:

an acid or base; and

an organic solvent,

in which a value represented by Formula (a) of the acid is 0 to 10 and a value represented by Formula (b) of the base is -5 to 0;

Formula (a) ClogP-pK_a

Formula (b) ClogP-pK_b

in Formulae (a) and (b), ClogP represents a value represented by a base-10 logarithm $\log P$ of P which is a 1-octanol/water partition coefficient representing a ratio of an equilibrium concentration in 1-octanol and water, pK_a represents an acid dissociation constant, and pK_b represents a base dissociation constant.

<14> The detergent composition as described in <13>,

in which the organic solvent is at least one selected from an aromatic compound, a saturated alicyclic compound, a cyclic ketone, or a cyclic terpene.

<15> The detergent composition as described in <13> or <14>,

in which the detergent composition includes an acid and the acid is at least one selected from a phosphoric acid, a phosphonic acid, a phosphinic acid, a sulfonic acid, or a carboxylic acid.

<16> The detergent composition as described in <13> or <14>,

in which the detergent composition includes a base and the base is at least one selected from an aliphatic amine, an aromatic amine, or a heterocyclic amine.

<17> The detergent composition as described in any one of <13> to <16>,

in which the mass ratio of the acid or base to the organic solvent is 0.0001:99.9999 to

50:50.

<18> The detergent composition as described in any one of <13> to <17>,

in which the silicone compound includes a polyether-modified silicone, a ratio represented by Formula (A) of the polyether-modified silicone is 80% or more, the content of the silicone compound in the temporary bonding material is 0.001% to 1.0% by mass, and the temporary bonding material includes a polystyrene-based elastomer;

Formula (A) $\{(MO+EO)/AO\} \times 100$

in Formula (A), MO is % by mole of methylene oxide included in the polyether structure in the polyether-modified silicone, EO is % by mole of ethylene oxide included in the polyether structure in the polyether-modified silicone, and AO is % by mole of alkylene oxide included in the polyether structure in the polyether-modified silicone.

<19> A method for manufacturing a semiconductor element, comprising removing a temporary bonding material including a silicone compound using a detergent composition including an acid or base and an organic solvent,

in which a value represented by Formula (a) of the acid is 0 to 10 and a value represented by Formula (b) of the base is -5 to 0;

Formula (a) ClogP-pKa

Formula (b) ClogP-pKb

in Formulae (a) and (b), ClogP represents a value represented by a base-10 logarithm $\log P$ of P which is a 1-octanol/water partition coefficient representing a ratio of an equilibrium concentration in 1-octanol and water, pKa represents an acid dissociation constant, and pKb represents a base dissociation constant.

<20> The method for manufacturing a semiconductor element as described in <19>,
in which the silicone compound is a silicone oil.

<21> The method for manufacturing a semiconductor element as described in <19>
or <20>,

in which the silicone compound includes a polyether-modified silicone.

<22> The method for manufacturing a semiconductor element as described in <21>,

in which a ratio represented by Formula (A) of the polyether-modified silicone is 80% or more;

Formula (A) $\{(MO+EO)/AO\} \times 100$

in Formula (A), MO is % by mole of methylene oxide included in the polyether structure in the polyether-modified silicone, EO is % by mole of ethylene oxide included in

the polyether structure in the polyether-modified silicone, and AO is % by mole of alkylene oxide included in the polyether structure in the polyether-modified silicone.

<23> The method for manufacturing a semiconductor element as described in any one of <19> to <22>,

in which a content of the silicone compound in the temporary bonding material is 0.001% to 1.0% by mass.

<24> The method for manufacturing a semiconductor element as described in any one of <19> to <23>,

in which the temporary bonding material includes an elastomer.

<25> The method for manufacturing a semiconductor element as described in <24>,
in which the elastomer is a polystyrene-based elastomer.

<26> The method for manufacturing a semiconductor element as described in <24>
or <25>,

in which the solubility of the elastomer in the organic solvent at 25°C is 18% to 40% by mass.

<27> The method for manufacturing a semiconductor element as described in any one of <19> to <26>,

in which the organic solvent is at least one selected from an aromatic compound, a saturated alicyclic compound, a cyclic ketone, or a cyclic terpene.

<28> The method for manufacturing a semiconductor element as described in any one of <19> to <27>,

in which the detergent composition includes an acid and the acid is at least one selected from a phosphoric acid, a phosphonic acid, a phosphinic acid, a sulfonic acid, or a carboxylic acid.

<29> The method for manufacturing a semiconductor element as described in any one of <19> to <27>,

in which the detergent composition includes a base and the base is at least one selected from an aliphatic amine, an aromatic amine, or a heterocyclic amine.

<30> The method for manufacturing a semiconductor element as described in any one of <19> to <29>,

in which the temporary bonding material is used for temporary adhesion between a carrier substrate and a substrate to be processed, and the temporary bonding material to be removed by the detergent composition is the temporary bonding material remaining on the

substrate to be processed after peeling off the carrier substrate, and the temporary bonding material remaining on the substrate to be processed after peeling off the carrier substrate and further peeling off the temporary bonding material.

[0006] According to the present invention, it is possible to provide a kit including a temporary bonding material and a detergent composition, the kit being capable of suitably removing a residue derived from the temporary bonding material including a silicone compound; a detergent composition; and a method for manufacturing a semiconductor element.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Fig. 1 is a schematic view of a first embodiment illustrating a method for manufacturing a semiconductor element.

Fig. 2 is a schematic view of a second embodiment illustrating a method for manufacturing a semiconductor element.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0008] Hereinafter, the contents of the present invention will be described in detail. Further, in the present specification, “(a value) to (a value)” is used to mean a range including the numerical values described before and after “to” as a lower limit value and an upper limit value, respectively.

In citations for a group (atomic group) in the present specification, in a case where the group (atomic group) is denoted without specifying whether it is substituted or unsubstituted, the group (atomic group) includes both a group (atomic group) not having a substituent and a group (atomic group) having a substituent. For example, an “alkyl group” includes not only an alkyl group not having a substituent (unsubstituted alkyl group) but also an alkyl group having a substituent (substituted alkyl group).

“Actinic rays” or “radiation” in the present specification means, for example, visible light, ultraviolet rays, far ultraviolet rays, electron beams, and X-rays.

“Exposure” in the present specification includes, unless otherwise specified, not only exposure using light but also writing using particle rays such as electron beams and ion beams. Further, examples of light used for exposure generally include actinic rays or radiation such as a bright line spectrum of a mercury lamp, far ultraviolet rays typified by an excimer laser, extreme ultraviolet rays (EUV light), X-rays, and electron beams.

In the present specification, the total solid content refers to a total mass of components excluding a solvent from a composition.

In the present specification, “(meth)acrylate” represents acrylate and methacrylate,

“(meth)acryl” represents acryl and methacryl, and “(meth)acryloyl” represents acryloyl and methacryloyl.

In the present specification, a weight-average molecular weight and a number-average molecular weight are each defined as a value in terms of polystyrene, as measured by means of gel permeation chromatography (GPC). In the present specification, the weight-average molecular weight (Mw) and the number-average molecular weight (Mn) can be determined, for example, by using HLC-8220GPC (manufactured by Tosoh Corporation), TSKgel Super AWM-H (manufactured by Tosoh Corporation, 6.0 mm (inner diameter (ID))×15.0 cm) as columns, and a 10-mmol/L lithium bromide N-methylpyrrolidone (NMP) solution as an eluent.

Furthermore, in embodiments described below, the members and the like in the drawings referred to above are simplified or omitted by attaching the same symbols or equivalent symbols to the drawings.

[0009] The kit of an embodiment of the present invention is a kit including a detergent composition including an acid or base and an organic solvent, and a temporary bonding material including a silicone compound, in which a value represented by Formula (a) of the acid is 0 to 10 and a value represented by Formula (b) of the base is -5 to 0;

Formula (a) ClogP-pKa

Formula (b) ClogP-pKb

in Formulae (a) and (b), ClogP represents a value represented by a base-10 logarithm $\log P$ of P which is a 1-octanol/water partition coefficient representing a ratio of an equilibrium concentration in 1-octanol and water, pKa represents an acid dissociation constant, and pKb represents a base dissociation constant.

By using the detergent composition, a residue can be effectively reduced even with a temporary bonding material including a silicone compound.

Hereinafter, the detergent composition and the temporary bonding material will be described in detail.

[0010] <Detergent Composition>

The detergent composition in the embodiment of the present invention is a detergent composition for a temporary bonding material including a silicone compound, which includes an acid or base and an organic solvent.

Here, the temporary bonding material refers to a bonding material used for temporary adhesion between a substrate and a substrate. Examples of the substrate include a carrier

substrate and a substrate to be processed (for example, a device wafer). The carrier substrate easily processes a substrate to be processed by temporary adhesion of the substrate to be processed onto a carrier substrate. Details thereof will be described later.

A residue derived from the temporary bonding material can be removed by an organic solvent to some degrees, usually by selecting an appropriate organic solvent. However, in a case of the temporary bonding material including a silicone compound, it was found that a residue derived from the silicone compound cannot be sufficiently removed only with an organic solvent. The residue derived from a silicone compound can cause the peeling of an insulating layer to be laminated thereafter. In the present invention, it is possible to appropriately remove a temporary bonding material including a silicone compound by using a detergent composition including an acid or base and an organic solvent.

[0011] <<Acid>>

In a case where the detergent composition includes an acid, a value represented by Formula (a) of the acid is preferably 0 to 10, more preferably 0.5 to 10, still more preferably 1 to 10, even still more preferably 1.5 to 9, and further still more preferably 2 to 8. By setting the values to such a range, the removability of the residue derived from a silicone compound is improved.

Formula (a) ClogP-pKa

Here, ClogP represents a value represented by a base-10 logarithm $\log P$ of P which is a 1-octanol/water partition coefficient representing a ratio of an equilibrium concentration in 1-octanol and water, and pKa represents an acid dissociation constant.

[0012] Furthermore, the acid is preferably at least one selected from phosphoric acid, phosphonic acid, phosphinic acid, sulfonic acid, or carboxylic acid, and more preferably at least one selected from sulfonic acid or carboxylic acid.

Examples of the phosphoric acid include monoalkyl phosphoric acids or dialkyl phosphoric acids such as methyl phosphate, dimethyl phosphate, ethyl phosphate, diethyl phosphate, butyl phosphate, dibutyl phosphate, butoxyethyl phosphate, and 2-ethylhexyl phosphate.

Examples of the phosphonic acid include vinylphosphonic acid, alkylphosphonic acids such as methylenediphosphonic acid, ethylphosphonic acid, propylphosphonic acid, 1,3-propylenediphosphonic acid, butylphosphonic acid, 1,4-butylenediphosphonic acid, pentylphosphonic acid, 1,5-pentylenediphosphonic acid, hexylphosphonic acid, 1,6-dihexylenephosphonic acid, octylphosphonic acid, decylphosphonic acid, and

dodecylphosphonic acid, and aromatic phosphonic acids such as phenylphosphonic acid, phenylenediphosphonic acid, xylylenediphosphonic acid, (4-hydroxyphenyl)phosphonic acid, (2-phenylethyl)phosphonic acid, o-xylenediphosphonic acid, benzhydrylphosphonic acid, cinnamylphosphonic acid, and (4-hydroxybenzyl)phosphonic acid.

Examples of the phosphinic acid include phenylphosphinic acid, 1-anilino-1-methylethylphosphinic acid, 1-(2-(n-ethyl-anilino)-ethylamino)-isopropylphosphinic acid, and tritylphosphinic acid.

Examples of the sulfonic acid include methanesulfonic acid, ethanesulfonic acid, trifluoromethanesulfonic acid, vinylsulfonic acid, 1,5-propanedisulfonic acid, 3-hydroxypropanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, p-ethylbenzenesulfonic acid, n-dodecylbenzenesulfonic acid, 2,4,5-trimethylbenzenesulfonic acid, nonafluoro-1-butanedisulfonic acid, 2-naphthalenesulfonic acid, 1,5-naphthalenedisulfonic acid, heptadecafluorooctasulfonic acid, 10-campersulfonic acid, 3-cyclohexylaminopropanesulfonic acid, m-xylene-4-sulfonic acid, p-xylene-2-sulfonic acid, dansyl acid, 4,4'-biphenyldisulfonic acid, 8-anilino-1-naphthalenesulfonic acid, 2-morpholinoethanesulfonic acid, 3-morpholinopropanesulfonic acid, and piperazine-1,4-bis(2-hydroxypropanesulfonic acid), 7-anilino-4-hydroxy-2-naphthalenesulfonic acid, 7-anilino-1-naphthol-3-sulfonic acid, 4-sulfophthalic acid, 2-hydroxy-3-morpholinopropanesulfonic acid, 4-nitrotoluene-2-sulfonic acid, picrylsulfonic acid, 5-sulfosalicylic acid, and 4-sulfo-2,3,5,6-tetrafluorobenzoic acid.

Examples of the carboxylic acid include saturated fatty acids such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, margaric acid, and stearic acid, unsaturated fatty acids such as oleic acid, linoleic acid, linolenic acid, arachidonic acid, eicosapentaenoic acid, docosahexaenoic acid, and sorbic acid, hydroxy acids such as lactic acid, malic acid, and citric acid, aromatic carboxylic acids such as benzoic acid, phthalic acid, isophthalic acid, terephthalic acid, salicylic acid, 3,4,5-trihydroxybenzoic acid, mellitic acid, and cinnamic acid, dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, fumaric acid, and maleic acid, tricarboxylic acids such as aconitic acid, oxocarboxylic acids such as pyruvic acid and oxaloacetic acid, and halogen-containing carboxylic acids such as chloroacetic acid, dichloroacetic acid, trichloroacetic acid, and trifluoroacetic acid.

[0013] A lower limit value of the content of the acid in the detergent composition of an

embodiment of the present invention is preferably 0.000008% by mass or more, more preferably 0.000080% by mass or more, still more preferably 0.000800% by mass or more, and even still more preferably 0.008000% by mass or more, with respect to the detergent composition.

An upper limit value of the content of the acid in the detergent composition of an embodiment of the present invention is preferably 1.0% by mass or less, more preferably 0.8% by mass or less, still more preferably 0.5% by mass or less, and even still more preferably 0.3% by mass or less, with respect to the detergent composition.

In a case where the detergent composition of the embodiment of the present invention contains an acid, it may include one kind or two or more kinds of the acids. In a case where the detergent composition includes two or more kinds of the acids, the total amount thereof is preferably within the range.

[0014] <<Base>>

In a case where the detergent composition includes a base, a value represented by Formula (b) of the base is -5 to 0, preferably -4.5 to 0, more preferably -4 to 0, still more preferably -3.5 to 0, even still more preferably -3 to 0, further still more preferably -2.5 to -0.5, and even further still more preferably -2 to -1.

Formula (b) ClogP-pKb

Here, ClogP represents a value represented by a base-10 logarithm $\log P$ of P which is a 1-octanol/water partition coefficient representing a ratio of an equilibrium concentration in 1-octanol and water, and pKb represents a base dissociation constant.

[0015] Moreover, the base is preferably at least one selected from amines, more preferably at least one selected from an aliphatic amine, an aromatic amine, or a heterocyclic amine, and still more preferably at least one selected from aliphatic amine and heterocyclic amine.

Examples of the aliphatic amine include methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, ethylenediamine, triethanolamine, N,N-diisopropylethylamine, tetramethylethylenediamine, hexamethylenediamine, spermidine, spermine, amantadine, and diethanolamine.

Examples of the aromatic amine include aniline, phenethylamine, toluidine, catecholamine, and 1,8-bis(dimethylamino)naphthalene.

Examples of the heterocyclic amine include pyrrolidine, piperidine, piperazine, morpholine, quinuclidine, pyrrole, pyrazole, imidazole, pyridine, pyridazine, pyrimidine, pyrazine, oxazole, thiazole, 4-dimethylaminopyridine, 1,4-diazabicyclo[2,2,2]octane,

1,5-diazabicyclo[4,3,0]-5-nonene, and 1,8-diazabicyclo[5,4,0]-7-undecene.

[0016] A lower limit value of the content of the base in the detergent composition of the embodiment of the present invention is preferably 0.000008% by mass or more, more preferably 0.000080% by mass or more, still more preferably 0.000800% by mass or more, and even still more preferably 0.008000% by mass or more, with respect to the detergent composition.

An upper limit value of the content of the base in the detergent composition of the embodiment of the present invention is preferably 1.0% by mass or less, more preferably 0.8% by mass or less, still more preferably 0.5% by mass or less, and still more preferably 0.3% by mass or less, with respect to the detergent composition.

In a case where the detergent composition of the embodiment of the present invention includes a base, it may include one kind or two or more kinds of the bases. In a case where the detergent composition includes two or more kinds of the bases, the total amount thereof is preferably within the range.

[0017] <<Organic Solvent>>

The detergent composition of the embodiment of the present invention includes an organic solvent. As the organic solvent, an organic solvent that dissolves a temporary bonding material, for example, a resin component of the temporary bonding material is used, and is preferably at least one selected from an aromatic compound, a saturated alicyclic compound, a cyclic ketone, or a cyclic terpene, more preferably at least one selected from an aromatic compound, an alicyclic compound, and a cyclic terpene, and still more preferably at least one selected from aromatic compounds.

Examples of the aromatic compound include benzene, toluene, xylene, ethylbenzene, cumene, n-butylbenzene, s-butylbenzene, t-butylbenzene, styrene, mesitylene, 1,2,4-trimethylbenzene, p-cymene, cyclohexylbenzene, diethylbenzene, pentylbenzene, Dipentylbenzene, dodecylbenzene, ethynylbenzene, tetralin, anisole, phenetole, butyl phenyl ether, pentylphenyl ether, veratrol, 1,3-dimethoxybenzene, 1,2,4-trimethoxybenzene, 3,4,5-trimethoxytoluene, 2-methoxytoluene, 2,5-dimethylanisole, o-chlorophenol, chlorobenzene, dichlorobenzene, trichlorobenzene, 1-chloronaphthalene, 1-bromonaphthalene, 1-methylnaphthalene, o-diiodobenzene, acetophenone, 2,3-benzofuran, 2,3-dihydrobenzofuran, 1,4-benzodioxane, phenyl acetate, methyl benzoate, cresol, aniline, and nitrobenzene.

Examples of the saturated alicyclic compound include cyclopropane, cyclobutane, cyclopentane, cyclohexane, methylcyclohexane, cycloheptane, cyclooctane, cyclononane,

cyclodecane, cycloundecane, cyclododecane, cyclobutene, cyclopropene, cyclohexene, cycloheptene, cyclooctene, dicycloundecane, decahydronaphthalene, norbornane, norbornadiene, cubane, basketane, and housane.

Examples of the cyclic ketone include cyclohexanone, cyclopentanone, isophorone, acetophenone, and benzophenone.

Examples of the cyclic terpene include monocyclic terpenes such as chrysanthemol, grandisol, junionone, thioterpineol, iridoid, secoiridoid, menthane, limonene, phellandrene, terpinolene, terpinene, cymene, menthol, pregall, piperitol, terpineol, carveol, thymol, dihydrocarveol, menthone, pulegone, ferrandrol, carvone, carbenone, piperitone, 1,8-cineol, 1,4-cineol, and ascaridole, and bicyclic terpenes such as carane, thujane, pinane, bornane, fenchane, isobornane, isocamphene, 3-carene, thujene, sabinene, thujone, thujanol, pinene, verbenol, verbenone, pinocarbon, camphor, borneol, isoborneol, fenchone, and fenchol fenchene.

[0018] The content of the organic solvent in the detergent composition of the embodiment of the present invention is preferably 50.0000% to 99.9999% by mass, and more preferably 99.0000% to 99.9990% by mass, with respect to the detergent composition.

In a case where the detergent composition of the embodiment of the present invention includes an organic solvent, it may include one kind or two or more kinds of the organic solvents. In a case where the detergent composition includes two or more kinds of the organic solvents, the total amount thereof is preferably within the range.

[0019] <<Acid or Base and Organic Solvent>>

The detergent composition of the embodiment of the present invention has a mass ratio of the acid or base to the organic solvent of preferably 0.0001:99.9999 to 50:50, more preferably 0.0010:99.9990 to 10:90, and still more preferably 0.0100:99.9900 to 1.0000:99.0000. By setting the ratio to the range, the removability of the temporary bonding material is more effectively improved.

[0020] <<Other Components>>

The detergent composition may include components other than the acid or base and the organic solvent. Examples of such other components include washing preparations such as sodium tripolyphosphate, 4-sodium pyrophosphate, potassium pyrophosphate, sodium aluminosilicate, sodium nitrilotriacetate, ethylenediamine tetraacetate acid, and sodium citrate, a micelle enhancer such as sodium sulfate, an inorganic alkali component such as sodium silicate and sodium carbonate, IRGAMET 30, IRGAMET 39, and IRGAMET 42 (all

manufactured by BASF Japan), Belclene 510, Belclene 511, Belclene 512, and Belclene 515 (all manufactured by BWA Water Additives), BT-120, BT-LX, CBT-1, TT-LX, TT-LYK, and JCL-400 (all manufactured by Johoku chemical Co., Ltd.), VERZONE Crystal #120, VERZONE MA-10, VERZONE A3-T, VERZONE Crystal #130, VERZONE Crystal #150, VERZONE Crystal #270, VERZONE Crystal #260, VERZONE SG Powder, VERZONE Green SH-K, VERZONE Oil #1022, VERZONE Origin Oil #1030, VERZONE Origin Oil #220, VERZONE OIL-HD, and VERZONE OIL-U (all manufactured by Daiwa Fine Chemicals Co., Ltd.), antirust agents such as a top antirust agent Y and a top antirust agent 511 (all manufactured by Okuno Chemical Industries Co., Ltd.), and CB Bright (manufactured by Ryoko Chemical Co., Ltd.), corrosion inhibitors such as IRGACOR L12, IRGACOR DSS G, IRGACOR NPA, IRGALUBE 349, and SARKOSYL O (all manufactured by BASF Japan), discoloration inhibitors for metal surfaces, such as VERZONE COR-280, Silver Rip, VERZONE DA-1, New Dain Silver S-1, New Dain Silver V-2, New Dain Silver, CU-Guard 1000R, CU-Guard 1000N, CU-Guard 1000, CU-Guard D, VERZONE NFS-Oil, VERZONE OA-386, VERZONE C-BTA, VERZONE TTA, and VERZONE Crystal #120 (all manufactured by Daiwa Fine Chemicals Co., Ltd.), Cu-423Y, Ag-422Y, and Ag-420Y (all manufactured by Dipsol Chemicals, Co., Ltd.), Entech CU-560, Entech CU-56, and Meldip AG-6801 (all manufactured by Meltex Inc.), Top Rinse CU-5 and Top Rinse CU-3 (both manufactured by Okuno Chemical Industries), BT-5, BT-7, BT-8, and BT-14 (all manufactured by ASAHI Co., Ltd.), metal oxide film removers such as CU-500 and CU-600 (both manufactured by ASAHI Co., Ltd.), S-Clean S-800, S-Clean S-800FR, S-Clean S-101PN, S-Pure SJ-400, S-Pure SJ gel, S-Clean SK-507, S-Clean W-2550, S-Clean S-105, S-Clean S-109, S-Clean AG-301, and S-Clean S-1000 (all manufactured by Sasaki Chemical Co., Ltd.), Pickle 25, Pickle 27, and Z-2218 (manufacture by Nippon Surface Chemical Co., Ltd.), antistatic agents, antioxidants, and surfactants.

Incidentally, the temporary bonding material used in the present invention can be used in an aspect in which it does not include a surfactant. Further, the temporary bonding material used in the present invention can be used in aspect in which components other than the acid or base and the organic solvent are not substantially included. An expression, substantially not including, means that the content of such other components is 3% by mass or less with respect to the detergent composition of the embodiment of the present invention, and the content is preferably 1% by mass or less, and more preferably 0.5% by mass or less.

[0021] <<Preparation of Detergent Composition>>

For the preparation of the detergent composition of the embodiment of the present invention, it is preferable that the respective components of the detergent composition are mixed, and then the mixture is filtered. The filtration is preferably performed using a filter having a pore diameter of 0.003 to 10 μm . By performing the filtration, the removability of the temporary bonding material tends to be further improved. The filter is preferably made of a polytetrafluoroethylene.

[0022] <Temporary Bonding Material>

<<Silicone Compound>>

The temporary bonding material used in the present invention includes a silicone compound. The silicone compound acts as a release agent and the temporary bonding material can be easily removed from a substrate to be processed.

The silicone compound is a compound including a Si-O bond, examples thereof include a silicone oil, a silane coupling agent, a silicone resin, a silicone rubber, and a cyclic siloxane, and the silane compound is preferably the silicone oil.

Furthermore, it is preferable that the silicone compound does not include a reactive group such as a polymerizable group.

The silicone compound is preferably a polyether-modified silicone.

[0023] The polyether-modified silicone used in the present invention has a ratio represented by Formula (A) of 80% or more.

Formula (A) $\{(MO+EO)/AO\} \times 100$

in Formula (A), MO is % by mole of methylene oxide included in the polyether structure in the polyether-modified silicone, EO is % by mole of ethylene oxide included in the polyether structure in the polyether-modified silicone, and AO is % by mole of alkylene oxide included in the polyether structure in the polyether-modified silicone.

The ratio represented by Formula (A) is preferably 90% or more, more preferably 95% or more, still more preferably 98% or more, even still more preferably 99% or more, and further still more preferably 100%.

[0024] A weight-average molecular weight of the polyether-modified silicone is preferably 500 to 100,000, more preferably 1,000 to 50,000, and still more preferably 2,000 to 40,000.

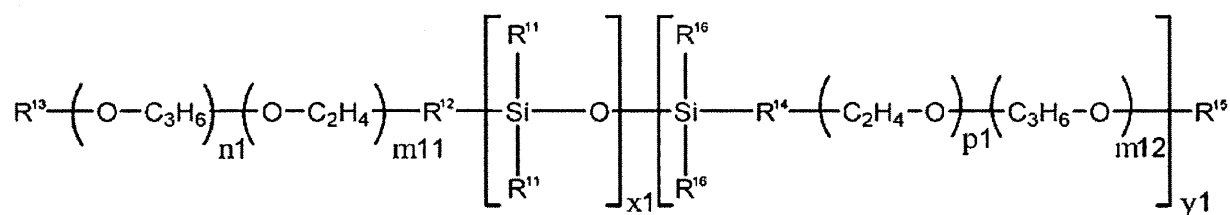
[0025] In the present invention, the polyether-modified silicone preferably has a mass reduction rate of 50% by mass or less in a case where the polyether-modified silicone is warmed from 20°C to 280°C at a temperature raising rate of 20°C/min in a nitrogen stream at 60 mL/min and maintained at a temperature of 280°C for 30 minutes. By using such a

compound, there is a tendency that a surface property of the substrate after processing including heating is further improved. The mass reduction rate of the polyether-modified silicone is preferably 45% by mass or less, more preferably 40% by mass or less, still more preferably 35% by mass or less, and even still more preferably 30% by mass or less. The lower limit value of the mass reduction rate of the polyether-modified silicone may be 0% by mass, but 15% by mass or more and 20% by mass or more of the mass reduction rates are also at sufficiently practically useful levels.

[0026] In the present invention, the light refractive index of the polyether-modified silicone is preferably 1.440 or less. The lower limit value is not particularly limited, but 1.400 or more of the light refractive index is also at a sufficiently practically useful level.

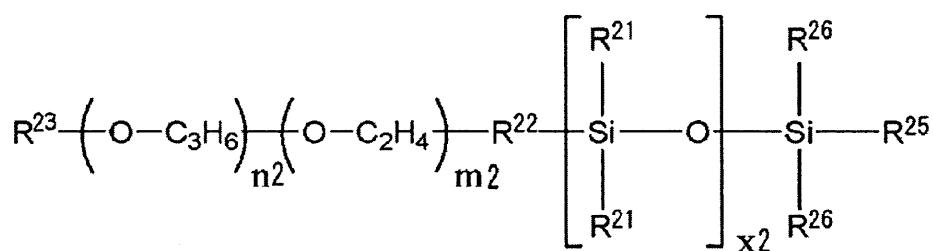
[0027] The polyether-modified silicone used in the present invention is preferably a polyether-modified silicone represented by any one of Formula (101) to Formula (104).

Formula (101)



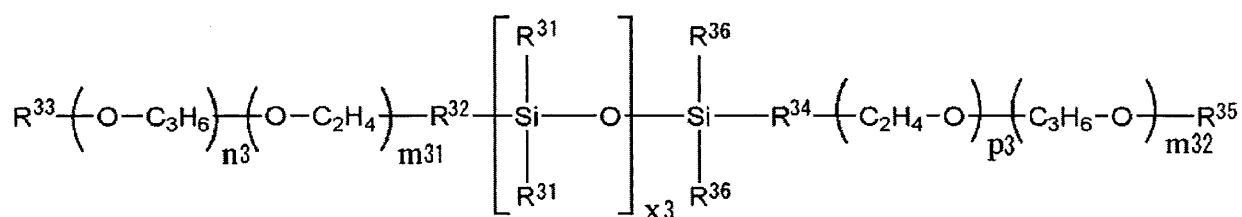
In Formula (101), R^{11} and R^{16} are each independently a substituent, R^{12} and R^{14} are each independently a divalent linking group, R^{13} and R^{15} are each a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, $m11$, $m12$, $n1$, and $p1$ are each independently a number of 0 to 20, and $x1$ and $y1$ are each independently a number of 2 to 100.

Formula (102)



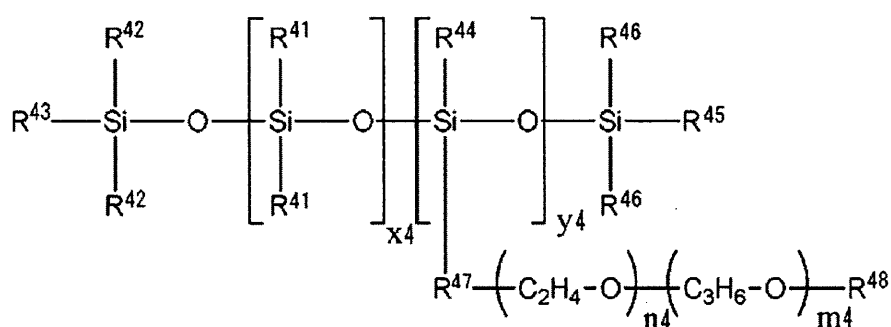
In Formula (102), R^{21} , R^{25} , and R^{26} are each independently a substituent, R^{22} is a divalent linking group, R^{23} is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, $m2$ and $n2$ are each independently a number of 0 to 20, and $x2$ is a number of 2 to 100.

Formula (103)



In Formula (103), R^{31} and R^{36} are each independently a substituent, R^{32} and R^{34} are each independently a divalent linking group, R^{33} and R^{35} are each a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, $m31$, $m32$, $n3$, and $p3$ are each independently a number of 0 to 20, and $x3$ is a number of 2 to 100.

Formula (104)



In Formula (104), R^{41} , R^{42} , R^{43} , R^{44} , R^{45} , and R^{46} are each independently a substituent, R^{47} is a divalent linking group, R^{48} is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, $m4$ and $n4$ are each independently a number of 0 to 20, and $x4$ and $y4$ are each independently a number of 2 to 100.

[0028] In Formula (101), R^{11} and R^{16} are each independently preferably a substituent, an alkyl group having 1 to 5 carbon atoms, or a phenyl group, and more preferably a methyl group.

In Formula (101), R^{12} and R^{14} are each independently a divalent linking group, preferably a carbonyl group, an oxygen atom, an alkylene group having 1 to 6 carbon atoms, a cycloalkylene group having 6 to 16 carbon atoms, an alkenylene group having 2 to 8 carbon atoms, an alkynylene group having 2 to 5 carbon atoms, and an arylene group having 6 to 10 carbon atoms, and preferably an oxygen atom.

In Formula (101), R^{13} and R^{15} are each a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, preferably a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and more preferably a hydrogen atom or an alkyl group having 1 to 3 carbon atoms.

[0029] In Formula (102), R^{21} , R^{25} and R^{26} are each independently a substituent and have the same definitions and preferred ranges as R^{11} and R^{16} in Formula (101).

In Formula (102), R^{22} is a divalent linking group and has the same definition and preferred range as R^{12} in Formula (101).

In Formula (102), R^{23} is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms and has the same definition and preferred range as R^{13} and R^{15} in Formula (101).

[0030] In Formula (103), R^{31} and R^{36} are each independently a substituent and have the same definitions and preferred ranges as R^{11} and R^{16} in Formula (101).

In Formula (103), R^{32} and R^{34} are each independently a divalent linking group and have the same definition and preferred range as R^{12} in Formula (101).

In Formula (103), R^{33} and R^{35} are each a hydrogen atom or an alkyl group having 1 to 5 carbon atoms and have the same definitions and preferred ranges as R^{13} and R^{15} in Formula (101).

[0031] In Formula (104), R^{41} , R^{42} , R^{43} , R^{44} , R^{45} , and R^{46} are each independently a substituent and have the same definitions and preferred ranges as R^{11} and R^{16} in Formula (101).

In Formula (104), R^{47} is a divalent linking group and has the same definition and preferred range as R^{12} in Formula (101).

In Formula (104), R^{48} is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms and has the same definitions and preferred ranges as R^{13} and R^{15} in Formula (101).

[0032] In Formula (101) to Formula (104), Formula (103) or Formula (104) is preferable, and Formula (104) is more preferable.

[0033] The content of the polyoxyalkylene groups in a molecule of the polyether-modified silicone used in the present invention is not particularly limited, but the content of the polyoxyalkylene groups is preferably more than 1% by mass in the total molecular weight.

The content ratio of the polyoxyalkylene groups is defined as “{(Formula mass of polyoxyalkylene groups in one molecule)/Molecular weight of one molecule}×100”.

[0034] Examples of the silane coupling agent include a fluorine atom-containing silane coupling agent, and the silane coupling agent is triethoxy(1H,1H,2H,2H-nonafluorohexyl)silane.

In addition, examples of the silane coupling agent include the surfactants described in each of JP1987-036663A (JP-S62-036663A), JP1986-226746A (JP-S61-226746A), JP1986-226745A (JP-S61-226745A), JP1987-170950A (JP-S62-170950A), JP1988-034540A (JP-S63-034540A), JP1995-230165A (JP-H07-230165A), JP1996-062834A (JP-H08-062834A), JP1997-054432A (JP-H09-054432A), JP1997-005988A (JP-H09-005988A), and JP2001-330953A, the contents of which are incorporated herein by reference.

[0035] As the silicone compound used in the present invention, commercially available

products can also be used.

Examples of the commercially available products include “ADVALON FA33”, “FLUID L03”, “FLUID L033”, “FLUID L051”, “FLUID L053”, “FLUID L060”, “FLUID L066”, “IM22”, and “WACKER-Belsil DMC 6038” (all manufactured by Wacker Asahikasei Silicone Co., Ltd.), “KF-352A”, “KF-353”, “KF-615A”, “KP-112”, “KP-341”, “X-22-4515”, “KF-354L”, “KF-355A”, “KF-6004”, “KF-6011”, “KF-6011P”, “KF-6012”, “KF-6013”, “KF-6015”, “KF-6016”, “KF-6017”, “KF-6017P”, “KF-6020”, “KF-6028”, “KF-6028P”, “KF-6038”, “KF-6043”, “KF-6048”, “KF-6123”, “KF-6204”, “KF-640”, “KF-642”, “KF-643”, “KF-644”, “KF-945”, “KP-110”, “KP-355”, “KP-369”, “KS-604”, “Polon SR-Conc”, “X-22-4272”, and “X-22-4952” (all manufactured by Shin-Etsu Chemical Co., Ltd.), “8526 ADDITIVE”, “FZ-2203”, “FZ-5609”, “L-7001”, “SF 8410”, “2501 COSMETIC WAX”, “5200 FORMULATION AID”, “57 ADDITIVE”, “8019 ADDITIVE”, “8029 ADDITIVE”, “8054 ADDITIVE”, “BY16-036”, “BY16-201”, “ES-5612 FORMULATION AID”, “FZ-2104”, “FZ-2108”, “FZ-2123”, “FZ-2162”, “FZ-2164”, “FZ-2191”, “FZ-2207”, “FZ-2208”, “FZ-2222”, “FZ-7001”, “FZ-77”, “L-7002”, “L-7604”, “SF8427”, “SF8428”, “SH 28 PAINR ADDITIVE”, “SH3749”, “SH3773M”, “SH8400”, and “SH8700” (all manufactured by Toray Dow Corning Co., Ltd.), “BYK-378”, “BYK-302”, “BYK-307”, “BYK-331”, “BYK-345”, “BYK-B”, “BYK-347”, “BYK-348”, “BYK-349”, and “BYK-377” (all manufactured by BYK Chemie-Japan), and “Silwet L-7001”, “Silwet L-7002”, “Silwet L-720”, “Silwet L-7200”, “Silwet L-7210”, “Silwet L-7220”, “Silwet L-7230”, “Silwet L-7605”, “TSF4445”, “TSF4446”, “TSF4452”, “Silwet Hydrostable 68”, “Silwet L-722”, “Silwet L-7280”, “Silwet L-7500”, “Silwet L-7550”, “Silwet L-7600”, “Silwet L-7602”, “Silwet L-7604”, “Silwet L-7607”, “Silwet L-7608”, “Silwet L-7622”, “Silwet L-7650”, “Silwet L-7657”, “Silwet L-77”, “Silwet L-8500”, “Silwet L-8610”, “TSF4440”, “TSF4441”, “TSF4450”, and “TSF4460” (all manufactured by Momentive Performance Materials Japan Co., Ltd.).

Furthermore, examples of the silicone compound include trade names “BYK-300”, “BYK-306”, “BYK-310”, “BYK-315”, “BYK-313”, “BYK-320”, “BYK-322”, “BYK-323”, “BYK-325”, “BYK-330”, “BYK-333”, “BYK-337”, “BYK-341”, “BYK-344”, “BYK-370”, “BYK-375”, “BYK-UV3500”, “BYK-UV3510”, “BYK-UV3570”, “BYK-3550”, “BYK-SILCLEAN3700”, and “BYK-SILCLEAN3720” (all manufactured by BYK Chemie-Japan), trade names “AC FS 180”, “AC FS 360”, and “AC S 20” (all manufactured by Algin Chemie), trade names “POLYFLOW KL-400X”, “POLYFLOW KL-400HF”,

“POLYFLOW KL-401”, “POLYFLOW KL-402”, “POLYFLOW KL-403”, “POLYFLOW KL-404”, and “POLYFLOW KL-700” (all manufactured by Kyoeisha Chemical Co., Ltd.), trade names “KP-301”, “KP-306”, “KP-109”, “KP-310”, “KP-310B”, “KP-323”, “KP-326”, “KP-341”, “KP-104”, “KP-110”, “KP-112”, “KP-360A”, “KP-361”, “KP-354”, “KP-357”, “KP-358”, “KP-359”, “KP-362”, “KP-365”, “KP-366”, “KP-368”, “KP-330”, “KP-650”, “KP-651”, “KP-390”, “KP-391”, and “KP-392” (all manufactured by Shin-Etsu Chemical Co., Ltd.), trade names “LP-7001”, “LP-7002”, “8032 ADDITIVE”, “FZ-2110”, “FZ-2105”, “67 ADDITIVE”, “8618 ADDITIVE”, “3 ADDITIVE”, “56 ADDITIVE” (all manufactured by Dow Corning Toray Co., Ltd.), “TEGO WET 270” (manufactured by Evonik Degussa Japan Co., Ltd.), “NBX-15” (manufactured by Neos Corporation), or the like can be used.

[0036] The content of the silicone compound in the temporary bonding material used in the present invention is preferably 0.001% to 1.0% by mass with respect to the solid content of the temporary bonding material. The lower limit of the content of the silicone compound is more preferably 0.004% by mass or more, still more preferably 0.006% by mass or more, even still more preferably 0.008% by mass or more, and further still more preferably 0.009% by mass or more. The upper limit of the content of the silicone compound is preferably 0.8% by mass or less, more preferably 0.6% by mass or less, still more preferably 0.3% by mass or less, even still more preferably 0.15% by mass or less, and further still more preferably 0.09% by mass or less.

The temporary bonding material used in the present invention may include one kind or two or more kinds of the silicone compounds. In a case where the temporary bonding material includes two or more kinds of the silicone compounds, the total amount thereof is preferably within the range.

[0037] <<Other Release Agents>>

In the present invention, other release agents other than the silicone compound may be included. Examples of such other release agents include a fluorine-based liquid-state compound.

In a case where such other release agents are contained, a content thereof is preferably in a range of 0.001% to 0.005% by mass. One kind or two or more kinds of such other release agents may be included. In a case where two or more kinds of such other release agents may be included, the total amount thereof is preferably within the range.

Furthermore, in the present invention, a configuration in which such other release agents are not substantially included may be adopted. A description of being not

substantially included means that the amount is 1% by mass or less with respect to the content of the silicone compound.

[0038] <<Resin>>

The temporary bonding material used in the present invention preferably includes at least one kind of resin.

Examples of the resin include a block copolymer, a random copolymer, and a graft copolymer, and the resin is preferably the block copolymer. With the block copolymer, it is possible to suppress the flow of the temporary bonding material during a heating process, and therefore, maintain the adhesion even during the heating process. Thus, an effect that the peelability is not changed can be expected even after the heating process.

[0039] In the temporary bonding material used in the present invention, the resin is preferably an elastomer. By using the elastomer as the resin, it is possible to form a temporary bonding material which follows fine irregularities of a substrate (a substrate to be processed, such as a carrier substrate and a device wafer) and has excellent adhesiveness by an appropriate anchoring effect. The elastomer can be used singly or in combination of two or more kinds thereof.

Furthermore, in the present specification, an elastomer represents a polymer compound which exhibits elastic deformation. That is, the polymer compound is defined as a polymer compound which has a property of instantaneously being deformed according to an external force at a time of the external force being applied and being recovered to the original shape in a short period of time at a time of the external force being removed.

[0040] <<<Elastomer>>>

In the present invention, the weight-average molecular weight of the elastomer is preferably 2,000 to 200,000, more preferably 10,000 to 200,000, and still more preferably 50,000 to 100,000. An elastomer having a weight-average molecular weight in the range has excellent solubility in a solvent, and therefore, in a case where the carrier substrate is peeled from a substrate to be processed and then residue derived from the elastomer remaining on a substrate to be processed or a carrier substrate is removed using a solvent, the residue is easily dissolved in the solvent and removed. As a result, there is an advantage that the residue does not remain on the substrate to be processed, the carrier substrate, or the like.

[0041] In the present invention, the elastomer is not particularly limited, and an elastomer including repeating units derived from styrene (polystyrene-based elastomer), a polyester-based elastomer, a polyolefin-based elastomer, a polyurethane-based elastomer, a

polyamide-based elastomer, a polyacrylic elastomer, a silicone-based elastomer, a polyimide-based elastomer, or the like can be used. In particular, the polystyrene-based elastomer, the polyester-based elastomer, or the polyamide-based elastomer is preferable, and from the viewpoints of heat resistance and peelability, the polystyrene-based elastomer is more preferable.

[0042] In the present invention, the elastomer is preferably a hydrogenated product. In particular, a hydrogenated product of a polystyrene-based elastomer is preferable. In a case where the elastomer is a hydrogenated product, the heat stability or the storage stability is improved. Moreover, the peelability and the removability of a temporary bonding material after peeling are improved. In a case where the hydrogenated product of the polystyrene-based elastomer is used, the effect is noticeable. Further, the hydrogenated product means a polymer with a structure in which an elastomer is hydrogenated.

[0043] In the present invention, a temperature for 5% of heat mass reduction of the elastomer at a time of using a temperature raising rate of 20°C/min from 25°C is preferably 250°C or higher, more preferably 300°C or higher, still more preferably 350°C or higher, and even still more preferably 400°C or higher. Further, the upper limit value is not particularly limited, but it is, for example, preferably 1,000°C or lower, and more preferably 800°C or lower. According to this aspect, a temporary bonding material having excellent heat resistance can be obtained.

The elastomer in the present invention can be deformed up to 200% by applying a small external force at room temperature (20°C) in a case where the original size is taken as 100%, and has a property of returning to the original size by 130% or less in a short period of time as the external force is eliminated.

[0044] <<<<Polystyrene-Based Elastomer>>>>

The polystyrene-based elastomer is not particularly limited and can be selected as appropriate depending on purposes thereof. It is preferably, for example, at least one polystyrene-based elastomer selected from a styrene-butadiene-styrene block copolymer (SBS), a styrene-isoprene-styrene block copolymer (SIS), a polystyrene-poly(ethylene-propylene) diblock copolymer (SEP), a polystyrene-poly(ethylene-propylene)-polystyrene triblock copolymer (SEPS), a polystyrene-poly(ethylene-butylene)-polystyrene triblock copolymer (SEBS), and polystyrene-poly(ethylene/ethylene-propylene)-polystyrene triblock copolymer (SEEPS).

[0045] The ratio of the repeating units derived from styrene in the polystyrene-based

elastomer is preferably 90% by mass or less, more preferably 55% by mass or less, still more preferably 48% by mass or less, even still more preferably 35% by mass or less, and further still more preferably 33% by mass or less. The lower limit of the ratio of the repeating units derived from styrene may be 0% by mass, and may also be 10% by mass or more. In a case where the ratio is within the range, it is possible to more effectively suppress warpage of a laminate formed by bonding substrates using a temporary bonding material.

[0046] In an embodiment of the polystyrene-based elastomer in the present invention, the elastomer may be used an elastomer to be used by combining an elastomer A containing repeating units derived from styrene at a ratio from 10% by mass to 55% by mass of all repeating units and an elastomer B containing repeating units derived from styrene at a ratio of more than 55% and 95% by mass or less of all repeating units. By using a combination of the elastomer A and the elastomer B, it is possible to effectively suppress the occurrence of warpage. A mechanism of obtaining such an effect can be assumed as follows. That is, since the elastomer A is formed of a relatively soft material, a temporary bonding material in a layer shape (temporary bonding layer) having elasticity is easily formed. Accordingly, in a case where a laminate of a substrate and a carrier substrate is produced using the temporary bonding material and the substrate is polished to obtain a thin film, the temporary bonding material (temporary bonding layer) can be made to easily return to the original shape as elastically deformed even in a case where a pressure at the time of polishing is locally applied. As the result, excellent flat polishability is obtained. Further, even in a case where the polished laminate of the carrier substrate, the substrate to be processed and temporary bonding material is subjected to a heating treatment and then cooled, the internal stress generated at the time of cooling can be relaxed and the occurrence of warpage can be effectively suppressed by the temporary bonding material (temporary bonding layer).

In addition, since the elastomer B is a relatively hard material, a temporary bonding material having excellent peelability can be obtained by incorporation the elastomer B into the temporary bonding material.

[0047] The mass ratio of the elastomer A to the elastomer B in a case where the both are blended is preferably elastomer A:elastomer B=1:99 to 99:1, more preferably 3:97 to 97:3, still more preferably 5:95 to 95:5, and even still more preferably 10:90 to 90:10. In a case where mass ratio is within the range, it is possible to more effectively suppress the occurrence of warpage.

[0048] As the polystyrene-based elastomer, a block copolymer of styrene and another resin is

preferable, a styrene block copolymer in which one terminal or both terminals are formed of styrene blocks is more preferable, and a styrene block copolymer in which both terminals are formed of styrene blocks is particularly preferable. In a case where the both ends of the polystyrene-based elastomer are formed of styrene blocks (repeating units derived from styrene), the heat stability tends to be further improved. This is because repeating units derived from styrene having excellent heat resistance are present at the terminals. In particular, in a case where a block site of the repeating unit derived from styrene is a reactive polystyrene-based hard block, the heat resistance and the chemical resistance tend to be more excellent, which is thus preferable. In addition, such an elastomer is more preferable from the viewpoints of the solubility in a solvent and the resistance to a resist solvent.

Furthermore, in a case where the polystyrene-based elastomer is a hydrogenated product, the stability with respect to heat is improved and deterioration such as decomposition and polymerization is unlikely to occur. In addition, this is more preferable from the viewpoints of the solubility in a solvent and the resistance to a resist solvent.

From the viewpoint of the peelability, the amount of unsaturated double bonds of the polystyrene-based elastomer is preferably less than 15 mmol, more preferably less than 5 mmol, and still more preferably less than 0.5 mmol per gram of the polystyrene-based elastomer. Further, the amount of the unsaturated double bonds as mentioned herein does not include unsaturated double bonds in a benzene ring derived from styrene. The amount of the unsaturated double bonds can be calculated by nuclear magnetic resonance (NMR) measurement.

[0049] Moreover, the “repeating unit derived from styrene” in the present specification is a constitutional unit derived from styrene contained in a polymer at the time of polymerizing styrene or a styrene derivative and may include a substituent. Examples of the styrene derivative include α -methylstyrene, 3-methylstyrene, 4-propylstyrene, and 4-cyclohexylstyrene. Examples of the substituent include an alkyl group having 1 to 5 carbon atoms, an alkoxy group having 1 to 5 carbon atoms, an alkoxyalkyl group having 2 to 5 carbon atoms, an acetoxy group, and a carboxyl group.

[0050] Examples of commercially available products of the polystyrene-based elastomer include TUFPRENE A, TUFPRENE 125, TUFPRENE 126S, SOLPRENE T, ASAPRENE T-411, ASAPRENE T-432, ASAPRENE T-437, ASAPRENE T-438, ASAPRENE T-439, TUFTEC H1272, TUFTEC P1500, TUFTEC H1052, TUFTEC H1062, TUFTEC M1943, TUFTEC M1911, TUFTEC H1041, TUFTEC MP10, TUFTEC M1913, TUFTEC H1051,

TUFTEC H1053, TUFTEC P2000, and TUFTEC H1043 (all manufactured by Asahi Kasei Corporation), ELASTOMER AR-850C, ELASTOMER AR-815C, ELASTOMER AR-840C, ELASTOMER AR-830C, ELASTOMER AR-860C, ELASTOMER AR-875C, ELASTOMER AR-885C, ELASTOMER AR-SC-15, ELASTOMER AR-SC-0, ELASTOMER AR-SC-5, ELASTOMER AR-710, ELASTOMER AR-SC-65, ELASTOMER AR-SC-30, ELASTOMER AR-SC-75, ELASTOMER AR-SC-45, ELASTOMER AR-720, ELASTOMER AR-741, ELASTOMER AR-731, ELASTOMER AR-750, ELASTOMER AR-760, ELASTOMER AR-770, ELASTOMER AR-781, ELASTOMER AR-791, ELASTOMER AR-FL-75N, ELASTOMER AR-FL-85N, ELASTOMER AR-FL-60N, ELASTOMER AR-1050, ELASTOMER AR-1060, and ELASTOMER AR-1040 (all manufactured by ARONKASEI Co., Ltd.), KRATON D1111, KRATON D1113, KRATON D1114, KRATON D1117, KRATON D1119, KRATON D1124, KRATON D1126, KRATON D1161, KRATON D1162, KRATON D1163, KRATON D1164, KRATON D1165, KRATON D1183, KRATON D1193, KRATON DX406, KRATON D4141, KRATON D4150, KRATON D4153, KRATON D4158, KRATON D4270, KRATON D4271, KRATON D4433, KRATON D1170, KRATON D1171, KRATON D1173, CARIFLEX IR0307, CARIFLEX IR0310, CARIFLEX IR0401, KRATON D0242, KRATON D1101, KRATON D1102, KRATON D1116, KRATON D1118, KRATON D1133, KRATON D1152, KRATON D1153, KRATON D1155, KRATON D1184, KRATON D1186, KRATON D1189, KRATON D1191, KRATON D1192, KRATON DX405, KRATON DX408, KRATON DX410, KRATON DX414, KRATON DX415, KRATON A1535, KRATON A1536, KRATON FG1901, KRATON FG1924, KRATON G1640, KRATON G1641, KRATON G1642, KRATON G1643, KRATON G1645, KRATON G1633, KRATON G1650, KRATON G1651, KRATON G1652 (G1652MU-1000), KRATON G1654, KRATON G1657, KRATON G1660, KRATON G1726, KRATON G1701, KRATON G1702, KRATON G1730, KRATON G1750, KRATON G1765, KRATON G4609, and KRATON G4610 (all manufactured by Kraton Corporation), TR2000, TR2001, TR2003, TR2250, TR2500, TR2601, TR2630, TR2787, TR2827, TR1086, TR1600, SIS5002, SIS5200, SIS5250, SIS5405, SIS5505, DYNARON 6100P, DYNARON 4600P, DYNARON 6200P, DYNARON 4630P, DYNARON 8601P, DYNARON 8630P, DYNARON 8600P, DYNARON 8903P, DYNARON 6201B, DYNARON 1321P, DYNARON 1320P, DYNARON 2324P, and DYNARON 9901P (all manufactured by JSR Corporation), Denka STR series (manufactured by Denka Seiken Co., Ltd.), QUINTAC 3520, QUINTAC 3433N, QUINTAC 3421, QUINTAC 3620, QUINTAC 3450, and QUINTAC 3460 (all manufactured by ZEON Corporation), TPE-SB

series (manufactured by Dainippon Sumitomo Pharma Co., Ltd.), RABALON series (manufactured by Mitsubishi Chemical Corporation), SEPTON 1001, SEPTON 8004, SEPTON 4033, SEPTON 2104, SEPTON 8007, SEPTON 2007, SEPTON 2004, SEPTON 2063, SEPTON HG252, SEPTON 8076, SEPTON 2002, SEPTON 1020, SEPTON 8104, SEPTON 2005, SEPTON 2006, SEPTON 4055, SEPTON 4044, SEPTON 4077, SEPTON 4099, SEPTON 8006, SEPTON V9461, SEPTON V9475, SEPTON V9827, HYBRAR 7311, HYBRAR 7125, HYBRAR 5127, and HYBRAR 5125 (all manufactured by Kuraray Co., Ltd.), SUMIFLEX (manufactured by Sumitomo Bakelite Company Limited), and LEOSTOMER and ACTYMER (both manufactured by Riken Technos Corporation).

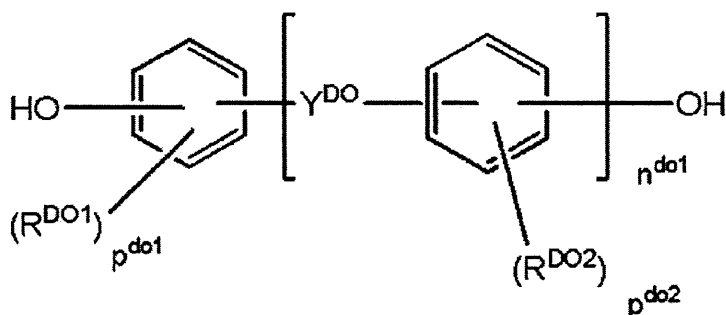
[0051] <<<<Polyester-Based Elastomer>>>>

The polyester-based elastomer is not particularly limited and can be selected as appropriate depending on the intended purpose thereof. Examples thereof include elastomers obtained by polycondensing dicarboxylic acid or a derivative thereof and a diol compound or a derivative thereof.

Examples of the dicarboxylic acid include aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, and naphthalene dicarboxylic acid; aromatic dicarboxylic acids in which these aromatic hydrogen atoms are substituted with a methyl group, an ethyl group, a phenyl group, or the like; aliphatic dicarboxylic acids having 2 to 20 carbon atoms, such as adipic acid, sebacic acid, and dodecanedicarboxylic acid; and alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid. These may be used singly or in combination of two or more kinds thereof.

Examples of the diol compound include an aliphatic diol such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,10-decanediol, or 1,4-cyclohexanediol, an alicyclic diol, and divalent phenol represented by the following structural formula.

[0052]



[0053] In the formula, Y^{DO} represents any one of an alkylene group having 1 to 10 carbon atoms, a cycloalkylene group having 4 to 8 carbon atoms, -O-, -S-, or -SO₂- or represents a

single bond. R^{DO1} and R^{DO2} each independently represent a halogen atom or an alkyl group having 1 to 12 carbon atoms. p^{do1} and p^{do2} each independently represent an integer of 0 to 4 and n^{do1} represents 0 or 1.

[0054] Specific examples of the divalent phenol r include bisphenol A, bis(4-hydroxyphenyl)methane, bis(4-hydroxy-3-methylphenyl)propane, and resorcin. There may be used singly or in combination of two or more kinds thereof.

Furthermore, as the polyester-based elastomer, a multi-block copolymer obtained by forming an aromatic polyester portion (for example, polybutylene terephthalate) with a hard segment component and forming an aliphatic polyester portion (for example, polytetramethylene glycol) with a soft segment component can be used. Examples of the multi-block copolymer include those with various grades depending on the difference between the types, the proportions, and the molecular weights of the hard segment or the soft segment. Specific examples thereof include HYTREL (manufactured by Du Pont-Toray Co., Ltd.), PELPRENE (manufactured by Toyobo Co., Ltd.), PRIMALLOY (manufactured by Mitsubishi Chemical Corporation), NUBERAN (manufactured by Teijin Limited), and ESPEL 1612 and 1620 (both manufactured by Hitachi Chemical Co., Ltd.).

[0055] <<<<Polyolefin-Based Elastomer>>>>

The polyolefin-based elastomer is not particularly limited and can be selected as appropriate depending on purposes thereof. Examples thereof include a copolymer of an α -olefin having 2 to 20 carbon atoms, such as ethylene, propylene, 1-butene, 1-hexene, and 4-methyl-1-pentene. Examples of the copolymer include an ethylene-propylene copolymer (EPR) and an ethylene-propylene-diene copolymer (EPDM). Further, other examples thereof include a copolymer of a non-conjugated diene and an α -olefin having 4 to 20 carbon atoms, such as dicyclopentadiene, 1,4-hexadiene, cyclooctadiene, methylene norbornene, ethylidene norbornene, butadiene, and isoprene. Further, a carboxy-modified nitrile rubber obtained by copolymerizing a methacrylic acid with a butadiene-acrylonitrile copolymer may also be included. Other examples thereof include an ethylene- α -olefin copolymer rubber, an ethylene- α -olefin-non-conjugated diene copolymer rubber, a propylene- α -olefin copolymer rubber, and a butene- α -olefin copolymer rubber.

Examples of commercially available products thereof include MILASTOMER (manufactured by Mitsui Chemicals, Inc.), THERMORUN (manufactured by Mitsubishi Chemical Corporation), EXACT (manufactured by Exxon Chemical Company, Inc.), ENGAGE (manufactured by The Dow Chemical Company), ESPOLEX (manufactured by

Sumitomo Chemical Co., Ltd.), Sarlink (manufactured by TOYOBO Co., Ltd.), NEWCON (manufactured by Japan Polypropylene Corporation), and EXCELINK (manufactured by JSR Corporation).

[0056] <<<<Polyurethane-Based Elastomer>>>>

The polyurethane-based elastomer is not particularly limited and can be selected as appropriate depending on the intended purpose thereof. Examples thereof include elastomers which include a constitutional unit having a hard segment formed of a low-molecular weight glycol and a diisocyanate and a soft segment formed of a high-molecular weight (long chain) diol and a diisocyanate.

Examples of the high-molecular weight (long chain) diol include polypropylene glycol, polytetramethylene oxide, poly(1,4-butylenedipate), poly(ethylene-1,4-butylenedipate), polycaprolactone, poly(1,6-hexylenecarbonate), and poly(1,6-hexylene-neopentylenedipate). The number average molecular weight of the high-molecular weight (long chain) diol is preferably in a range of 500 to 10,000.

As the low-molecular weight glycol, short chain diols such as ethylene glycol, propylene glycol, 1,4-butanediol, and bisphenol A can be used. The number average molecular weight of the short chain diol is preferably in a range of 48 to 500.

Examples of commercially available products of the polyurethane-based elastomer include PANDEX T-2185 and PANDEX T-2983N (both manufactured by DIC Corporation), MIRACTRAN (manufactured by Nippon Miractran Co., Ltd.), ELASTOLLAN (manufactured by BASF Japan Ltd.), RESAMINE (manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.), PELLETHANE (manufactured by The Dow Chemical Company), IRONRUBBER (manufactured by NOK Corporation), and MOBILON (manufactured by Nisshinbo Chemical Inc.).

[0057] <<<<Polyamide-Based Elastomer>>>>

The polyamide-based elastomer is not particularly limited and can be selected as appropriate depending on the purposes thereof. Examples thereof include an elastomer obtained by using a polyamide such as polyamide 6, polyamide 11, and polyamide 12 for a hard segment and an elastomer obtained by using a polyether and/or a polyester such as polyoxyethylene, polyoxypropylene, and polytetramethylene glycol for a soft segment. These elastomers are largely divided into two types of a polyether block amide type and a polyether ester block amide type.

Examples of commercially available products thereof include a UBE polyamide

elastomer and UBESTA XPA (both manufactured by Ube Industries, Ltd.), DAIAMIDE (manufactured by Daicel-Evonik Ltd.), PEBAX (manufactured by ARKEMA Inc.), GRILON ELX (manufactured by EMS-CHEMIE Japan Ltd.), NOVAMID (manufactured by DSM Engineering Plastics), GRELAX (manufactured by TOYOBO Co., Ltd.), polyether ester amides PA-200, PA-201, TPAE-12, and TPAE-32, and polyester amides TPAE-617 and TPAE-617C (both manufactured by T & K TOKA Co., Ltd.).

[0058] <<<<Polyacrylic Elastomer>>>>

The polyacrylic elastomer is not particularly limited and can be selected as appropriate depending on the purposes thereof. Examples thereof include an elastomer having an acrylic ester such as ethyl acrylate, butyl acrylate, methoxyethyl acrylate, and ethoxyethyl acrylate as a main component of a monomer material; and a copolymer of an acrylic ester, a glycidyl methacrylate, and an allyl glycidyl ether. Further, other examples thereof include a copolymer obtained by copolymerizing an acrylic ester and a cross-linking monomer such as acrylonitrile and ethylene. Specific examples thereof include an acrylonitrile-butyl acrylate copolymer, an acrylonitrile-butyl acrylate-ethyl acrylate copolymer, and an acrylonitrile-butyl acrylate-glycidyl methacrylate copolymer.

[0059] <<<<Other Elastomers>>>>

In the present invention, a rubber-modified epoxy resin (epoxy-based elastomer) can be used as the elastomer. The epoxy-based elastomer is obtained by modifying a part of or all epoxy groups of a bisphenol F type epoxy resin, a bisphenol A type epoxy resin, a salicylaldehyde type epoxy resin, a phenol novolak type epoxy resin, or a cresol novolak type epoxy resin with a both-terminal carboxylic acid-modified butadiene-acrylonitrile rubber, a terminal amino-modified silicone rubber, or the like.

[0060] <<<Other Polymer Compounds>>>

In the present invention, polymer compounds other than the above-mentioned resins (also referred to as other polymer compounds) can be used as the resin. Other polymer compounds can be used singly or in combination of two or more kinds thereof.

Specific examples of such other polymer compounds include a hydrocarbon resin, a novolak resin, a phenol resin, an epoxy resin, a melamine resin, a urea resin, an unsaturated polyester resin, an alkyd resin, a polyamide resin, a thermoplastic polyimide resin, a polyamide imide resin, a polybenzimidazole resin, a polybenzoxazole resin, a polyvinyl chloride resin, a polyvinyl acetate resin, a polyacetal resin, a polycarbonate resin, a polyphenylene ether resin, a polybutylene terephthalate resin, a polyethylene terephthalate

resin, a polyphenylene sulfide resin, a polysulfone resin, a polyether sulfone resin, a polyarylate resin, a polyether ether ketone resin, and a siloxane copolymer. Among these, the hydrocarbon resin, the thermoplastic polyimide resin, and the polycarbonate resin are preferable and the hydrocarbon resin is more preferable.

Moreover, in the present invention, a resin including a fluorine atom which will be described later can be used as the resin, but it is preferable that the resin including a fluorine atom (hereinafter also referred to as a fluorine resin) is not substantially included. The expression, substantially not including the fluorine resin, indicates that the content of such the fluorine resin is, for example, 0.1% by mass or less with respect to the total mass of the resin, and the content of the fluorine resin is preferably 0.05% by mass or less, and it is more preferable that the fluorine resin is not contained at all.

[0061] In the present invention, any of hydrocarbon resins can be used as the hydrocarbon resin.

The hydrocarbon resin means a resin basically formed of only carbon atoms and hydrogen atoms, but other atoms may be included in the side chain thereof as long as the basic skeleton is a hydrocarbon resin. That is, the concept of the hydrocarbon resin of the present invention includes a case where functional groups other than a hydrocarbon group are directly bonded to the main chain of the hydrocarbon resin formed of only carbon atoms and hydrogen atoms such as an acryl resin, a polyvinyl alcohol resin, a polyvinyl acetal resin, or a polyvinyl pyrrolidone resin. In this case, the content of a repeating unit formed by a hydrocarbon group being directly bonded to the main chain thereof is preferably 30% by mole or more with respect to the all repeating units of the resin.

Examples of the hydrocarbon resin that satisfies the conditions include a cyclic terpene resin, a cyclic terpene phenol resin, a modified cyclic terpene resin, a hydrogenated cyclic terpene resin, a hydrogenated cyclic terpene phenol resin, a rosin, a rosin ester, a hydrogenated rosin, a hydrogenated rosin ester, a polymerized rosin, a polymerized rosin ester, a modified rosin, a rosin-modified phenol resin, an alkylphenol resin, an aliphatic petroleum resin, an aromatic petroleum resin, a hydrogenated petroleum resin, a modified petroleum resin, an alicyclic petroleum resin, a coumarone petroleum resin, an indene petroleum resin, a polystyrene-polyolefin copolymer, an olefin polymer (for example, a methylpentene copolymer), and a cycloolefin polymer (for example, a norbornene-based copolymer, a dicyclopentadiene copolymer, and a tetracyclododecene copolymer).

[0062] The acryl resin in the present invention is a resin obtained by the polymerization of

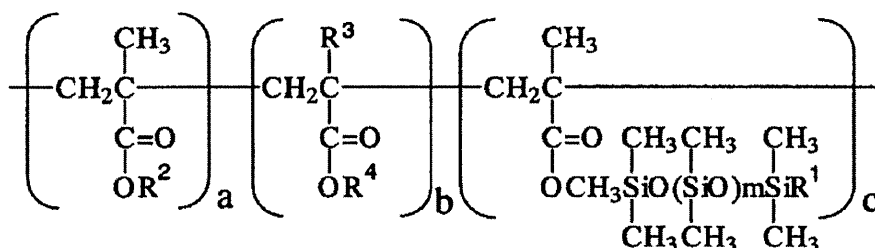
(meth)acrylate monomers.

Examples of the (meth)acrylate monomers include 2-ethylhexyl(meth)acrylate, ethyl (meth)acrylate, methyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, pentyl (meth)acrylate, n-octyl (meth)acrylate, isooctyl (meth)acrylate, isononyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, hexyl (meth)acrylate, n-nonyl (meth)acrylate, isoamyl (meth)acrylate, n-decyl (meth)acrylate, isodecyl (meth)acrylate, dodecyl (meth)acrylate, isobornyl (meth)acrylate, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate, and 2-methylbutyl (meth)acrylate.

In addition, other monomers can be copolymerized within a range where the spirit of the present invention is not impaired. In a case of copolymerizing other monomers, the amount of such other monomers is preferably 10% by mole or less of the all the monomers.

[0063] In the present invention, an acryl resin having an organopolysiloxane in a side chain is also preferable. Examples of the acryl resin having an organopolysiloxane in the side chain include an acryl resin represented by Formula (3).

Formula (3)



In Formula (3), in a case where a plurality of R¹'s are present, R¹'s may be the same as or different from each other and represent -CH₃, -C₂H₅, -CH₃(CH₂)₂, or -CH₃(CH₂)₃. In a case where a plurality of R²'s are present, R²'s may be the same as or different from each other and represent -H, -CH₃, -C₂H₅, -CH₃(CH₂)₂, or -CH₃(CH₂)₃. In a case where a plurality of R³'s are present, R³'s may be the same as or different from each other and represent -H or -CH₃. In a case where a plurality of R⁴'s are present, R⁴'s may be the same as or different from each other and represent -H, -CH₃, -C₂H₅, -CH₃(CH₂)₂, -CH₃(CH₂)₃, or an alkyl group having 1 to 6 carbon atoms substituted with at least one functional group selected from the group consisting of an epoxy group, a hydroxyl group, a carboxyl group, an amino group, an alkoxy group, a vinyl group, a silanol group, and an isocyanate group. a is 50 to 150, b is 50 to 150, and c is 80 to 600. In addition, m is 1 to 10.

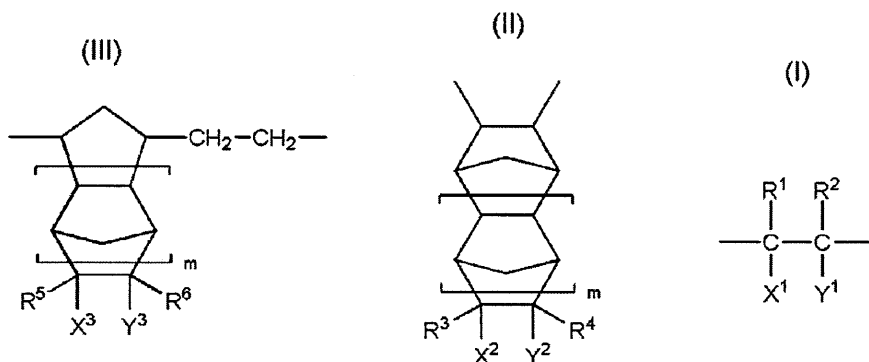
Specific examples of the acryl resin having an organopolysiloxane in the side chain include a silicone graft acryl resin, trade names: X-24-798A, X-22-8004 (R⁴: C₂H₄OH, a functional group equivalent: 3,250 g/mol), X-22-8009 (R⁴: a Si(OCH₃)₃-containing alkyl

group, a functional group equivalent: 6,200 g/mol), X-22-8053 (R^4 : H, a functional group equivalent: 900 g/mol), X-22-8084, X-22-8084EM, and X-22-8195 (R^4 : H, a functional group equivalent: 2,700 g/mol), manufactured by Shin-Etsu Chemical Co., Ltd., and SYMAC series (US-270, US-350, US-352, US-380, US-413, US-450, and the like), and RESEDA GS-1000 series (GS-1015, GS-1302, and the like), manufactured by TOAGOSEI Co., Ltd.

Moreover, in addition to the above resins, ACRYPET MF 001 manufactured by Mitsubishi Rayon Co., Ltd., and LC-5320 F1035 manufactured by 3M Japan are also exemplified.

[0064] Examples of the cycloolefin polymer include a norbornene-based copolymer, a polymer of a monocyclic olefin, a polymer of a cyclic conjugated diene, a vinyl alicyclic hydrocarbon polymer, and hydrides of these polymers. Preferred examples of the cycloolefin polymer include an addition (co)polymer having at least one repeating unit represented by Formula (II) and an addition (co)polymer formed by further having at least one repeating unit represented by Formula (I). In addition, other preferred examples of the cycloolefin polymer include a ring-opened (co)polymer having at least one cyclic repeating unit represented by Formula (III).

[0065]



[0066] In the formulae, m represents an integer of 0 to 4. R^1 to R^6 each represent a hydrogen atom or a hydrocarbon group having 1 to 10 carbon atoms, X^1 to X^3 and Y^1 to Y^3 each represent a hydrogen atom, a hydrocarbon group having 1 to 10 carbon atoms, a halogen atom, a hydrocarbon group having 1 to 10 carbon atoms and substituted with a halogen atom, $-(CH_2)_nCOOR^{11}$, $-(CH_2)_nOCOR^{12}$, $-(CH_2)_nNCO$, $-(CH_2)_nNO_2$, $-(CH_2)_nCN$, $-(CH_2)_nCONR^{13}R^{14}$, $-(CH_2)_nNR^{15}R^{16}$, $-(CH_2)_nOZ$, $-(CH_2)_nW$, or $(-CO)_2O$, $(-CO)_2NR^{17}$ constituted of X^1 and Y^1 and X^2 and Y^2 , or X^3 and Y^3 . R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , and R^{17} each represent a hydrogen atom or a hydrocarbon group (preferably a hydrocarbon group having 1 to 20 carbon atoms), Z represents a hydrocarbon group or a halogen-substituted hydrocarbon group, and W represents $SiR^{18}_pD_{3-p}$ (in which R^{18} represents a hydrocarbon group having 1 to 10 carbon atoms, D

represents a halogen atom, $-\text{OCOR}^{18}$ or $-\text{OR}^{18}$, and p represents an integer of 0 to 3). n represents an integer of 0 to 10.

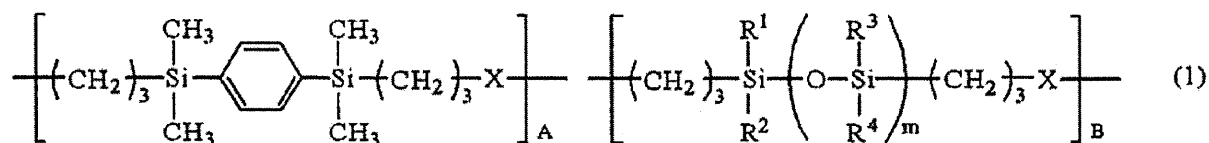
[0067] A norbornene-based polymer has been disclosed in JP1998-007732A (JP-H10-007732A), JP2002-504184A, US2004/229157A1 WO2004/070463A1, or the like. The norbornene-based polymer can be obtained by the addition polymerization of norbornene-based polycyclic unsaturated compounds. In addition, if necessary, it is possible to carry out addition polymerization of a norbornene-based polycyclic unsaturated compound with a conjugated diene such as ethylene, propylene, butene, butadiene or isoprene; or a non-conjugated diene such as ethylidene norbornene. This norbornene-based polymer was launched under the trade name of APEL from Mitsui Chemicals, Inc., in which there is a grade with a different glass transition temperature (T_g), for example, APL8008T (T_g 70°C), APL6013T (T_g 125°C) or APL6015T (T_g 145°C). Pellets such as TOPAS 8007, TOPAS 5013, TOPAS 6013, and TOPAS 6015 were launched from Polyplastics Co., Ltd. Further, Appear 3000 has been launched from Ferrania S.p.A.

[0068] A hydrogenated product of a norbornene-based polymer can be produced by subjecting a polycyclic unsaturated compound to addition polymerization or metathesis ring-opening polymerization and then hydrogenation, as disclosed in JP1989-240517A (JP-H01-240517A), JP1995-196736A (JP-H07-196736A), JP1985-026024A (JP-S60-026024A), JP1987-019801A (JP-S62-019801A), JP2003-1159767A, JP2004-309979A, or the like.

In Formula (III), R^5 and R^6 preferably represent a hydrogen atom or a methyl group, X^3 and Y^3 preferably represent a hydrogen atom, and the other groups are appropriately selected. A hydrogenated product of the norbornene-based polymer has been launched under the trade name of Arton G or Arton F from JSR Corporation, and is also commercially available under the trade name Zeonor ZF14 and ZF16, and ZEONEX 250, ZEONEX 280, and ZEONEX 480R from Zeon Corporation, which can be used.

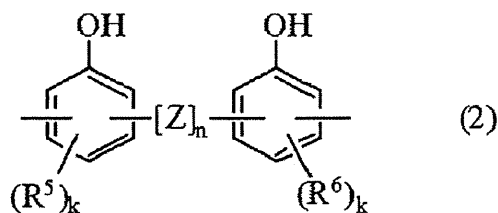
[0069] As the siloxane polymer, a siloxane polymer having a repeating unit represented by Formula (1) is preferable.

[0070]

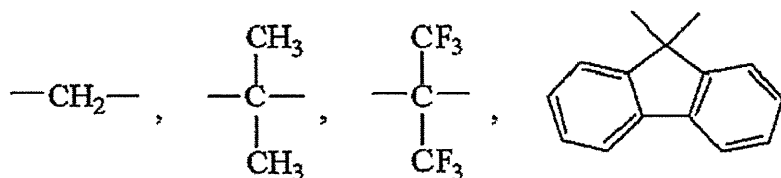


In Formula (1), R^1 to R^4 represent a monovalent hydrocarbon group such as an alkyl group having 1 to 8 carbon atoms, which may be the same as or different from each other. m

is an integer of 1 to 100, B is a positive number, and A is 0 or a positive number. X is a divalent organic group represented by Formula (2).



In Formula (2), Z is a divalent organic group selected from any of the following groups, and n is 0 or 1. R⁵ and R⁶ each independently represent an alkyl group having 1 to 4 carbon atoms or an alkoxy group having 2 to 4 carbon atoms, and may be the same as or different from each other. k's are each independently any one of 0, 1, or 2.



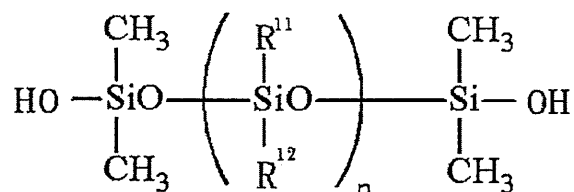
[0071] In Formula (1), specific examples of R¹ to R⁴ include a methyl group, an ethyl group, and a phenyl group, and m is preferably an integer of 3 to 60 and more preferably an integer of 8 to 40. In addition, B/A is 0 to 20, and particularly 0.5 to 5.

[0072] With regard to the details of the siloxane polymer, reference can be made to the descriptions in paragraph Nos. 0038 to 0044 of JP2013-243350A, the contents of which are incorporated herein by reference.

[0073] In addition, as the siloxane polymer, a thermoplastic siloxane polymer can be used.

The thermoplastic siloxane polymer is preferably a material in which an organopolysiloxane containing an R²¹R²²R²³SiO_{1/2} unit (R²¹, R²², and R²³ are each an unsubstituted or substituted monovalent hydrocarbon group having 1 to 10 carbon atoms or a hydroxyl group), and a SiO_{4/2} unit, with a molar ratio of the R²¹R²²R²³SiO_{1/2} unit/SiO_{4/2} unit of 0.6 to 1.7, and an organopolysiloxane represented by Formula (4) are partially subjected to dehydration condensation, the ratio of the organopolysiloxane and the organopolysiloxane to be subjected to dehydration condensation is 99:1 to 50:50, and the weight-average molecular weight is 200,000 to 1,500,000.

Formula (4)



(In Formula (4), R¹¹ and R¹² each independently represent a monovalent hydrocarbon group having 1 to 10 carbon atoms, which may have a substituent, and n is 5,000 to 10,000.)

[0074] In Formula (4), R¹¹ and R¹² are each specifically preferably a hydrocarbon group including an alkyl group such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, a t-butyl group, an n-pentyl group, a cyclopentyl group, and an n-hexyl group, a cycloalkyl group such as a cyclohexyl group, an aryl group such as a phenyl group, and a tolyl group, a group in which a part or whole of hydrogen atom(s) of the above groups is substituted by halogen atoms, and more preferably a methyl group or a phenyl group.

[0075] The weight-average molecular weight of the thermoplastic organopolysiloxane is preferably 200,000 or more and more preferably 350,000 or more, and 1,500,000 or less and more preferably 1,000,000 or less. Further, the content of a low molecular weight component having a molecular weight of 740 or less is 0.5% by mass or less, and more preferably 0.1% by mass or less.

Examples of commercially available products include SILRES 604 (manufactured by Wacker Asahikasei Silicone Co., Ltd.).

[0076] As the thermoplastic polyimide resin, a thermoplastic polyimide resin obtained by subjecting a tetracarboxylic dianhydride and a diamine to a condensation reaction by a known method can be used.

Examples of the known method include a method of performing dehydration ring closure on polyamic acid obtained by mixing the approximately equimolar amounts of tetracarboxylic dianhydride and diamine in an organic solvent, and reacting the mixture at a reaction temperature of 80°C or lower. Here, the equimolar amounts of tetracarboxylic dianhydride and diamine mean that the ratio between the molar amount of the tetracarboxylic dianhydride and the molar amount of the diamine is around 1:1. Further, as necessary, the compositional ratio between the tetracarboxylic dianhydride and the diamine may be adjusted such that the total amount of diamine to the total amount of 1.0 mol of tetracarboxylic dianhydride is in a range of 0.5 to 2.0 mol. By adjusting the compositional ratio between the tetracarboxylic dianhydride and the diamine to be within the above-mentioned range, the

weight-average molecular weight of the thermoplastic polyimide resin can be adjusted.

[0077] The tetracarboxylic anhydride is not particularly limited, and examples thereof include pyromellitic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 2,2',3,3'-biphenyltetracarboxylic dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride, 1,1-bis(3,4-dicarboxyphenyl)ethane dianhydride, bis(2,3-dicarboxyphenyl)methane dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, bis(3,4-dicarboxyphenyl)sulfone dianhydride, 3,4,9,10-perylenetetracarboxylic dianhydride, bis(3,4-dicarboxyphenyl)ether dianhydride, benzene-1,2,3,4-tetracarboxylic dianhydride, 3,4,3',4'-benzophenonetetracarboxylic dianhydride, 2,3,2',3'-benzophenonetetracarboxylic dianhydride, 2,3,3',4'-benzophenonetetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 1,2,4,5-naphthalenetetracarboxylic dianhydride, 2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic dianhydride, 2,7-dichloronaphthalene-1,4,5,8-tetracarboxylic dianhydride, 2,3,6,7-tetrachloronaphthalene-1,4,5,8-tetracarboxylic dianhydride, phenanthrene-1,8,9,10-tetracarboxylic dianhydride, pyrazine-2,3,5,6-tetracarboxylic dianhydride, thiophene-2,3,5,6-tetracarboxylic dianhydride, 2,3,3',4'-biphenyltetracarboxylic dianhydride, 3,4,3',4'-biphenyltetracarboxylic dianhydride, 2,3,2',3'-biphenyltetracarboxylic dianhydride, bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride, bis(3,4-dicarboxyphenyl)methylphenylsilane dianhydride, bis(3,4-dicarboxyphenyl)diphenylsilane dianhydride, 1,4-bis(3,4-dicarboxyphenyldimethylsilyl)benzene dianhydride, 1,3-bis(3,4-dicarboxyphenyl)-1,1,3,3-tetramethyldicyclohexane dianhydride, p-phenylenebis(trimellitate anhydride), ethylene tetracarboxylic dianhydride, 1,2,3,4-butanetetracarboxylic dianhydride, decahydronaphthalene-1,4,5,8-tetracarboxylic dianhydride, 4,8-dimethyl-1,2,3,5,6,7-hexahydronaphthalene-1,2,5,6-tetracarboxylic dianhydride, cyclopentane-1,2,3,4-tetracarboxylic dianhydride, pyrrolidine-2,3,4,5-tetracarboxylic dianhydride, 1,2,3,4-cyclobutanetetracarboxylic dianhydride, bicyclo-[2,2,2]-oct-7-ene-2,3,5,6-tetracarboxylic acid)dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2'-bis[4-(3,4-dicarboxyphenyl)phenyl]propane dianhydride,

2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride,
 2,2'-bis[4-(3,4-dicarboxyphenyl)phenyl]hexafluoropropane dianhydride,
 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride,
 1,4-bis(2-hydroxyhexafluoroisopropyl)benzenebis(trimellitate dianhydride),
 1,3-bis(2-hydroxyhexafluoroisopropyl)benzenebis(trimellitate dianhydride),
 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic dianhydride,
 tetrahydrofuran-2,3,4,5-tetracarboxylic dianhydride, 4,4'-oxydiphthalic dianhydride,
 1,2-(ethylene)bis(trimellitate anhydride), 1,3-(trimethylene)bis(trimellitate anhydride),
 1,4-(tetramethylene)bis(trimellitate anhydride), 1,5-(pentamethylene)bis(trimellitate anhydride),
 1,6-(hexamethylene)bis(trimellitate anhydride),
 1,7-(heptamethylene)bis(trimellitate anhydride), 1,8-(octamethylene)bis(trimellitate anhydride),
 1,9-(nonamethylene)bis(trimellitate anhydride),
 1,10-(decamethylene)bis(trimellitate anhydride), 1,12-(dodecamethylene)bis(trimellitate anhydride),
 1,16-(hexadecamethylene)bis(trimellitate anhydride), and
 1,18-(octadecamethylene)bis(trimellitate anhydride). These may be used singly or in combination of two or more kinds thereof. Among these, 3,4,3',4'-benzophenonetetracarboxylic dianhydride, 2,3,2',3'-benzophenonetetracarboxylic dianhydride, and 2,3,3',4'-benzophenonetetracarboxylic dianhydride are preferable, and 3,4,3',4'-benzophenonetetracarboxylic dianhydride is more preferable.

[0078] The diamine is not particularly limited and examples thereof include aromatic diamines such as o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 3,3'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, bis(4-amino-3,5-dimethylphenyl)methane, bis(4-amino-3,5-diisopropylphenyl)methane, 3,3'-diaminodiphenyldifluoromethane, 3,4'-diaminodiphenyldifluoromethane, 4,4'-diaminodiphenyldifluoromethane, 3,3'-diaminodiphenylsulfone, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfide, 3,4'-diaminodiphenyl sulfide, 4,4'-diaminodiphenyl sulfide, 3,3'-diaminodiphenyl ketone, 3,4'-diaminodiphenyl ketone, 4,4'-diaminodiphenyl ketone, 3-(4-aminophenyl)-1,1,3-trimethyl-5-aminoindane, 2,2-bis(3-aminophenyl)propane, 2,2'-(3,4'-diaminodiphenyl)propane, 2,2-bis(4-aminophenyl)propane, 2,2-bis(3-aminophenyl)hexafluoropropane, 2,2-(3,4'-diaminodiphenyl)hexafluoropropane, 2,2-bis(4-aminophenyl)hexafluoropropane, 1,3-bis(3-aminophenoxy)benzene, 1,4-bis(3-aminophenoxy)benzene,

1,4-bis(4-aminophenoxy)benzene, 3,3'-(1,4-phenylenebis(1-methylethylidene))bisaniiline,
 3,4'-(1,4-phenylenebis(1-methylethylidene))bisaniiline,
 4,4'-(1,4-phenylenebis(1-methylethylidene))bisaniiline,
 2,2-bis(4-(3-aminophenoxy)phenyl)propane,
 2,2-bis(4-(3-aminophenoxy)phenyl)hexafluoropropane,
 2,2-bis(4-(4-aminophenoxy)phenyl)hexafluoropropane,
 bis(4-(3-aminophenoxy)phenyl)sulfide, bis(4-(4-aminophenoxy)phenyl) sulfide,
 bis(4-(3-aminophenoxy)phenyl)sulfone, bis(4-(4-aminophenoxy)phenyl)sulfone,
 3,3'-dihydroxy-4,4'-diaminobiphenyl, and 3,5-diaminobenzoic acid,
 1,3-bis(aminomethyl)cyclohexane, 2,2-bis(4-aminophenoxyphenyl)propane,
 polyoxypropylenediamine, 4,9-dioxadodecane-1,12-diamine,
 4,9,14-trioxaheptadecane-1,17-diamine, 1,2-diaminoethane, 1,3-diaminopropane,
 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminoheptane,
 1,8-diaminooctane, 1,9-diaminononane, 1,10-diaminodecane, 1,11-diaminoundecane,
 1,12-diaminododecane, 1,2-diaminocyclohexane, and
 1,3-bis(3-aminopropyl)tetramethyldisiloxane.

Among these diamines, at least one selected from the group consisting of
 3-(4-aminophenyl)-1,1,3-trimethyl-5-aminoindane,
 1,3-bis(3-aminopropyl)tetramethyldisiloxane, polyoxypropylenediamine,
 2,2-bis(4-aminophenoxyphenyl)propane, 4,9-dioxadecane-1,12-diamine, 1,6-diaminohexane,
 and 4,9,14-trioxaheptadecane-1,17-diamine is preferable and
 3-(4-aminophenyl)-1,1,3-trimethyl-5-aminoindane is more preferable.

[0079] Examples of the solvent used in the reaction of the tetracarboxylic dianhydride with the diamine include N,N-dimethylacetamide, N-methyl-2-pyrrolidone, and N,N-dimethylformamide. In order to adjust the solubility of raw materials or the like, a non-polar solvent (for example, toluene and xylene) may be used together.

The reaction temperature of the tetracarboxylic dianhydride and the diamine is preferably lower than 100°C, and more preferably lower than 90°C. Further, imidization of polyamic acid is typically carried out by performing a heating treatment in an inert atmosphere (typically, in a vacuum or in a nitrogen atmosphere). The temperature of the heating treatment is preferably 150°C or higher and more preferably in a range of 180°C to 450°C.

[0080] The weight-average molecular weight (Mw) of the thermoplastic polyimide resin is

preferably 10,000 to 1,000,000, and more preferably 20,000 to 100,000.

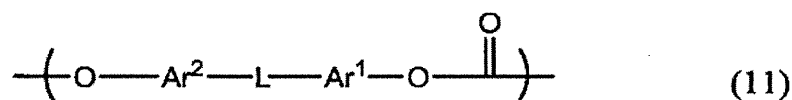
[0081] In the present invention, as the thermoplastic polyimide resin, a thermoplastic polyimide resin whose solubility in at least one solvent selected from γ -butyrolactone, cyclopentanone, N-methylpyrrolidone, N-ethyl-2-pyrrolidone, cyclohexanone, glycol ether, dimethyl sulfoxide, and tetramethylurea at 25°C is 10% by mass or more is preferable.

As the thermoplastic polyimide resin having such a solubility, a thermoplastic polyimide resin obtained by reacting 3,4,3',4'-benzophenonetetracarboxylic dianhydride and 3-(4-aminophenyl)-1,1,3-trimethyl-5-aminoindan may be exemplified. This thermoplastic polyimide resin has particularly excellent heat resistance.

[0082] As the thermoplastic polyimide resin, commercially available products may be used. Examples thereof include Durimide (registered trademark) 200, 208A, and 284 (all manufactured by Fujifilm Corporation), GPT-LT (manufactured by Gun Ei Chemical Industry Co., Ltd.), SOXR-S, SOXR-M, SOXR-U, and SOXR-C (all manufactured by Nippon Kodoshi Corporation), and EXTEM VH1003, VH1003F, VH1003M, and XH1015 (all manufactured by SABIC Japan Llc.).

[0083] In the present invention, it is preferable that the polycarbonate resin has a repeating unit represented by Formula (11).

[0084] Formula (11)



In Formula (11), Ar^1 and Ar^2 each independently represent an aromatic group, and L represents a single bond or a divalent linking group.

[0085] Ar^1 and Ar^2 in Formula (11) each independently represent an aromatic group. Examples of the aromatic group include a benzene ring, a naphthalene ring, a pentalene ring, an indene ring, an azulene ring, a heptalene ring, an indene ring, a perylene ring, a pentacene ring, an acenaphthylene ring, a phenanthrene ring, an anthracene ring, a naphthacene ring, a chrysene ring, a triphenylene ring, a fluorene ring, a biphenyl ring, a pyrrole ring, a furan ring, a thiophene ring, an imidazole ring, an oxazole ring, a thiazole ring, a pyridine ring, a pyrazine ring, a pyrimidine ring, a pyridazine ring, an indolizine ring, an indole ring, a benzofuran ring, a benzothiophene ring, an isobenzofuran ring, a quinolizine ring, a quinoline ring, a phthalazine ring, a naphthyridine ring, a quinoxaline ring, a quinoxaline ring, an isoquinoline ring, a carbazole ring, a phenanthridine ring, an acridine ring, a phenanthroline ring, a thianthrene ring, a chromene ring, a xanthene ring, a phenoxathiin

ring, a phenothiazine ring, and a phenazine ring. Among these, a benzene ring is preferable.

These aromatic groups may have a substituent, but it is preferable that these aromatic groups do not have a substituent.

Examples of the substituent which an aromatic group may have include a halogen atom, an alkyl group, an alkoxy group, and an aryl group.

Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.

As the alkyl group, an alkyl group having 1 to 30 carbon atoms may be exemplified. The number of carbon atoms of the alkyl group is more preferably in a range of 1 to 20 and still more preferably in a range of 1 to 10. The alkyl group may be linear or branched. Further, a part or all hydrogen atoms of the alkyl group may be substituted with halogen atoms. Examples of the halogen atoms include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom, and the halogen atom is preferably the fluorine atom.

As the alkoxy group, an alkoxy group having 1 to 30 carbon atoms is preferable. The number of carbon atoms of the alkoxy group is more preferably in a range of 1 to 20 and still more preferably in a range of 1 to 10. The alkoxy group may be linear, branched, or cyclic.

As the aryl group, an aryl group having 6 to 30 carbon atoms is preferable and an aryl group having 6 to 20 carbon atoms is more preferable.

[0086] The weight-average molecular weight (Mw) of the polycarbonate resin is preferably in 1,000 to 1,000,000, and more preferably 10,000 to 80,000. In a case where the weight-average molecular weight is in the range, the solubility in a solvent and the heat resistance are excellent.

[0087] Examples of commercially available products of the polycarbonate resin include PCZ-200, PCZ-300, PCZ-500, and PCZ-800 (all manufactured by Mitsubishi Gas Chemical Company, Inc.), APEC9379 (manufactured by BAYER AG), and PANLITE L-1225LM (manufactured by Teijin Limited).

[0088] <<<Tensile Elastic Modulus E of Resin>>>

A tensile elastic modulus E of the resin at 25°C in accordance with Japanese Industrial Standards (JIS) K 7161:1994 is preferably from 1 MPa to 4,000 MPa, more preferably from 1 MPa to 100 MPa, still more preferably from 1 MPa to 60 MPa, even still more preferably from 1 MPa to 35 MPa, even still further more preferably from 1 MPa to 20 MPa, even still further more preferably from 1 MPa to 15 MPa, and particularly still more

preferably from 3 MPa to 10 MPa. By setting the tensile elastic modulus E to be within such a range, it is possible to more effectively suppress the warpage.

[0089] <<<Blend Amount of Resin>>>

The temporary bonding material used in the present invention includes a resin at a ratio of preferably 50.00% to 99.99% by mass, more preferably 70.00% to 99.99% by mass, and particularly preferably 88.00% to 99.99% by mass, in the total solid content of the temporary bonding material. In a case where the content of the resin is within the range, the adhesiveness and the peelability are excellent.

In a case where an elastomer is used as the resin, the elastomer is included at a ratio of preferably 50.00% to 99.99% by mass, more preferably 70.00% to 99.99% by mass, and particularly preferably 88.00% to 99.99% by mass, in the total solid content of the temporary bonding material. In a case where the content of the elastomer is within the range, the adhesiveness and the peelability are excellent. In a case where two or more kinds of the elastomers are used, the total amount thereof is preferably within the range.

Furthermore, in a case where an elastomer is used as the resin, the content of the elastomer in the total mass of the resin is preferably 50% to 100% by mass, more preferably 70% to 100% by mass, still more preferably 80% to 100% by mass, and even still more preferably 90 to 100% by mass. Further, the resin may be formed substantially only with an elastomer. In addition, in a case where the resin is formed substantially only with an elastomer, the content of the elastomer in the total mass of the resin is preferably 99% by mass or more, and more preferably 99.9% by mass or more, and still more preferably, the resin is formed of only the elastomers.

[0090] <<Plasticizer>>

The temporary bonding material used in the present invention may contain a plasticizer as necessary. By blending a plasticizer, a temporary bonding layer having all the performances can be formed.

As the plasticizer, a phthalic ester, a fatty acid ester, an aromatic polyvalent carboxylic ester, a polyester, or the like can be used.

[0091] Examples of the phthalic ester include DMP, DEP, DBP, #10, BBP, DOP, DINP, and DIDP (all manufactured by Daihachi Chemical Industry Co., Ltd.), PL-200 and DOIP (both manufactured by CO Ester Corporation), and SANISO CIZER DUP (manufactured by New Japan Chemical Co., Ltd.).

Examples of the fatty acid ester include butyl stearate, UNISTER M-9676, UNISTRE

M-2222SL, UNISTER H-476, UNISTER H-476D, PANACET 800B, PANACET 875, and PANACET 810 (all manufactured by NOF Corporation), and DBA, DIBA, DBS, DOA, DINA, DIDA, DOS, BXA, DOZ, and DESU (all manufactured by Daihachi Chemical Industry Co., Ltd.).

Examples of the aromatic polyvalent carboxylic ester include TOTM (manufactured by Daihachi Chemical Industry Co., Ltd.), MONOCIZER W-705 (manufactured by Daihachi Chemical Industry Co., Ltd), and UL-80 and UL-100 (both manufactured by ADEKA Corporation).

Examples of the polyester include POLYCIZER TD-1720, POLYCIZER S-2002, and POLYCIZER S-2010 (all manufactured by DIC Corporation), and BAA-15 (both manufactured by Daihachi Chemical Industry Co., Ltd.).

Among the plasticizers, DIDP, DIDA, TOTM, UNISTER M-2222SL, and POLYCIZER TD-1720 are preferable, DIDA and TOTM are more preferable, and TOTM is particularly preferable.

The plasticizers may be used singly or in combination of two or more kinds thereof. [0092] From the viewpoint of preventing sublimation during heating, as the weight change of the plasticizer is measured under conditions of raising the temperature at a constant rate of 20°C/min in a nitrogen stream, the temperature at which the weight thereof is decreased by 1% by mass is preferably 250°C or higher, more preferably 270°C or higher, and particularly preferably 300°C or higher. The upper limit is not particularly limited, but can be set to, for example, 500°C or lower.

[0093] The amount of the plasticizer to be added is preferably from 0.01% by mass to 5.0% by mass, and more preferably from 0.1% by mass to 2.0% by mass, with respect to the total solid content of the temporary bonding material.

[0094] <<Solvent>>

The temporary bonding material used in the present invention contains a solvent. As the solvent, a known solvent can be used without limitation and an organic solvent is preferable.

Examples of the organic solvent include esters such as ethyl acetate, n-butyl acetate, isobutyl acetate, amyl formate, isoamyl acetate, isobutyl acetate, butyl propionate, isopropyl butyrate, ethyl butyrate and butyl butyrate, methyl lactate, ethyl lactate, alkyloxyalkyl acetate (such as alkyloxymethyl acetate, alkyloxyethyl acetate, alkyloxybutyl acetate (for example, methoxymethyl acetate, methoxyethyl acetate, methoxybutyl acetate, ethoxymethyl acetate,

and ethoxyethyl acetate)), 3-alkyloxyalkyl propionate esters (such as 3-alkyloxymethyl propionate and 3-alkyloxyethyl propionate (for example, 3-methoxymethyl propionate, 3-methoxyethyl propionate, 3-ethoxyethyl propionate, and 3-ethoxymethyl propionate)), 2-alkyloxyalkyl propionate esters (such as 2-alkyloxymethyl propionate, 2-alkyloxyethyl propionate, and 2-alkyloxypropyl propionate (for example, 2-methoxymethyl propionate, 2-methoxyethyl propionate, 2-methoxypropyl propionate, 2-ethoxymethyl propionate, and 2-ethoxyethyl propionate)), 2-alkyloxy-2-methyl methyl propionate and 2-alkyloxy-2-methylethyl propionate (for example, 2-methoxy-2-methylmethyl propionate and 2-ethoxy-2-methylethyl propionate), methyl pyruvate, ethyl pyruvate, propyl pyruvate, methyl acetoacetate, ethyl acetoacetate, methyl 2-oxobutanoate, ethyl 2-oxobutanoate, and 1-methoxy-2-propyl acetate;

ethers such as diethylene glycol dimethyl ether, tetrahydrofuran, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, methyl cellosolve acetate, ethyl cellosolve acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, and propylene glycol monopropyl ether acetate;

ketones such as methylethyl ketone, cyclohexanone, 2-heptanone, 3-heptanone, N-methyl-2-pyrrolidone, and γ -butyrolactone;

aromatic hydrocarbons such as toluene, xylene, anisole, mesitylene, ethylbenzene, propylbenzene, cumene, n-butylbenzene, sec-butylbenzene, isobutylbenzene, t-butylbenzene, amylbenzene, isoamylbenzene, (2,2-dimethylpropyl)benzene, 1-phenylhexane, 1-phenylheptane, 1-phenyloctane, 1-phenylnonane, 1-phenyldecane, cyclopropylbenzene, cyclohexylbenzene, 2-ethyltoluene, 1,2-diethylbenzene, o-cymene, indane, 1,2,3,4-tetrahydronaphthalene, 3-ethyltoluene, m-cymene, 1,3-diisopropylbenzene, 4-ethyltoluene, 1,4-diethylbenzene, p-cymene, 1,4-diisopropylbenzene, 4-t-butyltoluene, 1,4-di-t-butylbenzene, 1,3-diethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 4-t-butyl-o-xylene, 1,2,4-triethylbenzene, 1,3,5-triethylbenzene, 1,3,5-triisopropylbenzene, 5-t-butyl-m-xylene, 3,5-di-t-butyltoluene, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, and pentamethyl benzene; and

hydrocarbons such as limonene, p-menthane, nonane, decane, dodecane, and decalin.

Among these, mesitylene, t-butylbenzene, 1,2,4-trimethylbenzene, p-menthane, γ -butyrolactone, anisole, 3-ethoxymethyl propionate, 3-ethoxyethyl propionate, ethyl

cellosolve acetate, ethyl lactate, diethylene glycol dimethyl ether, butyl acetate, 3-methoxymethyl propionate, 2-heptane, cyclohexanone, ethylcarbitol acetate, butylcarbitol acetate, propylene glycol methyl ether, and propylene glycol methyl ether acetate are preferable, cyclohexanone and mesitylene are more preferable, and cyclohexanone is even more preferable.

[0095] An aspect in which two or more kinds of the solvents are mixed is also preferable from the viewpoint of improving the coating surface properties. In this case, particularly preferred is a mixed solution constituted of two or more selected from mesitylene, t-butylbenzene, 1,2,4-trimethylbenzene, p-menthane, γ -butyrolactone, anisole, 3-ethoxymethyl propionate, 3-ethoxyethyl propionate, ethyl cellosolve acetate, ethyl lactate, diethylene glycol dimethyl ether, butyl acetate, 3-methoxymethyl propionate, 2-heptane, cyclohexanone, cyclopentane, ethylcarbitol acetate, butylcarbitol acetate, propylene glycol methyl ether, and propylene glycol methyl ether acetate.

[0096] The content of the solvent in the temporary bonding material is such an amount that the total solid content concentration of the temporary bonding material is preferably 5% to 80% by mass, more preferably 10% to 50% by mass, and particularly preferably 15% to 40% by mass from the viewpoint of coatability.

Only one kind or two or more kinds of the solvents may be used. In a case where two or more kinds of the solvents are used, the total amount thereof is preferably within the above range.

In addition, the content ratio of the solvent in a temporary bonding layer obtained by applying the temporary bonding material in the shape of a layer and drying is preferably 1% by mass or less, and more preferably 0.1% by mass or less, and it is particularly preferable that the temporary bonding material does not contain the solvent at all.

[0097] <<Antioxidant>>

The temporary bonding material used in the present invention may contain an antioxidant. As the antioxidant, a phenol-based antioxidant, a sulfur-based antioxidant, a phosphorus-based antioxidant, a quinone-based antioxidant, an amine-based antioxidant, or the like can be used.

Examples of the phenol-based antioxidant include p-methoxyphenol, 2,6-di-tert-butyl-4-methylphenol, Irganox 1010, Irganox 1330, Irganox 3114, and Irganox 1035 (all manufactured by BASF Japan Ltd.), and Sumilizer MDP-S and Sumilizer GA-80 (both manufactured by Sumitomo Chemical Co., Ltd.).

Examples of the sulfur-based antioxidant include 3,3'-thiodipropionate distearyl, Sumilizer TPL-R, and Sumilizer TPM, Sumilizer TPS, Sumilizer MB, and Sumilizer TP-D (all manufactured by Sumitomo Chemical Co., Ltd.).

Examples of the phosphorus-based antioxidant include tris(2,4-di-tert-butylphenyl)phosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphate, poly(dipropyleneglycol)phenyl phosphite, diphenyl isodecyl phosphite, 2-ethylhexyldiphenyl phosphite, triphenyl phosphite, Irgafos168, and irgafos38 (all manufactured by BASF Japan Ltd.), and Sumilizer GP (manufactured by Sumitomo Chemical Co., Ltd.).

Examples of the quinone-based antioxidant include p-benzoquinone, and 2-tert-butyl-1,4-benzoquinone.

The examples of the amine-based antioxidant include dimethylaniline and phenothiazine.

As the antioxidant, Irganox 1010, Irganox 1330, 3,3'-thiodipropionate distearyl, or Sumilizer TP-D is preferable, Irganox 1010 or Irganox 1330 is more preferable, and Irganox 1010 is particularly preferable.

Furthermore, among the antioxidants, a combination of a phenol-based antioxidant and a sulfur-based antioxidant or a phosphorus-based antioxidant is preferably used, and a combination of a phenol-based antioxidant and a sulfur-based antioxidant is most preferably used. Particularly, in a case where a polystyrene-based elastomer is used as an elastomer, a combination of a phenol-based antioxidant and a sulfur-based antioxidant is preferably used. By combining a phenol-based antioxidant and a sulfur-based antioxidant, an effect of efficiently suppressing deterioration of the temporary bonding material due to an oxidation reaction can be expected. In a case where a phenol-based antioxidant and a sulfur-based antioxidant are used in combination, the ratio of the mass of the phenol-based antioxidant to the mass of the sulfur-based antioxidant is preferably 95:5 to 5:95, and more preferably 25:75 to 75:25 of the phenol-based antioxidant:the sulfur-based antioxidant.

As the combination of antioxidants, a combination of Irganox 1010 and Sumilizer TP-D, a combination of Irganox 1330 and Sumilizer TP-D, and a combination of Sumilizer GA-80 and Sumilizer TP-D are preferable, a combination of Irganox 1010 and Sumilizer TP-D and a combination of Irganox 1330 and Sumilizer TP-D are more preferable, and a combination of Irganox 1010 and Sumilizer TP-D is particularly preferable.

[0098] From the viewpoint of preventing sublimation during heating, the molecular weight of the antioxidant is preferably 400 or more, more preferably 600 or more, and particularly

preferably 750 or more.

[0099] In a case where the temporary bonding material contains an antioxidant, the content of the antioxidant is preferably 0.001% to 20.0% by mass, and more preferably 0.005% to 10.0% by mass, with respect to the total solid content of the temporary bonding material.

The antioxidant may be used singly or in combination of two or more kinds thereof. In a case where two or more kinds of the antioxidants are used, the total amount thereof is preferably within the range.

[0100] <<Other Additives>>

As necessary, various additives such as a surfactant, a curing agent, a curing catalyst, a filler, an adhesion promoter, an ultraviolet absorbing agent, and an aggregation inhibitor can be blended into the temporary bonding material used in the present invention within a range where the spirit of the present invention is not impaired. In a case where these additives are blended into the temporary bonding material, the total amount of the additives to be blended is preferably 3% by mass or less of the total solid content of the temporary bonding material.

[0101] It is preferable that the temporary bonding material used in the present invention does not include impurities such as a metal. The content of impurities included in these materials is preferably 1 part per million (ppm) by mass or less, more preferably 100 parts per trillion (ppt) by mass or less, and still more preferably 10 ppt by mass or less. It is particularly preferable that the temporary bonding material substantially does not include impurities (below the detection limit of a measurement device).

As a method for removing impurities such as a metal from the temporary bonding material, a method of filtration using a filter may be exemplified. As the pore diameter of the filter, a pore size is preferably 10 nm or less, more preferably 5 nm or less, and still more preferably 3 nm or less. As the material of the filter, a filter made of polytetrafluoroethylene, a filter made of polyethylene, or a filter made of nylon is preferable. Further, a filter which has been washed with an organic solvent in advance may be used. In the filtration through a filter step, a plurality of filters may be connected in series or in parallel. In a case where a plurality of filters are used, filters having different pore diameters and/or being formed of different materials may be used in combination. Further, various filter materials may be filtered multiple times, and a step of performing filtration multiple times may be a circulation filtration step.

Furthermore, examples of a method for reducing impurities such as a metal included in the temporary bonding material include a method of performing distillation under

conditions of suppressing contamination as much as possible by selecting a raw material having a small amount of metal as the raw material constituting the temporary bonding material, performing filtration through a filter on the raw material constituting the temporary bonding material, performing lining the inside the device using Teflon (registered trademark), and the like. Preferred conditions for performing filtration through a filter on the raw material constituting the temporary bonding material are the same as the conditions described above.

In addition to the filtration through a filter, impurities may be removed using an adsorbent and a combination of filtration through a filter and an adsorbent may be used. A known adsorbent can be used as the adsorbent and examples thereof include inorganic adsorbents such as silica gel or zeolite and organic adsorbents such as activated carbon.

[0102] <<Formation of Temporary Bonding Layer>>

A temporary bonding layer can be formed by applying the temporary bonding material onto a substrate by a spin coating method, a spray method, a roller coating method, a flow coating method, a doctor coating method, a dip coating method, or the like.

The temporary bonding layer is formed on the surface of at least one of two substrates to be temporarily adhered as described above. The temporary bonding layer may be formed on only one substrate and adhered to the other substrate, or the temporary bonding layers may be provided on both the substrates and then adhered to each other.

Subsequently, since the temporary bonding material usually includes a solvent, the solvent is volatilized by performing heating. The heating temperature is preferably a temperature higher than the boiling point of the solvent, more preferably 110°C or higher, still more preferably 130°C to 200°C, and particularly preferably 160°C to 190°C.

[0103] <<Preparation of Temporary Bonding Material>>

The temporary bonding material used in the present invention can be prepared by mixing the above-described respective components. The mixing of the respective components is usually performed in a range of 0°C to 100°C. Further, after mixing the respective components, the mixture is preferably filtered through, for example, a filter. The filtration may be performed in multiple steps or may be repeated plural times. In addition, the filtered liquid may also be refiltered.

Any filter which has been used in the filtration applications or the like from the related art can be used without particular limitation. Examples of the filter include fluorine resins such as polytetrafluoroethylene (PTFE), polyamide-based resins such as nylon-6 and

nylon 6,6, and polyolefin resins (including a high-density polyolefin and an ultrahigh-molecular weight polyolefin) such as polyethylene and polypropylene (PP). Among these materials, polypropylene and nylon are preferable.

The pore diameter of the filter is suitably, for example, approximately 0.003 to 5.0 μm . By setting the pore diameter to be within the range, it is possible to reliably remove fine impurities, aggregates, or the like included in the composition while suppressing filtration clogging.

In a case where a filter is used, different filters may be combined. At this time, the filtration with the first filter may be performed once or may also be performed twice or more times. In a case of performing filtration twice or more times through a combination of different filters, the pore diameter at the second run or later is preferably the same as or smaller than that of the first filtration run. Further, the first filter having different pore diameters may be combined within the above-mentioned range. For the pore diameter as mentioned herein, reference can be made to a nominal value of a filter maker. As a commercially available filter, a filter can be selected from various filters provided by, for example, Nihon Pall Ltd., Advantec Toyo Kaisha, Ltd., Nihon Entegris K. K, Nihon Mykrolis Ltd., and Kitz Micro Filter Corporation.

[0104] <Detergent Composition and Temporary Bonding Material>

In the present invention, in a case where the temporary bonding material includes a resin and an elastomer, an organic solvent included in the detergent composition has a solubility of the elastomer in the organic solvent at 25°C of preferably 18% to 40% by mass, and more preferably 20% to 32% by mass.

By setting the solubility to be within such a range, the removability can be further improved.

In particular, the detergent composition of the embodiment of the present invention is effective to remove the following temporary bonding material;

the silicone compound includes a polyether-modified silicone,

the ratio represented by Formula (A) of the polyether-modified silicone is 80% or more,

the content of the silicone compound in the temporary bonding material is 0.001% to 1.0% by mass, and

the temporary bonding material includes a styrene-based elastomer;

Formula (A) $\{(MO+EO)/AO\} \times 100$

in Formula (A), MO is % by mole of methylene oxide included in the polyether structure in the polyether-modified silicone, EO is % by mole of ethylene oxide included in the polyether structure in the polyether-modified silicone, and AO is % by mole of alkylene oxide included in the polyether structure in the polyether-modified silicone.

[0105] <Method for Producing Semiconductor Element>

The method for manufacturing a semiconductor element of an embodiment of the present invention includes removing a temporary bonding material including a silicone compound using a detergent composition including an acid or base and an organic solvent. By using such a configuration, the temporary bonding material including a silicone compound can be effectively removed.

Examples of an aspect in which the temporary bonding material including a silicone compound is removed include removing a temporary bonding layer on a substrate to be processed, removing excess temporary bonding materials in a step of temporary adhesion between a substrate to be processed and a carrier substrate, and removing a temporary bonding material remaining on a carrier substrate for a reuse of a carrier substrate.

Furthermore, it is needless to say that the temporary bonding material to be removed in the present invention includes components derived from the temporary bonding material. The components derived from the temporary bonding material are included in a case where the temporary bonding material includes a solvent, and examples thereof include components after removing a solvent from the temporary bonding material, and a part of components (for example, a resin and a silicone compound) included in the temporary bonding material.

With respect to details of the temporary bonding material including a silicone compound, and the detergent composition including an acid or base and an organic solvent, reference can be made to each of the descriptions of the temporary bonding material and the detergent composition as described above, and preferred ranges thereof are also the same.

In the method for manufacturing a semiconductor element of the embodiment of the present invention, the temporary bonding material is used for temporary adhesion between a carrier substrate and a substrate to be processed, the temporary bonding material to be removed by the detergent composition is preferably the temporary bonding material remaining on the substrate to be processed after peeling off the carrier substrate, or the temporary bonding material remaining on the substrate to be processed after peeling off the carrier substrate and further peeling off the temporary bonding material. The peel-off is preferably performed at a temperature of 40°C or lower, and more preferably at a temperature of 10°C to

40°C. In addition, the peel-off is preferably manual peeling and mechanical peeling.

Examples of the substrate to be processed include a device wafer which has silicon, glass, a compound semiconductor such as SiC, GaN, and GaAs, a mold resin, or the like as a substrate, and a structure formed between the surface of the substrate and the internal portion.

[0106] <<First Embodiment>>

Hereinafter, a first embodiment of a method for manufacturing a semiconductor element will be described with reference to Fig. 1. In addition, the present invention is not limited to the following embodiments.

Figs. 1(A) to 1(E) are each cross-sectional views (Figs. 1(A) and 1(B)) schematically describing temporary adhesion between a carrier substrate and a device wafer; a cross-sectional view (Fig. 1(C)) schematically illustrating a state in which the device wafer temporarily adhering to the carrier substrate is made thinner; a cross-sectional view (Fig. 1(D)) schematically illustrating a state in which the carrier substrate and the device wafer are peeled from each other; and a cross-sectional view (Fig. 1(E)) schematically illustrating a state in which the temporary bonding material has been removed from the device wafer.

[0107] In this embodiment, as illustrated in Fig. 1(A), first, a bonding carrier substrate 100 formed by providing a temporary bonding layer 11 on a carrier substrate 12 is prepared.

The temporary bonding layer 11 is formed using a temporary bonding material including a silicone compound, and is preferably in an aspect in which the temporary bonding layer 11 does not substantially include a solvent.

A device wafer 60 is formed by providing a plurality of device chips 62 on a surface 61a of a silicon substrate 61.

The thickness of the silicon substrate 61 is preferably, for example, 200 to 1,200 μm . It is preferable that the device chip 62 is preferably, for example, a metal structure and the height of the structure is more preferably 10 to 100 μm .

In the step of forming a temporary bonding layer, a step of washing the rear surface of the carrier substrate and the device wafer with the detergent composition of the embodiment of the present invention, a peeling liquid which will be described later, or an organic solvent (hereinafter referred to as “the detergent composition of the embodiment of the present invention or the like” in some cases) may be provided. Specifically, it is possible to prevent contamination of a device by removing a residue of the temporary bonding layer adhering to the end surface or the rear surface of the carrier substrate or the device wafer with the detergent composition of the embodiment of the present invention or the like, whereby it is

possible to decrease a total thickness variation (TTV) of a thin device wafer.

[0108] Next, as illustrated in Fig. 1(B), the adhesive carrier substrate 100 and the device wafer 60 are compressed to each other to perform temporary adhesion between the carrier substrate 12 and the device wafer 60.

It is preferable that the device chip 62 is completely covered with the temporary bonding layer 11. Further, it is preferable that the relationship of " $X+100 \geq Y > X$ " is satisfied in a case where the height of the device chip is denoted as $X \mu\text{m}$ and the thickness of the temporary bonding layer is denoted as $Y \mu\text{m}$.

The complete coverage of the device chip 62 with the temporary bonding layer 11 is effective in a case where the total thickness variation (TTV) of the thin device wafer is intended to be further decreased (that is, in a case where the flatness of the thin device wafer is intended to be further improved).

That is, at the time of making the device wafer thinner, it is possible to almost eliminate an uneven shape from the contact surface with the carrier substrate 12 by protecting the plurality of device chips 62 with the temporary bonding layer 11. Therefore, even in a case where the device wafer is made thinner, a possibility that a shape derived from the plurality of device chips 62 is transferred to a rear surface 61b1 of the thin device wafer is decreased, and as the result, the TTV of the thin device wafer to be finally obtained can be further reduced.

[0109] Next, as illustrated in Fig. 1(C), the rear surface 61b of the silicon substrate 61 is subjected to a mechanical or chemical treatment (the treatment is not particularly limited and examples thereof include a treatment for making a thinner film, such as gliding and chemical and mechanical polishing (CMP), a treatment at a high temperature in vacuo such as chemical vapor deposition (CVD) and physical vapor deposition (PVD), a treatment using chemicals such as an organic solvent, an acidic treatment liquid, and a basic treatment liquid, a plating treatment, irradiation with actinic rays, a heating treatment, and a cooling treatment). In Fig. 1(C), the thickness of the silicon substrate 61 is decreased (for example, the silicon substrate 61 is made thinner to the above-mentioned thickness), thereby obtaining a thin device wafer 60a.

[0110] After the device wafer is made thinner, a step of washing a temporary bonding layer protruding to the outside the area of the substrate surface of the device wafer with the detergent composition of the embodiment of the present invention, or the like may be provided at the stage of before the treatment under a high temperature condition in a vacuum

is performed. Specifically, the deformation or deterioration of the temporary bonding layer caused by directly subjecting the treatment under a high temperature condition in a vacuum to the temporary bonding layer can be prevented by removing the protruding portion of the temporary bonding layer with the detergent composition of the embodiment of the present invention, or the like after the device wafer is made thinner.

In the present invention, it is preferable that the area of the film surface of the temporary bonding layer is smaller than the area of the substrate surface of the carrier substrate. Further, in the present invention, in a case where the diameter of the substrate surface of the carrier substrate is denoted as $C \mu\text{m}$, the diameter of the substrate surface of the device wafer is denoted as $D \mu\text{m}$, and the diameter of the film surface of the temporary bonding layer is denoted as $T \mu\text{m}$, it is more preferable that the relationship of “ $(C-200) \geq T \geq D$ ” is satisfied. Further, in a case where the diameter of the substrate surface of the carrier substrate is denoted as $C \mu\text{m}$, the diameter of the substrate surface of the device wafer is denoted as $D \mu\text{m}$, the diameter of the film surface of the temporary bonding layer on a side where the temporary bonding layer is in contact with the carrier substrate is set to $T_C \mu\text{m}$, and the diameter of the film surface of the temporary bonding layer on a side where the temporary bonding layer is in contact with the device wafer is set to $T_D \mu\text{m}$, it is preferable that the relationship of “ $(C-200) \geq T_C > T_D \geq D$ ” is satisfied. By adopting this configuration, the deformation or deterioration of the temporary bonding layer caused by directly subjecting the treatment at a high temperature in vacuo to the temporary bonding layer can be further suppressed.

Furthermore, the area of the film surface of the temporary bonding layer indicates the area as it is viewed from a direction perpendicular to the carrier substrate and the unevenness of the film surface will not be considered. The same applies to the substrate surface of the device wafer. That is, the substrate surface of the device wafer as mentioned herein indicates the surface corresponding to the surface 61a of Fig. 1 and this is the surface on a side where device chips are provided. The same applies to the diameter of the film surface of the temporary bonding layer or the like.

In addition, a diameter T of the film surface of the temporary bonding layer is obtained using an equation of “ $T = (T_C + T_D) / 2$ ” in a case where the diameter of the film surface of the temporary bonding layer on a side where the temporary bonding layer is in contact with the carrier substrate is denoted as $T_C \mu\text{m}$ and the diameter of the film surface of the temporary bonding layer on a side where the temporary bonding layer is in contact with the device wafer

is denoted as T_D μm . The diameter of the substrate surface of the carrier substrate and the diameter of the substrate surface of the device wafer indicate the diameter of the surface on a side where the temporary bonding layer is in contact with the carrier substrate or the device wafer.

Moreover, in the carrier substrate or the like, the term “diameter” is used for definition, the carrier substrate or the like does not need to be circular (perfect circle) in a mathematical sense. It is sufficient that the carrier substrate or the like is substantially circular. In a case where the carrier substrate or the like does not have a shape of a perfect circle, the diameter as converted to a perfect circle with the same area is defined as the diameter.

In addition, as the mechanical or chemical treatment, a treatment of forming a through-hole (not illustrated) penetrating the silicon substrate from the rear surface 61b1 of the thin device wafer 60a and then thrilling a through-silicon electrode (not illustrated) in the through-hole may be performed after the treatment for making a film thinner.

Furthermore, a heating treatment may be performed after the carrier substrate 12 and the device wafer 60 are temporarily adhered to each other and before the carrier substrate 12 and the device wafer 60 are peeled from each other. As an example of the heating treatment, a treatment of performing heating during the mechanical or chemical treatment may be exemplified.

The highest temperature to be reached during the heating treatment is preferably 80°C to 400°C, more preferably 130°C to 400°C, and still more preferably 180°C to 350°C. It is preferable that the highest temperature during the heating treatment is set to be lower than the decomposition temperature of the temporary bonding layer. It is preferable that the heating treatment is performed by heating the surface at the highest temperature for 30 seconds to 30 minutes, and it is more preferable that the heating treatment is performed by heating the surface at the highest temperature for 1 minute to 10 minutes.

[0111] Next, the carrier substrate 12 is peeled from the thin device wafer 60a (device wafer which has been subjected to a mechanical or chemical treatment) as illustrated in Fig. 1(D). The temperature at the time of peeling is preferably 40°C or lower, or can also be set to 30°C or lower. The lower limit value of the temperature at the time of peeling is, for example, 0°C or higher, and preferably 10°C or higher. The peeling in the present invention is highly valuable in that it can be performed at a normal temperature of approximately 15°C to 35°C.

The peeling method is not particularly limited, but it is preferable that the thin device wafer 60a is fixed, the carrier substrate 12 is peeled off by pulling the end portion up to the

direction perpendicular to the device wafer 60a from the end portion. At this time, it is preferable that the peeling at an interface is performed at the interface between the carrier substrate 12 and the temporary bonding layer 11. The pulling speed at a time of peeling is preferably a speed of 30 to 100 mm/min, and more preferably a speed of 40 to 80 mm/min. In this case, it is preferable that an adhesion strength A at the interface between the carrier substrate 12 and the temporary bonding layer 11 and an adhesion strength B between the surface 61a of the device wafer and the temporary bonding layer 11 satisfy the following formula.

$$A < B \quad \dots \text{Formula (A1)}$$

Furthermore, the force of pulling the end portion at the time of peeling is preferably 0.33 N/mm or less, and can also be set to 0.2 N/mm or less. The lower limit value thereof is preferably 0.07 N/mm or more. The force at this time can be measured using a force gauge. [0112] In addition, a thin device wafer can be obtained by removing the temporary bonding layer 11 from the thin device wafer 60a as illustrated in Fig. 1(E).

Examples of the method of removing the temporary bonding layer 11 include a method of removing the temporary bonding layer using a the detergent composition of the embodiment of the present invention (a method of peeling and removing the temporary bonding layer after the temporary bonding layer is swollen by the detergent composition of the embodiment of the present invention, a method of destroying and removing the temporary bonding layer by spraying the detergent composition of the embodiment of the present invention to the temporary bonding layer, a method of dissolving and removing the temporary bonding layer by dissolving the temporary bonding layer in the detergent composition of the embodiment of the present invention, and the like), and a method of removing the temporary bonding layer by irradiating the temporary bonding layer with actinic rays, radiation, or heat so that the temporary bonding layer is decomposed and vaporized.

From the viewpoint of reducing the amount of a solvent to be used, it is preferable that the temporary bonding layer is peeled and removed (peeled off) while its state is maintained in the shape of a film. The method of peeling and removing the temporary bonding layer while its state is maintained in the shape of a film means that the temporary bonding layer is peeled and removed (peeled off) by maintaining the state of the temporary bonding material in the shape of a film while not being subjected to a chemical treatment using the detergent composition of the embodiment of the present invention, or the like. In a case where the temporary bonding layer is peeled and removed while its state is maintained in

the shape of a film, manual peeling or mechanical peeling is preferable. In order to peel and remove the temporary bonding layer while its state is maintained in the shape of a film, it is preferable that an adhesion strength B between the surface 61a of the device wafer and the temporary bonding layer 11 satisfies Formula (B1).

$$B \leq 4 \text{ N/cm} \cdots \text{Formula (B1)}$$

Furthermore, the peeling liquid in the present invention means that it does not include an acid or a base as a peeling liquid of a temporary bonding material including water or an organic solvent. Examples of the organic solvent include an organic solvent used as the detergent composition of the embodiment of the present invention.

[0113] The carrier substrate 12 is peeled from the thin device wafer 60a, and then the thin device wafer 60a is subjected to various known treatments, thereby manufacturing a semiconductor element having the thin device wafer 60a.

[0114] <<Second Embodiment>>

A second embodiment of a method for manufacturing a semiconductor will be described with reference to Fig. 2. The same elements as those in the first embodiment described above are denoted by the same reference numerals and the description thereof will not be repeated.

Figs. 2(A) to 2(E) are respectively cross-sectional views (Figs. 2(A) and 2(B)) schematically describing temporary adhesion between a carrier substrate and a device wafer, a cross-sectional view (Fig. 2(C)) schematically illustrating a state in which the device wafer temporarily adhering to the carrier substrate is made thinner, a cross-sectional view (Fig. 2(D)) schematically illustrating a state in which the carrier substrate and the device wafer are peeled from each other, and a cross-sectional view (Fig. 2(E)) schematically illustrating a state after the temporary bonding layer has been removed from the device wafer.

This embodiment is different from the first embodiment described above in that the temporary bonding layer is formed on the surface 61a of the device wafer as illustrated in Fig. 2(A).

In a case where a temporary bonding layer 11a is provided on the surface 61a of the device wafer 60, the temporary bonding layer can be formed by applying a temporary bonding material to the surface 61a of the device wafer 60 (preferably the surface is coated with the temporary bonding material) and then drying (baking) the surface thereof. Drying can be performed, for example, at 60°C to 150°C for 10 seconds to 2 minutes.

Next, as illustrated in Fig. 2(B), the carrier substrate 12 and the device wafer 60 are

compressed to each other to perform temporary adhesion between the carrier substrate 12 and the device wafer 60. Next, a rear surface 61b of the silicon substrate 61 is subjected to a mechanical or chemical treatment as illustrated in Fig. 2(C), and then the thickness of the silicon substrate 61 is reduced as illustrated in Fig. 2(C), thereby obtaining a thin device wafer 60a. Next, as illustrated in Fig. 2(D), the carrier substrate 12 is peeled from the thin device wafer 60a. Further, the temporary bonding layer 11a is removed from the thin device wafer 60a as illustrated in Fig. 2(E).

[0115] The method for manufacturing a semiconductor element of the embodiment of the present invention is not limited to the above-mentioned embodiments, and modifications, improvements, and the like can be made as appropriate.

Furthermore, in the above-mentioned embodiments, a silicon substrate is exemplified as a device wafer, but the embodiments are not limited thereto and any of members to be treated which can be provided for the mechanical or chemical treatment in the method for manufacturing a semiconductor element can be used.

In addition, in the above-mentioned embodiments, a treatment for making a device wafer thinner and a treatment for forming a through-silicon electrode are exemplified as the mechanical or chemical treatment for the device wafer (silicon substrate), but the embodiments are not limited thereto and any treatment which is required for the method for manufacturing a semiconductor element can be exemplified.

In addition, the shape, the dimension, the number, the arrangement sites, and the like of the device chips in the device wafer which are exemplified in the above-mentioned embodiments are optional and are not limited.

Examples

[0116] Hereinafter, the present invention will be described in more detail with reference to Examples, but the present invention is not limited to Examples below unless it departs from the scope of the present invention. Further, “part” and “%” are on a mass basis unless otherwise specified.

[0117] <Preparation of Temporary Adhesive>

As shown below, the respective components of a temporary bonding material were mixed to obtain a homogeneous solution, and the solution was then filtered using a polytetrafluoroethylene-made filter having a pore diameter of 0.2 μm , thereby preparing a temporary bonding material.

[0118] <<Composition of Temporary Adhesive (Examples 1 to 21 and Comparative Examples

1 to 5)>>

- SEPTON 4033 (manufactured by Kuraray Co., Ltd., polystyrene-based elastomer): 98 parts by mass

- Irganox 1010 (manufactured by BASF Japan): 1 part by mass
- Sumilizer TP-D (manufactured by Sumitomo chemical Co., Ltd.): 1 part by mass
- Silicone compound, the compound described in Table 1: 0.04 parts by mass
- Mesitylene (manufactured by Toyo Gosei Co., Ltd.): 400 parts by mass

[0119] <<Composition of Temporary Adhesive (Example 22)>>

- SILRES 604 (siloxane copolymer, manufactured by Wacker Asahikasei Silicone Co., Ltd.): 100 parts by mass
- Silicone compound, the compound described in Table 1: 0.04 parts by mass
- Methyl isobutyl ketone (manufactured by Sankyo Chemical Co., Ltd.): 300 parts by mass

[0120] <<Composition of Temporary Adhesive (Example 23)>>

- LC-5320F1035 (acryl resin, manufactured by 3M Limited, Japan): 100 parts by mass
- Silicone compound, the compound described in Table 1: 0.04 parts by mass

[0121] <Preparation of Detergent Composition>

As shown below, the respective components of a detergent composition were mixed to obtain a homogeneous solution, and the solution was then filtered using a polytetrafluoroethylene-made filter having a pore diameter of 0.2 μm , thereby preparing a detergent composition.

Furthermore, with regard to some of Examples and Comparative Examples, some of the components shown below are not described in Table 1, which means that the components are not blended in such Examples or Comparative Examples.

<<Composition of Detergent Composition>>

- Compound 1 described in Table 1: Amount described in Table 1
- Compound 2 described in Table 1: Amount described in Table 1
- Solvent described in Table 1: Amount described in Table 1

[0122] <Formation of Laminate>

<<Formation of Laminate A>>

Using a silicon wafer in the shape of a disc having a diameter of 12 inches (1 inch is 2.54 cm) as a carrier substrate, the temporary bonding material was formed into the shape of a

layer on the surface of the silicon wafer with a coating device (EVG 101, manufactured by EV Group, Japan). The layer was heated at 100°C for 3 minutes using a hot plate (EVG 105, manufactured by EV Group, Japan), and further heated at 180°C for 3 minutes to obtain a laminate A in which the temporary bonding layer is formed on the surface of the carrier substrate. The thickness of the temporary bonding layer was 60 μm .

The carrier substrate of the obtained laminate A was set on the low side in a coating device (EVG 101, manufactured by EV Group, Japan), and a bevel portion of the carrier substrate was subjected to a back side rinse (BSR) treatment with mesitylene at a flow rate of 20 mL/min while increasing the rotation speed to 2,000 rpm from a rotation speed of 1,250 rpm at an acceleration speed of 50 rpm/s, thereby removing the temporary bonding layer attached onto the bevel portion.

[0123] <<Bonding Treatment>>

A substrate to be processed on which a titanium layer with a thickness of 10 nm and a copper layer with a thickness of 50 nm were formed in this order on the surface of a silicon wafer in the shape of a disc having a diameter of 12 inches by sputtering was obtained.

The laminate A obtained above and the substrate to be processed obtained above were thermally compressed at a temperature 200°C and a pressure of 0.3 MPa for 1 minute under an atmospheric pressure of 1 Pa, using a wafer bonding device (EVG 540, manufactured by EV Group, Japan), thereby obtaining a laminate B. For the compression, the copper layer and the temporary bonding layer were arranged to be in contact with each other.

[0124] <<Back Grinding Processing>>

The rear surface (as side on which the temporary bonding layer was not provided) of the substrate to be processed in the laminate B obtained above was polished using a back grinder (DFG8540, manufactured by DISCO Corporation) to a thickness of 40 μm , thereby obtaining a back grinding-processed (thin) laminate C.

[0125] <<Temporary Adhesion Performance>>

The surface which had been subjected to a back grinding processing in the laminate C was set to the lower side and the silicon wafer on the lower side was fixed to the center of a dicing tape together with a dicing frame using a dicing tape mounter. Thereafter, using a wafer debonder device (Synapse Z, manufactured by Tokyo Electron Limited), the silicon wafer on the upper side was pulled upward at a speed of 3 mm/min in a vertical direction to the silicon wafer on the lower side and was peeled off at 25°C, thereby obtaining a laminate D formed of a temporary bonding layer (or a residue derived from the temporary bonding

material) and a substrate to be processed. It was checked if the silicon wafer on the upper side was able to be peeled off while the silicon wafer on the low side was not cracked. Evaluation was performed in accordance with the following standards.

A: It was possible to peel the wafer.

B: The adhesive force was weak, a periphery of the wafer was partly detached but it was possible to peel the wafer, or the wafer was cracked at a pulling speed of 3 mm/min, but it was possible to peel the wafer at a pulling speed of 2 mm/min.

C: Not corresponded to Any of A and B.

[0126] <<Evaluation of Residues>>

The temporary bonding material (including a residue derived from the temporary bonding material) of the laminate D obtained by performing the evaluation of the peeling was removed by supplying a detergent composition while rotating the laminate D, using a wafer debonder device (manufactured by Tokyo Electron Limited, Synapse Z).

The surface of the substrate to be processed after washing was measured with a monochromatic Al-K α -ray (energy value; 1486.6 eV, output: 25 W, voltage; 15 kV, and beam diameter of 200 μm) as an X-ray source, using a Quantera SXM device (manufactured by ULVAC PHI, Inc.). The measurement was performed in a measurement region of 1,400 $\times$ 700 μm^2 under measurement conditions of a pass energy=140 eV, a step size=0.1 eV, and a cumulative number of 1 to 3, and the existence ratios of carbon atoms and silicon atoms were evaluated in accordance with the following standards.

<<<Existence Ratio of Carbon Atoms>>>

A: Carbon atoms exist at a ratio of less than 40% by mole.

B: Carbon atoms exist at a ratio of 40% by mole or more and less than 50% by mole.

C: Carbon atoms exist at a ratio of 50% by mole or more and less than 60% by mole.

D: Carbon atoms exist at a ratio of 60% by mole or more.

<<<Existence Ratio of Silicon Atoms>>>

A: Silicon atoms exist at a ratio of less than 0.1% by mole.

B: Silicon atoms exist at a ratio of 0.1% by mole or more and less than 1% by mole.

C: Silicon atoms exist at a ratio of 1% by mole or more and less than 3% by mole.

D: Silicon atoms exist at a ratio of 3% by mole or more.

[0127] [Table 1]

	Silicone compound included in temporary bonding material	Detergent composition					Evaluation			
		Compound 1	Parts by mass	Compound 2	Parts by mass	Solvent	Parts by mass	Evaluation of temporary adhesion performance	Existence ratio of carbon atoms	Existence ratio of silicon atoms
Example 1	Si-1	A-1	0.1	-	-	S-1	100	A	A	A
Example 2	Si-2	A-2	0.1	-	-	S-1	100	A	A	A
Example 3	Si-3	A-3	0.1	-	-	S-1	100	A	A	A
Example 4	Si-5	A-3	0.1	-	-	S-1	100	C	A	A
Example 5	Si-6	A-3	0.1	-	-	S-1	100	C	A	A
Example 6	Si-7	A-3	0.1	-	-	S-1	100	B	A	A
Example 7	Si-4	A-8	0.1	-	-	S-1	100	A	A	A
Example 8	Si-1	A-9	0.1	-	-	S-1	100	A	A	A
Example 9	Si-2	A-10	0.1	-	-	S-1	100	A	A	A
Example 10	Si-3	A-3	0.001	-	-	S-1	100	A	A	B
Example 11	Si-4	A-3	0.0001	-	-	S-1	100	A	A	C
Example 12	Si-1	A-3	0.1	-	-	S-2	100	A	A	A
Example 13	Si-2	A-3	0.1	-	-	S-3	100	A	A	A
Example 14	Si-3	A-3	0.1	-	-	S-4	100	A	C	A
Example 15	Si-4	A-3	0.1	-	-	S-5	100	A	B	A
Example 16	Si-1	A-3	0.1	-	-	S-6	100	A	B	A
Example 17	Si-1	A-3	0.05	A-2	0.05	S-1	100	A	A	A
Example 18	Si-2	A-3	0.1	-	-	S-4	100	C	B	C
Example 19	Si-3	A-3	0.1	-	-	S-4	100	C	C	A
Comparative Example 1	-	A-3	0.1	-	-	S-1	100	D	A	A
Comparative Example 2	Si-1	-	0.1	-	-	S-1	100	A	A	D
Comparative	Si-2	-	0.1	-	-	S-5	100	A	B	D

[0128] The compounds described in Table 1 are as follows.

[Table 2]

Symbol	Trade name	Manufacturer	Structure	EO ratio/%
Si-1	TSF4445	Momentive Performance Materials Japan Co., Ltd.	Polyether-modified organopolysiloxane	100
Si-2	TSF4446	Momentive Performance Materials Japan Co., Ltd.	Polyether-modified organopolysiloxane	100
Si-3	Silwet L-7605	Momentive Performance Materials Japan Co., Ltd.	Polyether-modified organopolysiloxane	100
Si-4	KF-6017	Shin-Etsu Chemical Co., Ltd.	Polyether-modified organopolysiloxane	100
Si-5	Silwet L-7200	Momentive Performance Materials Japan Co., Ltd.	Polyether-modified organopolysiloxane	75
Si-6	KP-323	Shin-Etsu Chemical Co., Ltd.	Silicone single product	0
Si-7	Triethoxy(1H,1H,2H,2H-nonafluorohexyl)silane	Tokyo Chemical Industry Co., Ltd.	Fluorine atom-containing silane coupling agent	-

In the table, Si-1 to Si-5 are modified silicone oils.

[0129] [Table 3]

Symb ol	Trade name	Manufacturer	CAS No.	Type	ClogP	pKa	pKb	(ClogP-pKa) or (ClogP-pKb)
A-1	p-Toluenesulfonic acid	Tokyo Chemical Industry Co., Ltd.	104-15-4	Acid	-0.15	-2.8		2.65
A-2	p-Ethylbenzenesulfonic acid	Sigma-Aldrich Japan Co., LLC	98-69-1	Acid	0.38	-2		2.38
A-3	n-Dodecylbenzenesulfonic acid	Kanto Chemical Co., Inc.	27176-87-0	Acid	5.67	-1.84		7.51
A-4	Dichloroacetic acid	Tokyo Chemical Industry Co., Ltd.	79-43-6	Acid	0.98	1.29		-0.31
A-5	Lauric acid	Tokyo Chemical Industry Co., Ltd.	143-07-7	Acid	4.85	5.02		-0.17
A-6	Aniline	Nippon Refine Co., Ltd.	62-53-3	Base	0.81		9.1	-8.29
A-7	Diethanolamine	Tokyo Chemical Industry Co., Ltd.	111-42-2	Base	-1.54		5.1	-6.64
A-8	Triethylamine	Tokyo Chemical Industry Co., Ltd.	121-44-8	Base	1.61		3.3	-1.69
A-9	Piperidine	Tokyo Chemical Industry Co., Ltd.	110-89-4	Base	0.94		2.9	-1.96
A-10	1,5-Diazabicyclo[4,3,0]-5-nonene	San-Apro Ltd.	3001-72-7	Base	0.02		1.3	-1.28

[0130] [Table 4]

Symbol	Trade name	Manufacturer	CAS	Type
S-1	Mesitylene	Toyo Gosei Co., Ltd.	108-67-8	Aromatic compound
S-2	t-Butylbenzene	Toyo Gosei Co., Ltd.	98-06-6	Aromatic compound
S-3	p-Diethylbenzene	Toray Co., Ltd.	105-05-5	Aromatic compound
S-4	Cyclohexanone	Ube Industries, Ltd.	108-94-1	Cyclic ketone
S-5	p-Menthane	Nippon Terpene Chemical Co., Ltd.	99-82-1	Cyclic terpene
S-6	Decahydronaphthalene	Nippon Steel & Sumikin Chemical Co., Ltd.	91-17-8	Saturated alicyclic compound
S-7	Water	-	7732-18-5	Water

[0131] As clearly seen from Table 1, in a case where the detergent composition of the embodiment of the present invention was used, the removability of the temporary bonding material was excellent and there was a small amount of the residue (Examples 1 to 19).

On the other hand, in a case where a silicone compound was not included in the temporary bonding material (Comparative Example 1), the temporary adhesion performance was evaluated to be deteriorated.

In a case where the detergent composition did not include an acid and a base (Comparative Examples 2 and 3), the (ClogP-pKa) of the acid was in the range of 0 to 10 (Comparative Examples 6 and 7), and the (ClogP-pKb) of the base was in the range of -5 to 0 (Comparative Examples 8 and 9), the existence ratio of the silicon atoms were remarkably increased.

Furthermore, in a case where water other than an organic solvent was used as the solvent, the existence ratio of carbon atoms was remarkably increased (Comparative Examples 4 and 5).

In particular, a kit with a temporary bonding material including a styrene-based elastomer and a polyether-modified silicone having a ratio represented by Formula (A) of 80% or more, and the detergent composition of the embodiment of the present invention accomplished high peelability and had a small amount of a residue (Examples 1 to 4, and Examples 7 to 19).

Explanation of References

[0132] 11, 11a: temporary bonding layer

12: carrier substrate

60: device wafer

60a: thin device wafer

61: silicon substrate

61a: surface

61b, 61b1: rear surface

62: device chip

100: adhesive carrier substrate

WHAT IS CLAIMED IS:

1. A kit comprising:

a detergent composition including an acid or base and an organic solvent; and

a temporary bonding material including a silicone compound,

wherein a value represented by Formula (a) of the acid is 0 to 10 and a value represented by Formula (b) of the base is -5 to 0;

Formula (a) ClogP-pKa

Formula (b) ClogP-pKb

in Formulae (a) and (b), ClogP represents a value represented by a base-10 logarithm logP of P which is a 1-octanol/water partition coefficient representing a ratio of an equilibrium concentration in 1-octanol and water, pKa represents an acid dissociation constant, and pKb represents a base dissociation constant.

2. The kit according to claim 1,

wherein the silicone compound is a silicone oil.

3. The kit according to claim 1 or 2,

wherein the silicone compound includes a polyether-modified silicone.

4. The kit according to claim 3,

wherein a ratio represented by Formula (A) of the polyether-modified silicone is 80% or more;

Formula (A) $\{(\text{MO}+\text{EO})/\text{AO}\}\times 100$

in Formula (A), MO is % by mole of methylene oxide included in the polyether structure in the polyether-modified silicone, EO is % by mole of ethylene oxide included in the polyether structure in the polyether-modified silicone, and AO is % by mole of alkylene oxide included in the polyether structure in the polyether-modified silicone.

5. The kit according to any one of claims 1 to 4,

wherein a content of the silicone compound in the temporary bonding material is 0.001% to 1.0% by mass.

6. The kit according to any one of claims 1 to 5,
wherein the temporary bonding material includes an elastomer.
7. The kit according to claim 6,
wherein the elastomer is a polystyrene-based elastomer.
8. The kit according to claim 6 or 7,
wherein a solubility of the elastomer in the organic solvent at 25°C is 18% to 40% by mass.
9. The kit according to any one of claims 1 to 8,
wherein the organic solvent is at least one selected from an aromatic compound, a saturated alicyclic compound, a cyclic ketone, or a cyclic terpene.
10. The kit according to any one of claims 1 to 9,
wherein the detergent composition includes an acid and the acid is at least one selected from a phosphoric acid, a phosphonic acid, a phosphinic acid, a sulfonic acid, or a carboxylic acid.
11. The kit according to any one of claims 1 to 9,
wherein the detergent composition includes a base and the base is at least one selected from an aliphatic amine, an aromatic amine, or a heterocyclic amine.
12. The kit according to any one of claims 1 to 11,
wherein the mass ratio of the acid or base to the organic solvent is 0.0001:99.9999 to 50:50.
13. A detergent composition for a temporary bonding material including a silicone compound, comprising:
an acid or base; and
an organic solvent,
wherein a value represented by Formula (a) of the acid is 0 to 10 and a value represented by Formula (b) of the base is -5 to 0;

Formula (a) ClogP-pKa

Formula (b) ClogP-pKb

in Formulae (a) and (b), ClogP represents a value represented by a base-10 logarithm logP of P which is a 1-octanol/water partition coefficient representing a ratio of an equilibrium concentration in 1-octanol and water, pKa represents an acid dissociation constant, and pKb represents a base dissociation constant.

14. The detergent composition according to claim 13,

wherein the organic solvent is at least one selected from an aromatic compound, a saturated alicyclic compound, a cyclic ketone, or a cyclic terpene.

15. The detergent composition according to claim 13 or 14,

wherein the detergent composition includes an acid and the acid is at least one selected from a phosphoric acid, a phosphonic acid, a phosphinic acid, a sulfonic acid, or a carboxylic acid.

16. The detergent composition according to claim 13 or 14,

wherein the detergent composition includes a base and the base is at least one selected from an aliphatic amine, an aromatic amine, or a heterocyclic amine.

17. The detergent composition according to any one of claims 13 to 16,

wherein the mass ratio of the acid or base to the organic solvent is 0.0001:99.9999 to 50:50.

18. The detergent composition according to any one of claims 13 to 17,

wherein the silicone compound includes a polyether-modified silicone, a ratio represented by Formula (A) of the polyether-modified silicone is 80% or more,

the content of the silicone compound in the temporary bonding material is 0.001% to 1.0% by mass, and

the temporary bonding material includes a polystyrene-based elastomer;

Formula (A) $\{(\text{MO}+\text{EO})/\text{AO}\}\times 100$

in Formula (A), MO is % by mole of methylene oxide included in the polyether structure in the polyether-modified silicone, EO is % by mole of ethylene oxide included in

the polyether structure in the polyether-modified silicone, and AO is % by mole of alkylene oxide included in the polyether structure in the polyether-modified silicone.

19. A method for manufacturing a semiconductor element, comprising removing a temporary bonding material including a silicone compound using a detergent composition including an acid or base and an organic solvent,

wherein a value represented by Formula (a) of the acid is 0 to 10 and a value represented by Formula (b) of the base is -5 to 0;

Formula (a) ClogP-pKa

Formula (b) ClogP-pKb

in Formulae (a) and (b), ClogP represents a value represented by a base-10 logarithm $\log P$ of P which is a 1-octanol/water partition coefficient representing a ratio of an equilibrium concentration in 1-octanol and water, pKa represents an acid dissociation constant, and pKb represents a base dissociation constant.

20. The method for manufacturing a semiconductor element according to claim 19, wherein the silicone compound is a silicone oil.

21. The method for manufacturing a semiconductor element according to claim 19 or 20, wherein the silicone compound includes a polyether-modified silicone.

22. The method for manufacturing a semiconductor element according to claim 21, wherein a ratio represented by Formula (A) of the polyether-modified silicone is 80% or more;

Formula (A) $\{(\text{MO}+\text{EO})/\text{AO}\}\times 100$

in Formula (A), MO is % by mole of methylene oxide included in the polyether structure in the polyether-modified silicone, EO is % by mole of ethylene oxide included in the polyether structure in the polyether-modified silicone, and AO is % by mole of alkylene oxide included in the polyether structure in the polyether-modified silicone.

23. The method for manufacturing a semiconductor element according to any one of claims 19 to 22,

wherein a content of the silicone compound in the temporary bonding material is

0.001% to 1.0% by mass.

24. The method for manufacturing a semiconductor element according to any one of claims 19 to 23,

wherein the temporary bonding material includes an elastomer.

25. The method for manufacturing a semiconductor element according to claim 24,

wherein the elastomer is a polystyrene-based elastomer.

26. The method for manufacturing a semiconductor element according to claim 24 or 25,

wherein the solubility of the elastomer in the organic solvent at 25°C is 18% to 40% by mass.

27. The method for manufacturing a semiconductor element according to any one of claims 19 to 26,

wherein the organic solvent is at least one selected from an aromatic compound, a saturated alicyclic compound, a cyclic ketone, or a cyclic terpene.

28. The method for manufacturing a semiconductor element according to any one of claims 19 to 27,

wherein the detergent composition includes an acid and the acid is at least one selected from a phosphoric acid, a phosphonic acid, a phosphinic acid, a sulfonic acid, or a carboxylic acid.

29. The method for manufacturing a semiconductor element according to any one of claims 19 to 27,

wherein the detergent composition includes a base and the base is at least one selected from an aliphatic amine, an aromatic amine, or a heterocyclic amine.

30. The method for manufacturing a semiconductor element according to any one of claims 19 to 29,

wherein the temporary bonding material is used for temporary adhesion between a carrier substrate and a substrate to be processed, and

the temporary bonding material to be removed by the detergent composition is the temporary bonding material remaining on the substrate to be processed after peeling off the carrier substrate, and the temporary bonding material remaining on the substrate to be processed after peeling off the carrier substrate and further peeling off the temporary bonding material.