

KIT, METHOD FOR MANUFACTURING SEMICONDUCTOR ELEMENT, AND METHOD FOR CLEANING SUBSTRATE OF SEMICONDUCTOR ELEMENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a kit, a method for manufacturing a semiconductor element, and a method for cleaning a substrate of 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, JP2016-011361A discloses a peeling composition for peeling a bonding material including a styrene-based hydrogenated elastomer, in which the peeling composition includes at least one of a cyclic terpene-based solvent, a nonionic surfactant, or a silicon-based surfactant.

Furthermore, JP2006-505629A discloses a composition including A) a water-soluble organic solvent, B) a sulfonic acid or a salt corresponding thereto, and C) water.

In addition, JP2004-307725A discloses a cleaning liquid composition used in cleaning a semiconductor substrate having a contact angle of the surface of 70 degrees or more upon dropwise addition of water, in which the cleaning liquid composition includes aliphatic polycarboxylic acids and an organic solvent having a hydroxyl group and/or an ether group, and a contact angle upon dropwise addition of the cleaning liquid composition onto a semiconductor substrate is 40° or less.

SUMMARY OF THE INVENTION

[0004] However, according to the studies conducted by the present inventors, it was found that in a case where a temporary bonding material including a silicone compound or a precursor of the silicone compound (hereinafter simply referred to as a “silicon-containing compound” in some cases) is cleaned with such a detergent composition as described above, carbon atom residues or silicon atom residues derived from the temporary bonding material remain. In this regard, the present applicant has studied on removal of the residues using a composition including an organic sulfonic acid and an organic solvent. However, it was found that in a case where a temporary bonding material including a silicon-containing compound is cleaned with a composition including an organic sulfonic acid and an organic solvent, sulfur atom residues derived from the organic sulfonic acid remain. With such sulfur atom residues, acid

components may cause corrosion of a metal surface, disconnection of a metal wiring, or the like in a case where a substrate to be processed, which is subjected to temporary bonding, has a metal such as a copper and there are many irregularities on the surface of the metal. The present invention has been made to solve such problems, and thus has an object to provide a kit which includes a temporary bonding material including a silicon-containing compound and a detergent for the temporary bonding material and is capable of appropriately cleaning various residues; a method for manufacturing a semiconductor element; and a method for cleaning a substrate of a semiconductor element.

[0005] The present inventors have studied so as to achieve the objects, and as a result, they have found that by cleaning a temporary bonding material including a silicon-containing compound with a detergent composition including an organic sulfonic acid and the like, and then further cleaning the temporary bonding material with a detergent composition including an organic carboxylic acid, water, and the like, it is possible to effectively remove residues derived from the silicon-containing compound, and also effectively remove residues derived from the organic sulfonic acid and the like, thereby leading to completion of the present invention.

Specifically, according to <1>, and preferably according to <2> to <29>, the objects were accomplished.

<1> A kit comprising:

a temporary bonding material including at least one silicon-containing compound selected from the group consisting of a silicone compound and a precursor of the silicone compound;

a detergent composition A including at least one organic acid in which an acid group included in the organic acid contains a sulfur atom or a phosphorus atom, and an organic solvent; and

a detergent composition B including an organic carboxylic acid compound and at least one of water or a water-soluble solvent.

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

in which the organic acid includes at least one organic acid selected from the group consisting of an organic sulfonic acid, an organic phosphoric acid, and an organic phosphonic acid.

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

in which the silicon-containing compound includes a silicone oil.

- <4> The kit as described in any one of <1> to <3>,
in which the silicon-containing compound includes a polyether-modified silicone.
- <5> The kit as described in any one of <1> to <4>,
in which a content of the silicon-containing 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 any one of <1> to <7>,
in which an acid dissociation constant pKa of the organic acid is -4 to 5.
- <9> The kit as described in any one of <1> to <8>,
in which the organic acid is selected from the group consisting of an alkylsulfonic acid, an aromatic sulfonic acid, an alkylphosphoric acid, an aromatic phosphoric acid, an alkylphosphonic acid, and an aromatic phosphonic acid.
- <10> The kit as described in any one of <1> to <9>,
in which the organic solvent included in the detergent composition A includes an aromatic hydrocarbon-based solvent having an alkyl group.
- <11> The kit as described in <10>,
in which the aromatic hydrocarbon-based solvent having an alkyl group is a solvent having a benzene ring and 1 to 3 alkyl groups having 1 to 10 carbon atoms.
- <12> The kit as described in any one of <1> to <11>,
in which a mass ratio of the organic acid to the organic solvent in the detergent composition A is 0.0001:99.9999 to 50:50.
- <13> The kit as described in any one of <1> to <12>,
in which the organic carboxylic acid compound is selected from the group consisting of a saturated fatty acid, an unsaturated fatty acid, a hydroxy acid, and an aromatic carboxylic acid.
- <14> The kit as described in any one of <1> to <13>,
in which a value represented by a base-10 logarithm $\log P$ of P which is a 1-octanol/water partition coefficient representing a ratio of equilibrium concentrations of the organic carboxylic acid compound in 1-octanol and water is -5 to 6.
- <15> The kit as described in any one of <1> to <14>,

in which the solvent included in the detergent composition B includes water.

<16> The kit as described in any one of <1> to <15>,

in which an acid dissociation constant pKa of the organic carboxylic acid compound is 1 to 7.

<17> The kit as described in any one of <1> to <16>,

in which a mass ratio of the organic carboxylic acid compound to the solvent in the detergent composition B is 0.0001:99.9999 to 50:50.

<18> The kit as described in any one of <1> to <17>, further comprising a rinsing composition C including at least one of water or an alcohol.

<19> A method for manufacturing a semiconductor element, comprising:

a step of cleaning a substrate having a silicone compound on a surface thereof using a detergent composition A; and

a step of further cleaning the cleaned substrate using a detergent composition B,

in which the detergent composition A includes at least one organic acid in which an acid group included in the organic acid contains a sulfur atom or a phosphorus atom, and an organic solvent, and

the detergent composition B includes an organic carboxylic acid compound and at least one of water or a water-soluble solvent.

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

in which the organic acid includes at least one organic acid selected from the group consisting of an organic sulfonic acid, an organic phosphoric acid, and an organic phosphonic acid.

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

in which a temporary bonding layer formed from a temporary bonding material is provided on the substrate, at least a part of the temporary bonding layer is cleaned with the organic acid, and the temporary bonding material includes at least one of the silicone compound or a precursor of the silicone compound.

<22> The method for manufacturing a semiconductor element as described in any one of <19> to <21>,

in which the step of performing cleaning using the detergent composition A and the step of performing cleaning using the detergent composition B are performed by a single wafer method.

<23> The method for manufacturing a semiconductor element as described in any one of <19> to <22>, further comprising a drying step after each of the step of performing cleaning using the detergent composition A and the step of performing cleaning using the detergent composition B.

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

in which a period from the start of the step of performing cleaning using the detergent composition A to the end of the step of performing cleaning using the detergent composition B for one sheet of the substrate is 30 to 300 seconds.

<25> The method for manufacturing a semiconductor element as described in any one of <19> to <24>, further comprising a step of performing a rinsing treatment using a rinsing composition C including at least one of water or an alcohol after the step of performing cleaning using the detergent composition B.

<26> The method for manufacturing a semiconductor element as described in any one of <19> to <25>, using the kit as described in any one of <1> to <18>.

<27> A method for cleaning a substrate of a semiconductor element, comprising:
a step of cleaning a substrate having a silicone compound on a surface thereof using a detergent composition A; and

a step of further cleaning the cleaned substrate using a detergent composition B,
in which the detergent composition A includes at least one organic acid in which an acid group included in the organic acid contains a sulfur atom or a phosphorus atom, and an organic solvent, and the detergent composition B includes an organic carboxylic acid compound and at least one of water or a water-soluble solvent.

<28> The method for cleaning a substrate of a semiconductor element as described in <27>, further comprising performing a rinsing treatment using a rinsing composition C including at least one of water or an alcohol after the step of performing cleaning using the detergent composition B.

<29> The method for cleaning a substrate of a semiconductor element as described in <27> or <28>, using the kit as described in any one of <1> to <18>.

[0006] According to the present invention, it is possible to provide a kit which includes a temporary bonding material including a silicon-containing compound and a detergent for the temporary bonding material and is capable of appropriately cleaning various residues; a method for manufacturing a semiconductor element; and a method for cleaning a substrate of a

semiconductor element.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0007] 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).

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-8220 (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.

[0008] Kit

The kit of an embodiment of the present invention is a kit including a temporary bonding material including at least one silicon-containing compound selected from the group consisting of a silicone compound and a precursor of the silicone compound; a detergent composition A including at least one organic acid in which an acid group included in the organic acid contains a sulfur atom or a phosphorus atom (hereinafter simply referred to as an “organic acid” in some cases), and an organic solvent; and a detergent composition B including an organic carboxylic acid compound and at least one of water or a water-soluble solvent. By using such a composition, various residues can be effectively removed. In a semiconductor process, residues derived from the silicon-containing compound on a metal

cause peeling of an insulating layer or failure of adhesion of a solder, and therefore, is required to be appropriately removed. It is conceivable to use a detergent composition including the organic acid as such a detergent. However, in a case where there is unevenness on a metal surface of a substrate to be processed, it is easy for sulfur or phosphorus derived from the detergent composition including the organic acid to remain in a concave portion. In a case where sulfur or phosphorus remains on the concave portion, it causes corrosion of the metal surface, disconnection of the wiring, or the like, and therefore, it is necessary to immediately clean the sulfur or phosphorus components.

In the present invention, the problems are successfully solved by appropriately removing the residues derived from the silicon-containing compound using a detergent composition A including an organic acid and an organic solvent, and appropriately removing the residues derived from the organic acid using the detergent composition B including the organic carboxylic acid compound, water, and the like. In addition, it is also possible to effectively suppress the discoloration of the copper layer by using the kit of the embodiment of the present invention. It is presumed that the discoloration of the copper layer is due to protection of the surface of the copper layer by the coordination of an organic carboxylic acid compound.

The kit of the embodiment of the present invention may further include a rinsing composition C including at least one of water or an alcohol.

Hereinafter, the kit of the embodiment of the present invention will be described in detail.

[0009] <Temporary Bonding Material>

<<Silicone Compound or Precursor of Silicone Compound>>

The temporary bonding material which is used in the present invention includes at least one silicon-containing compound selected from the group consisting of a silicone compound and a precursor of the silicone compound. The silicon-containing compound acts as a release agent, by which it is possible to easily remove the temporary bonding material from the substrate to be processed.

As the silicon-containing compound, a silicone oil is preferable. The silicone oil refers to a compound which is liquid at 25°C.

Furthermore, it is preferable that the silicon-containing compound does not contain a reactive group such as a polymerizable group.

The silicon-containing compound is preferably a polyether-modified silicone.

[0010] The polyether-modified silicone which is 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%.

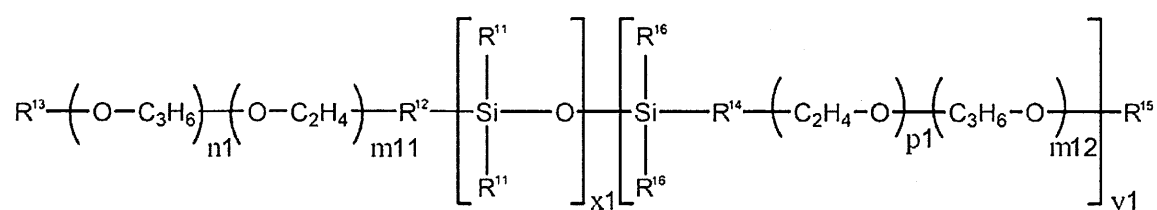
[0011] A weight-average molecular weight of the polyether-modified silicone is preferably 500 to 100,000, more preferably 1,000 to 50,000, and still more preferably 2,000 to 40,000.

[0012] 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.

[0013] 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.

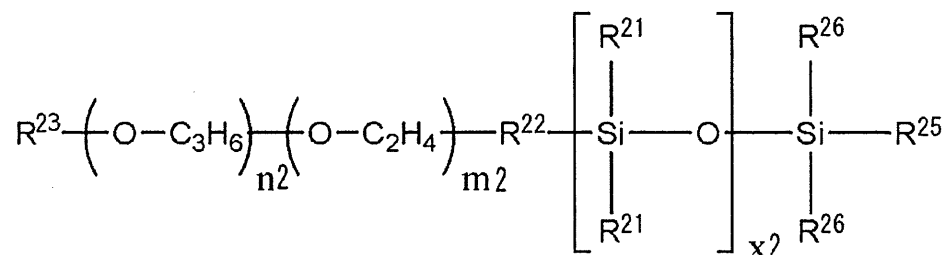
[0014] The polyether-modified silicone which is used in the present invention is preferably a polyether-modified silicone represented by any one of Formula (101) to Formula (104).

Formula (101)



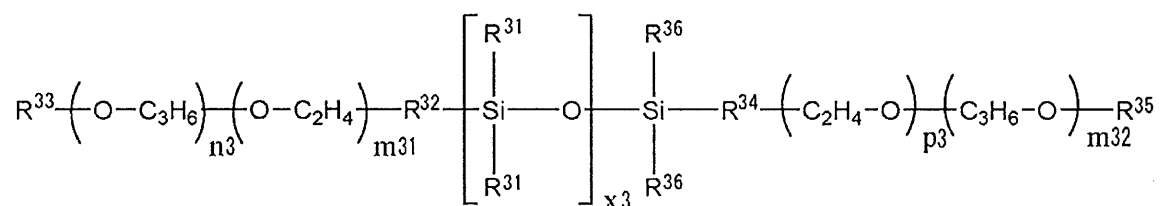
In Formula (101), R^{11} and R^{16} are each independently a substituent, R^{12} and R^{14} are each independently a divalent linking group, R^{13} and R^{15} are each a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, $m11$, $m12$, $n1$, and $p1$ are each independently a number of 0 to 20,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

Formula (102)



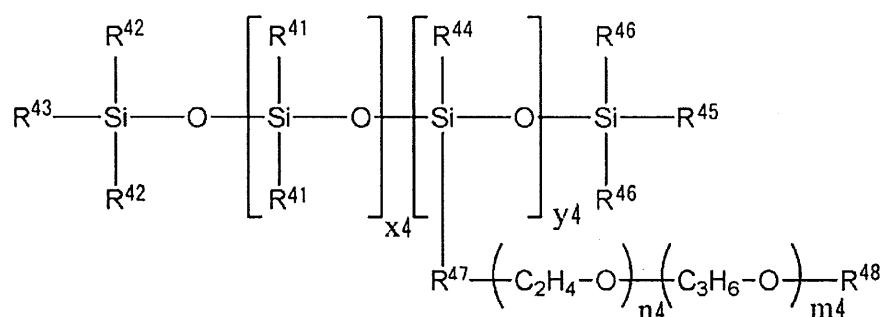
In Formula (102), R^{21} , R^{25} , and R^{26} are each independently a substituent, R^{22} is a divalent linking group, R^{23} is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, $m2$ and $n2$ are each independently a number of 0 to 20, and $x2$ is a number of 2 to 100.

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.

[0015] 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 more 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.

[0016] 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).

[0017] 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 definitions and preferred ranges 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).

[0018] 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 definition and preferred range as R^{13} and R^{15} in Formula (101).

[0019] In Formula (101) to Formula (104), Formula (103) or Formula (104) is preferable, and Formula (104) is more preferable.

[0020] The content of the polyoxyalkylene groups in a molecule of the polyether-modified silicone which is 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”.

[0021] Examples of a precursor of the silicone compound include a silane coupling agent. Examples of the silane coupling agent include a fluorine atom-containing silane coupling agent, and triethoxy(1H,1H,2H,2H-nonafluorohexyl)silane is preferable.

In addition, examples of the silane coupling agent also include the surfactants described in each publication 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.

[0022] As the silicon-containing compound which is 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 silicon-containing 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 Kyoisha 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 also be used.

[0023] The content of the silicon-containing compound in the temporary bonding material which is 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 silicon-containing 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 silicon-containing 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 which is used in the present invention may include one kind or two or more kinds of the silicon-containing compounds. In a case where the temporary bonding material includes two or more kinds of the silicon-containing compounds, the total amount thereof is preferably within the range.

[0024] <<Other Release Agents>>

In the present invention, other release agents other than the silicon-containing 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 silicon-containing compound.

[0025] <<Resin>>

The temporary bonding material which is 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.

[0026] In the temporary bonding material which is 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.

[0027] <<<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.

[0028] 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.

[0029] 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.

[0030] 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 preferably 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.

[0031] <<<<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), or polystyrene-poly(ethylene/ethylene-propylene)-polystyrene triblock copolymer (SEEPS).

[0032] 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.

[0033] In an embodiment of the polystyrene-based elastomer in the present invention, the elastomer may 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% by mass 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 the 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.

[0034] 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 the mass ratio is within the range, it is possible to more effectively suppress the occurrence of warpage.

[0035] As the polystyrene-based elastomer, a block copolymer of styrene and another monomer is preferable, a block copolymer in which one terminal or both terminals are formed of styrene blocks is more preferable, and a 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 resistance 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.

[0036] 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 have 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.

[0037] 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).

[0038] As an elastomer other than the polystyrene-based elastomer, a polyester-based elastomer, a polyolefin-based elastomer, a polyurethane-based elastomer, a polyamide-based elastomer, a polyacrylic elastomer, or the like can be used.

[0039] <<<Blend Amount of Resin>>>

The temporary bonding material which is used in the present invention preferably includes a resin at a ratio of 50.00% to 99.99% by mass, more preferably includes the resin at a ratio of 70.00% to 99.99% by mass, and particularly preferably includes the resin at a ratio of 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 preferably included at a ratio of 50.00% to 99.99% by mass, more preferably included at a ratio of 70.00% to 99.99% by mass, and particularly preferably included at a ratio of 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.

[0040] <<Plasticizer>>

The temporary bonding material which is 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.

[0041] 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 SANSO 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.

[0042] 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.

[0043] The amount of the plasticizer to be added is preferably a ratio of 0.01% by mass to 5.0% by mass, and more preferably 0.1% by mass to 2.0% by mass, with respect to the total solid content of the temporary bonding material.

[0044] <<Solvent>>

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

Suitable examples of the organic solvent include esters such as ethyl acetate, n-butyl acetate, isobutyl acetate, amyl formate, isoamyl acetate, butyl propionate, isopropyl butyrate, ethyl butyrate, 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-oxy-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, tert-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-tert-butyltoluene, 1,4-di-tert-butylbenzene, 1,3-diethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 4-tert-butyl-o-xylene, 1,2,4-triethylbenzene, 1,3,5-triethylbenzene, 1,3,5-triisopropylbenzene, 5-tert-butyl-m-xylene, 3,5-di-tert-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, tert-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.

[0045] 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, tert-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-heptanone, cyclohexanone, cyclopentanone, ethylcarbitol acetate, butylcarbitol acetate, propylene glycol methyl ether, and propylene glycol methyl ether acetate.

[0046] 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 a ratio of 5% to 80% by mass, more preferably a ratio of 10% to 50% by mass, and particularly preferably a ratio of 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 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.

[0047] <<Antioxidant>>

The temporary bonding material which is 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.

[0048] 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.

[0049] In a case where the temporary bonding material contains an antioxidant, the content of the antioxidant is preferably a ratio of 0.001% to 20.0% by mass, and more preferably a ratio of 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.

[0050] <<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 which is used in the present invention within a range where the effect 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.

[0051] <<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 slit coating 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 bonded. 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.

[0052] <<Preparation of Temporary Bonding Material>>

The temporary bonding material which is 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 filters with fluorine resins such as polytetrafluoroethylene (PTFE), polyamide-based resins such as nylon-6 and nylon 6,6, polyolefin resins such as polyethylene and polypropylene (PP), or the like. 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 filtration run or later is preferably the same as or smaller than that of the first filtration run. Further, the plurality of the first filters 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.

[0053] <Detergent Composition A>

The detergent composition A in the present invention includes at least one organic acid in which an acid group included in the organic acid contains a sulfur atom or a phosphorus atom, and an organic solvent. With such a configuration, it is possible to effectively remove the residues derived from the silicon-containing compound, and then effectively suppress the peeling of an insulating layer to be laminated.

[0054] <<Organic Acid>>

The organic acid which is used in the present invention may be a low-molecular-weight compound (for example, having a molecular weight of less than 1,000 or a molecular weight of 500 or less, with a lower limit thereof being, for example, 98 or more), or a polymer compound (for example, having a molecular weight of 1,000 or more or a molecular weight of 2,000 or more, with an upper limit thereof being, for example, 5,000 or less). The organic acid which is used in the present invention is preferably a low-molecular-weight compound.

An acid dissociation constant pK_a of the organic acid which is used in the present invention is preferably -4 to 5, and more preferably -3 to 4.

With regard to the organic acid which is used in the present invention, the value represented by a base-10 logarithm $\log P$ of P which is a 1-octanol/water partition coefficient representing a ratio of equilibrium concentrations of the organic acid in 1-octanol and water is preferably -5 to 6, and more preferably -3 to 5.

The organic acid which is used in the present invention is preferably selected from an alkylsulfonic acid, an aromatic sulfonic acid, an alkylphosphoric acid, an aromatic phosphoric acid, an alkylphosphonic acid, and an aromatic phosphonic acid. Here, the aromatic organic acid may be an aromatic hydrocarbon or an aromatic heterocycle, but is preferably an aromatic hydrocarbon.

The organic acid which is used in the present invention preferably includes at least one organic acid selected from the group consisting of an organic sulfonic acid, an organic phosphoric acid, an organic phosphonic acid, an organic sulfinic acid, and an organic phosphinic acid, more preferably includes at least one organic acid selected from the group consisting of an organic sulfonic acid, an organic phosphoric acid, and an organic phosphonic acid, still more preferably includes at least one organic sulfonic acid, and even still more preferably includes at least one of an alkylsulfonic acid having a cyclic group or an aromatic sulfonic acid.

The organic acid which is used in the present invention may or may not have an acid group other than the acid group containing a sulfur atom or a phosphorus atom. In the present invention, the organic acid is preferably an organic acid not having a carboxyl group, and more preferably an organic acid not having an acid group other than a sulfonic acid group, a phosphoric acid group, and a phosphonic acid group.

[0055] Examples of the organic sulfonic acid include methanesulfonic acid, ethanesulfonic acid, trifluoromethanesulfonic acid, butanesulfonic acid, vinylsulfonic acid, 1,5-propanedisulfonic acid, 3-hydroxypropanesulfonic acid, benzenesulfonic acid, paratoluenesulfonic acid, p-ethylbenzenesulfonic acid, dodecylbenzenesulfonic acid, 2,4,5-trimethylbenzenesulfonic acid, nonafluoro-1-butanesulfonic acid, 2-naphthalenesulfonic acid, 1,5-naphthalenedisulfonic acid, heptadecafluorooctasulfonic acid, camphorsulfonic 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, piperazine-1,4-bis(2-hydroxypropanesulfonic acid), 7-anilino-4-hydroxy-2-naphthalenesulfonic acid, 7-anilino-1-naphthol-3-sulfonic acid, 4-sulphophthalic acid, 2-hydroxy-3-morpholinopropanesulfonic acid, 4-nitrotoluene-2-sulfonic acid, and picrylsulfonic acid. The organic sulfonic acid is preferably an alkylsulfonic acid or an aromatic sulfonic acid, and more preferably an aromatic sulfonic acid.

[0056] Examples of the organic phosphoric acid include alkyl phosphoric acids such as methyl phosphate, dimethyl phosphate, ethyl phosphate, diethyl phosphate, butyl phosphate, dibutyl phosphate, butoxyethyl phosphate, and 2-ethylhexyl phosphate, and aromatic phosphoric acids such as phenylphosphoric acid and diphenylphosphoric acid. The organic phosphoric acid is preferably an alkylphosphoric acid or an aromatic phosphoric acid, more preferably an aromatic phosphoric acid, and still more preferably a diarylphosphoric acid.

Examples of the organic phosphonic acid include alkylphosphonic acids such as vinylphosphonic acid, methylenediphosphonic acid, ethylphosphonic acid, propylphosphonic acid, 1,3-propylenediphosphonic acid, butylphosphonic acid, 1,4-butylenediphosphonic acid, pentylphosphonic acid, 1,5-pentylene phosphonic acid, hexylphosphonic acid, 1,6-dihexylene phosphonic 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. The organic phosphonic acid is preferably an alkylphosphonic acid or an aromatic phosphonic acid, and more preferably an aromatic phosphonic acid.

[0057] The content of the organic acid in the detergent composition A is preferably 0.08 mg to 0.8 g with respect to 1 L of the organic solvent included in the detergent composition A.

Moreover, the content of the organic acid in the detergent composition A 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, even still more preferably 0.008000% by mass or more, and even still more preferably 0.08% by mass or more, with respect to the detergent composition. The content of the organic acid in the detergent composition in 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.

The detergent composition A may include one kind or two or more kinds of the organic acids. In a case where the detergent composition A includes two or more kinds of the organic acids, the total amount thereof is preferably within the range.

[0058] <<Organic Solvent>>

The detergent composition A includes an organic solvent. In a case where the temporary bonding material includes an elastomer, the organic solvent is preferably an organic solvent that dissolves an elastomer, more 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, or a cyclic terpene, and still more preferably at least one selected from aromatic compounds.

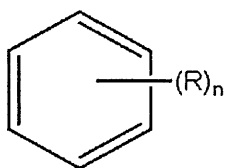
The organic solvent as the aromatic compound preferably includes an aromatic hydrocarbon-based solvent having an alkyl group, and is more preferably a solvent having a

benzene ring and 1 to 3 alkyl groups having 1 to 10 carbon atoms.

[0059] The alkyl group constituting the aromatic hydrocarbon-based solvent having an alkyl group which is used in the present invention is a linear, branched, or cyclic alkyl group, and preferably a linear or branched alkyl group. The number of carbon atoms constituting the alkyl group is preferably 1 to 10, more preferably 1 to 6, and still more preferably 1 to 4.

The aromatic hydrocarbon-based solvent having an alkyl group which is used in the present invention is preferably a solvent having a benzene ring and 1 to 3 alkyl groups having 1 to 10 carbon atoms, and more preferably a solvent represented by Formula (X).

Formula (X)



In Formula (X), R is an alkyl group having 1 to 4 carbon atoms, and n is an integer of 1 to 3.

R is preferably a linear or branched alkyl group having carbon atoms 1 to 4, and more preferably a methyl group, an ethyl group, or a tert-butyl group. Further, the total number for carbon atoms constituting R is preferably an integer of 2 to 5, and more preferably 3 or 4.

[0060] The boiling point of the aromatic hydrocarbon-based solvent having an alkyl group which is used in the present invention is preferably 50°C to 250°C, more preferably 80°C to 200°C, and still more preferably 120°C to 170°C.

[0061] Specific examples of the aromatic hydrocarbon-based solvent having an alkyl group which is used in the present invention include toluene, xylene, trimethylbenzene (preferably 1,3,5-trimethylbenzene (mesitylene) or 1,2,4-trimethylbenzene (pseudocumene)), ethylbenzene, propylbenzene, 1-methylethylbenzene, butylbenzene (preferably n-butylbenzene, sec-butylbenzene, isobutylbenzene, or tert-butylbenzene, and more preferably tert-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 (2-isopropyltoluene), 3-ethyltoluene, m-cymene, 1,3-diisopropylbenzene, 4-ethyltoluene, 1,4-diethylbenzene, p-cymene, 1,4-diisopropylbenzene, 4-tert-butyltoluene, 1,4-di-tert-butylbenzene, 1,3-diethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 4-tert-butyl-o-xylene, 1,2,4-triethylbenzene, 1,3,5-triethylbenzene, 1,3,5-triisopropylbenzene, 5-tert-butyl-m-xylene, 3,5-di-tert-butyltoluene, 1,2,3,5-tetramethylbenzene,

1,2,4,5-tetramethylbenzene, and pentamethylbenzene.

[0062] The aromatic hydrocarbon-based solvent having an alkyl group is preferably at least one of toluene, xylene, trimethylbenzene (preferably mesitylene), butylbenzene (preferably tert-butylbenzene), or diethylbenzene, and more preferably at least one of xylene, trimethylbenzene, or butylbenzene.

[0063] Examples of the saturated alicyclic compound include cyclopropane, cyclobutane, cyclopentane, cyclohexane, methylcyclohexane, cycloheptane, cyclooctane, cyclononane, cyclodecane, cycloundecane, cyclododecane, cyclopropene, cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, bicycloundecane, 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, terpeneol, carveol, thymol, dihydrocarveol, menthone, pulegone, ferrandrul, 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, sarbinen, thujone, thujanol, pinene, verbenol, verbenone, pinocarbon, camphor, borneol, isoborneol, fenchone, and fenchol fenchene.

[0064] The content of the organic solvent in the detergent composition A 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 A.

The detergent composition of the present invention 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.

In addition, the mass ratio of the organic acid to the organic solvent in the detergent composition A is 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 mass ratio to such a range, the removability of the temporary bonding material is more effectively improved.

[0065] <<Other Components>>

The detergent composition A may include components other than the organic acid and

the organic solvent. Examples of such other components include cleaning 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, 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.

[0066] <<Preparation of Detergent Composition A>>

For the preparation of the detergent composition A, it is preferable that the respective components of the detergent composition A 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, it is possible to reduce contamination of a substrate surface due to impurities derived from the detergent composition A. The filter is preferably made of polytetrafluoroethylene.

[0067] As a storage container for the detergent composition A which is used in the present invention, a storage container known in the related art can be used. Further, as the storage container, it is also preferable to use a multilayer bottle having an inner wall constituted with six layers from six kinds of resins or a bottle having a 7-layer structure from 6 kinds of resins for the purpose of suppressing incorporation of impurities into raw materials or compositions. Examples of such a container include the containers described in JP2015-123351A.

[0068] <Detergent Composition B>

The detergent composition in the present invention includes an organic carboxylic acid compound and at least one of water or a water-soluble solvent. By adopting such a configuration, it is possible to effectively remove residues derived from the organic acid.

[0069] <<Organic Carboxylic Acid Compound>>

The organic carboxylic acid compound which is used in the present invention may be a low-molecular-weight compound (for example, having a molecular weight of less than 1,000 or a molecular weight of 500 or less, with a lower limit thereof being, for example, 46 or more), or may be a polymer compound (for example, having a molecular weight of 1,000 or more or a molecular weight of 2,000 or more, with an upper limit thereof being, for example, 5,000 or less). The organic carboxylic acid compound which is used in the present invention is preferably a low-molecular-weight compound.

An acid dissociation constant pK_a of the organic carboxylic acid compound which is used in the present invention is preferably 1 to 7, more preferably 2 to 7, and still more preferably 2 to 5, and may be 2 to 4.

With regard to the organic carboxylic acid compound which is used in the present invention, a value represented by a base-10 logarithm $\log P$ of P which is a 1-octanol/water partition coefficient representing a ratio of equilibrium concentrations in 1-octanol and water is preferably -5 to 2, and more preferably -5 to 1.

The organic carboxylic acid which is used in the present invention is preferably a monocarboxylic acid, a dicarboxylic acid, or a tricarboxylic acid, and more preferably a monocarboxylic acid or a dicarboxylic acid.

The organic carboxylic acid compound which is used in the present invention is preferably selected from the group consisting of a saturated fatty acid, an unsaturated fatty

acid, a hydroxy acid, an aromatic carboxylic acid, an oxocarboxylic acid, and a halogen-containing carboxylic acid, more preferably selected from the group consisting of a saturated fatty acid, an unsaturated fatty acid, a hydroxy acid, and an aromatic carboxylic acid, and still more preferably selected from the group consisting of a saturated fatty acid and an aromatic carboxylic acid.

The saturated fatty acid, the unsaturated fatty acid, and the hydroxy acid are each preferably a monocarboxylic acid, and the aromatic carboxylic acid is more preferably a monocarboxylic acid or a dicarboxylic acid.

The organic carboxylic acid compound which is used in the present invention may or may not have an acid group other than the carboxyl group. It is preferable that the organic carboxylic acid compound which is used in the present invention does not have a sulfonic acid group, a phosphoric acid group, and a phosphonic acid group, and it is more preferable that the organic carboxylic acid compound does not have an acid group other than the carboxyl group.

[0070] Examples of the organic carboxylic acid compound 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, sorbic acid, and aconitic 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, cinnamic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, fumaric acid, and maleic acid; oxocarboxylic acids such as pyruvic acid and oxalacetic acid; and halogen-containing carboxylic acids such as chloroacetic acid, dichloroacetic acid, trichloroacetic acid, and trifluoroacetic acid.

[0071] The content of the organic carboxylic acid compound in the detergent composition B is preferably 0.8 mg to 1.6 g with respect to 1 L of the solvent included in the detergent composition B.

Moreover, the content of the organic carboxylic acid compound in the detergent composition B is preferably 0.0016% by mass or more, more preferably 0.0016% by mass or more, still more preferably 0.1600% by mass or more, and even still more preferably 1.6000% by mass or more, with respect to the detergent composition B. The content of the organic carboxylic acid compound in the detergent composition B of the present invention is preferably 10.0% by mass or less, more preferably 8.0% by mass or less, still more preferably

5.0% by mass or less, and even still more preferably 4.0% by mass or less, with respect to the detergent composition B.

The detergent composition B may include one kind or two or more kinds of the organic carboxylic acid compounds. In a case where the detergent composition B includes two or more kinds of the organic carboxylic acid compounds, the total amount thereof is preferably within the range.

[0072] <<Solvent>>

The solvent included in the detergent composition B is at least one solvent including water and a water-soluble solvent, and preferably water.

The water-soluble solvent means an organic compound having a solubility in water of 1,000 mg/L or more, and examples thereof include methanol, ethanol, 1-propanol, 2-propanol, tert-butyl alcohol, and ethylene glycol.

[0073] The content of the solvent in the detergent composition B 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 B.

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

In addition, the mass ratio of the organic carboxylic acid compound to the solvent in the detergent composition B is 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 mass ratio to such a range, the removability of the residues derived from the detergent composition A is more effectively improved.

[0074] <<Other Components>>

The detergent composition B may include components other than organic carboxylic acid compound and the solvent. Specifically, such other components as mentioned for the detergent composition A can be used.

[0075] <<Preparation of Detergent Composition B>>

For the preparation of the detergent composition B, it is preferable that the respective components of the detergent composition B 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, it is possible to reduce contamination of a substrate surface due to impurities derived from the detergent composition B. The filter is preferably made of

polytetrafluoroethylene.

[0076] As a storage container for the detergent composition B which is used in the present invention, a storage container known in the related art can be used. Further, as the storage container, it is also preferable to use a multilayer bottle having an inner wall constituted with six layers from six kinds of resins or a bottle having a 7-layer structure from 6 kinds of resins for the purpose of suppressing incorporation of impurities into raw materials or compositions. Examples of such a container include the containers described in JP2015-123351A.

[0077] <Detergent Composition A and Detergent Composition B>

In the present invention, a difference between the acid dissociation constant pK_a of the organic carboxylic acid compound and the acid dissociation constant pK_a of the organic acid is preferably 2 to 10. By setting the difference to such a range, the effect of the present invention is more effectively exhibited.

In addition, in the present invention, the equivalents of the acid included in the detergent composition B with respect to the equivalents of the acid include in the detergent composition A is preferably 2 to 100 times. By setting the equivalents to such a range, the effect of the present invention is more effectively exhibited.

[0078] <Rinsing Composition C>

The kit of the embodiment of the present invention may further include a rinsing composition C.

The rinsing composition includes at least one of water or an alcohol. As the alcohol, an alcohol including a linear or branched alkyl group having 1 to 10 carbon atom and a hydroxyl group is preferable.

Specific examples of the alcohol include methanol, ethanol, 1-propanol, 2-propanol, tert-butyl alcohol, and ethylene glycol.

[0079] <<Other Components>>

The rinsing composition C may include components other than at least one of water or an alcohol. Specifically, such other components as mentioned for the detergent composition A can be used.

[0080] <<Preparation of Rinsing Composition C>>

For the preparation of the rinsing composition C, it is preferable that the respective components of the rinsing composition C 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, there is a tendency that removability of residues derived from the

detergent compositions A and B is further improved. The filter is preferably made of a polytetrafluoroethylene.

[0081] Method for Manufacturing Semiconductor Element

The method for manufacturing a semiconductor element of an embodiment of the present invention includes a step of cleaning a substrate having a silicone compound on a surface thereof using a detergent composition A, and a step of further cleaning the cleaned substrate using a detergent composition B, in which the detergent composition A includes at least one organic acid in which an acid group included in the organic acid contains a sulfur atom or a phosphorus atom, and an organic solvent, and the detergent composition B includes an organic carboxylic acid compound and at least one of water or a water-soluble solvent. It is preferable that the method for manufacturing a semiconductor element of the embodiment of the present invention includes a step of performing a rinsing treatment using a rinsing composition C including at least one of water or an alcohol after the step of performing cleaning using the detergent composition B.

[0082] It is also preferable that a temporary bonding layer formed from a temporary bonding material is included on the substrate, at least a part of the temporary bonding layer is cleaned with the organic acid, and the temporary bonding material includes at least one of the silicone compound or a precursor of the silicone compound. Accordingly, examples of the substrate having the silicon-containing compound on a surface thereof include a substrate to be processed and a carrier substrate.

Examples of an aspect for removing the temporary bonding material including a silicon-containing compound include removal of a temporary bonding layer on a substrate to be processed, removal of excess temporary bonding materials in a step of temporarily bonding a substrate to be processed to a carrier substrate, and removal of a temporary bonding material remaining on a carrier substrate for reuse of the carrier substrate.

[0083] In the method for manufacturing a semiconductor element of the embodiment of the present invention, it is preferable that the temporary bonding material is used for the temporary bonding between a carrier substrate and a substrate to be processed, the substrate to be processed is cleaned by removing a part or whole of the temporary bonding material using the detergent composition A, and then the substrate to be processed is further cleaned using the detergent composition B. The temporary bonding material to be removed using the detergent composition A is preferably a temporary bonding material which remains on the substrate to be processed after peeling the carrier substrate, or a temporary bonding material which

remains on the temporary bonding layer or the substrate to be processed after peeling the carrier substrate and further peeling off the temporary bonding layer. The peel-off of the temporary bonding layer is preferably performed at a temperature of 40°C or lower, and more preferably performed at a temperature of 10°C to 40°C. In addition, the peel-off of the temporary bonding layer is preferably manual peeling or mechanical peeling.

Examples of the substrate to be processed include a device wafer which has silicon, glass, a compound semiconductor of SiC, GaN, GaAs, or the like, a mold resin, or the like as a substrate, and a structure formed on the surface and the inside of the substrate. Particularly, in the present invention, a metal layer, and more preferably a copper layer is preferably placed as a structure on the surface of the substrate to be processed. In the method for manufacturing a semiconductor element of the embodiment of the present invention, it is possible to effectively remove sulfur atom residues or phosphorus atom residues derived from the detergent composition A, which remain on the surface of the copper layer, by using the detergent composition B.

Moreover, the method for manufacturing a semiconductor element of the embodiment of the present invention is preferably used in an aspect in which a copper layer is placed on the surface of a substrate and a solder ball is provided on the surface of the copper layer. In a case where the solder ball is provided, a use of the method for manufacturing a semiconductor element of the embodiment of the present invention is of high value from the viewpoint of an effect of enhancing the adhesiveness between the solder ball and the copper layer by removing impurities.

In addition, irregularity steps exist on a wiring layer including a copper layer due to the structure of the semiconductor in some case. Particularly, it is easy for residues containing sulfur atoms or phosphorus atoms derived from the detergent composition A to remain on the bottom surface of a copper pad having a depth of 5 to 50 μm , in which a concave portion is formed in the shape of a circular basin having a diameter of 400 to 800 μm . [0084] Furthermore, the step of performing cleaning using the detergent composition A and the step of performing cleaning using the detergent composition B are preferably performed by a single wafer method. Incidentally, in the step of performing a rinsing treatment, drying and cleaning are also preferably performed by the single wafer method.

In addition, a drying step is preferably included after each of the step of performing cleaning using the detergent composition A and the step of performing cleaning using the detergent composition B. By providing the drying step after each of the cleaning steps, the

effect of the present invention is more effectively exhibited. In addition, a drying step is also preferably included after the step of performing a rinsing treatment.

Drying after performing cleaning using the detergent composition A is preferably performed at 80°C to 200°C. The drying time is preferably 30 to 180 seconds. It is preferable that cleaning is performed using the detergent composition B within 180 seconds after the drying. Drying after performing cleaning using the detergent composition B is preferably performed at 80°C to 200°C. The drying time is preferably 30 to 180 seconds. It is preferable that the rinsing is performed using the rinsing composition C within 30 seconds after the drying. It is preferable to start drying within 3 seconds after application of the rinsing treatment. Drying after the rinsing treatment is preferably performed at 80°C to 200°C using the rinsing composition C. The drying time is preferably 30 to 180 seconds.

[0085] In the method of manufacturing a semiconductor element of the embodiment of the present invention, a period from the start of the step of performing cleaning using the detergent composition A to the end of the step of performing cleaning using the detergent composition B for one sheet of the substrate is preferably 30 to 540 seconds, and more preferably 60 to 240 seconds. With such a period, it is possible to effectively remove the temporary bonding material and the residues of the silicon-containing compound in one step. In addition, a period from the time of starting the cleaning using the detergent composition A to the time of ending the cleaning using the rinsing composition C is preferably 60 to 660 seconds, and more preferably 90 to 540 seconds.

Furthermore, a ratio of a period A from the start of the step of performing cleaning using the detergent composition A to the start of the step of performing cleaning using the detergent composition B to a period B from the start of the step of performing cleaning using the detergent composition B to the start of the step of performing cleaning using the rinsing composition C is preferably 1:10 to 10:1, and more preferably 4:6 to 6:4. With such a ratio, the cleaning effect of each substrate in the single wafer treatment can further accelerate homogenization.

[0086] The detergent composition A, the detergent composition B, the rinsing composition C, and the temporary bonding material in the method for manufacturing a semiconductor element of the embodiment of the present invention have the same definitions as the above-mentioned detergent composition A, detergent composition B, rinsing composition C, and temporary bonding material, respectively. Therefore, in the method for manufacturing a semiconductor element of the embodiment of the present invention, the kit of the embodiment of the present

invention can be preferably used.

In addition, with respect to the method for manufacturing a semiconductor element, in particular, the method for temporary bonding, reference can be made to the description in paragraphs 0074 to 0099 and Figs. 1 to 3 of WO2016/181879A, the contents of which are herein incorporated by reference.

[0087] Method for Cleaning Substrate of Semiconductor Element

The method for cleaning a substrate of a semiconductor element of an embodiment of the present invention includes a step of cleaning a substrate having a silicone compound on a surface thereof using a detergent composition A; and a step of further cleaning the cleaned substrate using a detergent composition B, in which the detergent composition A includes at least one organic acid in which an acid group included in the organic acid contains a sulfur atom or a phosphorus atom, and an organic solvent, and the detergent composition B includes an organic carboxylic acid compound and at least one of water or a water-soluble solvent.

The method for cleaning a substrate of a semiconductor element of the embodiment of the present invention preferably includes a step of performing a rinsing treatment using a rinsing composition C including at least one of water or an alcohol after the step of performing cleaning using the detergent composition B.

[0088] In the method for cleaning a substrate of a semiconductor element of the embodiment of the present invention, the detergent composition A, the detergent composition B, the rinsing composition C, and the temporary bonding material have the same definitions as the above-mentioned detergent composition A, detergent composition B, rinsing composition C, and temporary bonding material, respectively. Accordingly, in the method for cleaning a substrate of a semiconductor element of the embodiment of the present invention, the kit of the embodiment of the present invention can be preferably used.

Examples

[0089] 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, “parts” and “%” are on a mass basis unless otherwise specified.

[0090] <Preparation of Temporary Bonding Material>

As shown in Table 1 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.

[0091] [Table 1]

Temporary bonding material	Elastomer 1		Elastomer 2		Antioxidant 1		Antioxidant 2		Silicon-containing compound 1		Silicon-containing compound 2		Solvent	
	Type	% by mass	Type	% by mass	Type	% by mass	Type	% by mass	Type	% by mass	Type	% by mass	Type	% by mass
1	P-1	25.86	None	0	A-1	0.26	A-2	0.26	Si-1	0.01	None	0	S-1	73.61
2	P-1	25.86	None	0	A-1	0.26	A-2	0.26	Si-2	0.01	None	0	S-1	73.61
3	P-1	25.86	None	0	A-1	0.26	A-2	0.26	Si-3	0.01	None	0	S-1	73.61
4	P-1	25.86	None	0	A-1	0.26	A-2	0.26	Si-4	0.01	None	0	S-1	73.61
5	P-1	25.86	None	0	A-1	0.26	A-2	0.26	Si-5	0.01	None	0	S-1	73.61
6	P-1	25.86	None	0	A-1	0.26	A-2	0.26	Si-6	0.01	None	0	S-1	73.61
7	P-1	25.86	None	0	A-1	0.26	A-2	0.26	Si-7	0.01	None	0	S-1	73.61
8	P-2	25.86	None	0	A-1	0.26	A-2	0.26	Si-2	0.01	None	0	S-1	73.61
9	P-3	25.86	None	0	A-1	0.26	A-2	0.26	Si-2	0.01	None	0	S-1	73.61
10	P-2	15.52	P-1	10.34	A-1	0.26	A-2	0.26	Si-1	0.005	Si-6	0.005	S-1	73.61
11	P-2	15.52	P-1	10.34	A-1	0.26	A-2	0.26	Si-2	0.005	Si-4	0.005	S-1	73.61

[0092] Details of the compounds used are as follows.

<<Elastomer>>

P-1: SEPTON 4033 (manufactured by Kuraray Co., Ltd., polystyrene-based elastomer)

P-2: SEPTON 2104 (manufactured by Kuraray Co., Ltd., polystyrene-based elastomer)

P-3: SEPTON 8004 (manufactured by Kuraray Co., Ltd., polystyrene-based elastomer)

[0093] <<Silicon-Containing Compound>>

Si-1: TSF4446 (manufactured by Momentive Performance Materials Japan Co., Ltd., polyether-modified organopolysiloxane)

Si-2: TSF4445 (manufactured by Momentive Performance Materials Japan Co., Ltd., polyether-modified organopolysiloxane)

Si-3: Silwet L-7605 (manufactured by Momentive Performance Materials Japan Co., Ltd., polyether-modified organopolysiloxane)

Si-4: KF-6017 (manufactured by Shin-Etsu Chemical Co., Ltd., polyether-modified organopolysiloxane)

Si-5: Silwet L-7200 (manufactured by Momentive Performance Materials Japan Co., Ltd., polyether-modified organopolysiloxane)

Si-6: KP-323 (manufactured by Shin-Etsu Chemical Co., Ltd., silicone single substance)

Si-7: Fluorine atom-containing silane coupling agent (a precursor of a silicone compound) (manufactured by Tokyo Chemical Industry Co., Ltd., triethoxy(1H,1H,2H,2H-nonafluorohexyl)silane)

[0094] <<Other Additives>>

A-1: Irganox1010 (manufactured by BASF Japan)

A-2: Sumilizer TP-D (manufactured by Sumitomo Chemical Co., Ltd.)

[0095] <<Organic Solvent>>

S-1: 1,3,5-Trimethylbenzene (mesitylene, manufactured by Toyo Gosei Co., Ltd.)

[0096] <Preparation of Detergent Composition A>

As shown in Tables 2 and 3 below, the respective components of a detergent composition A 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 the detergent composition A.

[Table 2]

	Organic acid	pKa	LogP (octanol/H ₂ O)
S1	Methanesulfonic acid	-1.86	-2.38
S2	Butanesulfonic acid	4.82	0.79
S3	Benzenesulfonic acid	-2.8	-2.25
S4	Paratoluenesulfonic acid	-2.8	-0.62
S5	Camphorsulfonic acid	1.2	-0.17
S6	Dodecylbenzenesulfonic acid	2.55	4.78
S7	Diphenylphosphoric acid	3.88	2.88
S8	Phenylphosphonic acid	1.83	0.54
A1	m-Cresol	10.09	1.96

[0097] [Table 3]

Detergent composition A	Organic acid 1	Amount (% by mass) of organic acid 1	Organic acid 2	Amount (% by mass) of organic acid 2	Organic solvent 1	Amount (% by mass) of organic solvent 1	Organic solvent 2	Amount (% by mass) of organic solvent 2
CS1	S1	0.1	None	0	Mesitylene	99.9	None	0
CS2	S2	0.1	None	0	Mesitylene	99.9	None	0
CS3	S3	0.1	None	0	Mesitylene	99.9	None	0
CS4	S4	0.1	None	0	Mesitylene	99.9	None	0
CS5	S5	0.1	None	0	Mesitylene	99.9	None	0
CS6	S6	0.1	None	0	Mesitylene	99.9	None	0
CS7	S7	0.1	None	0	Mesitylene	99.9	None	0
CS8	S8	0.1	None	0	Mesitylene	99.9	None	0
CS9	S6	0.1	None	0	tert-Butylbenzene	99.9	None	0
CS10	S6	0.1	None	0	Cyclohexane	99.9	None	0
CS11	S6	0.05	S4	0.05	Cyclohexane	99.9	None	0
CS12	S6	0.1	None	0	Cyclohexane	49.9	Mesitylene	50.0
CA1	A1	0.05	None	0	Mesitylene	99.95	None	0
CA2	None	None	None	0	Mesitylene	100	None	0

[0098] <Preparation of Detergent Composition B>

As shown in Tables 4 and 5 below, the respective components of a detergent composition B 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 the detergent composition B.

[0099] [Table 4]

	Organic carboxylic acid compound	pKa	LogP (octanol/H ₂ O)
C1	Formic acid	3.77	-0.54
C2	Acetic acid	4.76	-0.17
C3	Propionic acid	4.88	0.33
C4	Oxalic acid (pKa1)	1.27	-2.22
C5	Malonic acid (pKa1)	2.85	-0.81
C6	Citric acid (pKa1)	2.79	-1.64
C7	Lactic acid	3.86	-0.72
C8	Capric acid	4.9	4.09
A2	Hydrochloric acid	-3.7	0.25

[0100] [Table 5]

Detergent composition B	Organic carboxylic acid compound 3	Amount (% by mass) of organic carboxylic acid compound 3	Organic carboxylic acid compound 4	Amount (% by mass) of organic carboxylic acid compound 4	Solvent 3	Amount (% by mass) of solvent 3	Solvent 4	Amount (% by mass) of solvent 4
CW1	C1	3.0	None	0.0	Water	97.0	None	0
CW2	C2	3.0	None	0.0	Water	97.0	None	0
CW3	C3	3.0	None	0.0	Water	97.0	None	0
CW4	C4	3.0	None	0.0	Water	97.0	None	0
CW5	C5	3.0	None	0.0	Water	97.0	None	0
CW6	C6	3.0	None	0.0	Water	97.0	None	0
CW7	C7	3.0	None	0.0	Water	97.0	None	0
CW8	C8	3.0	None	0.0	Water	97.0	None	0
CW9	C3	1.0	C6	2.0	Water	97.0	None	0
CW10	C6	5.0	C6	0.0	Water	-1.2	Isopropyl alcohol	-0.8
CA2	None	None	None	0	Mesitylene	100	None	0
CA3	A2	0.1	None	0	Water	99.9	None	0
CA4	None	None	None	0	Water	100	None	0

[0101] <Preparation of Rinsing Composition C>

As shown in Table 6 below, the respective components of a rinsing composition C were filtered using a polytetrafluoroethylene-made filter having a pore diameter of 0.2 μm , thereby preparing the rinsing composition C.

[Table 6]

Rinsing	Composition
R1	Water
R2	Isopropyl alcohol

[0102] Evaluation Method

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 was 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 lower 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 cleaning the temporary bonding layer attached onto the bevel portion.

[0103] 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 prepared 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.

[0104] The rear surface (a 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.

[0105] 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 bonder device (manufactured by Tokyo Electron Limited, Synapse Z), 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. The silicon wafer on the upper side was able to be peeled off while the silicon wafer on the lower side was not cracked.

[0106] The laminate D that was able to be subjected to the peeling was cleaned by supplying the detergent composition A while rotating the substrate to be processed of the laminate D, using a wafer bonder device (manufactured by Tokyo Electron Limited, Synapse Z). The substrate to be processed after cleaning was dried by heating at 110°C for 2 minutes.

[0107] <Observation of Surface (Carbon Atom Residues and Silicon Atom Residues)>

Cleaning was performed using the detergent composition A, and the surface of the substrate to be processed after drying 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 (carbon atom residues and silicon atom residues) were evaluated in accordance with the following standards.

<<Carbon Atom Residues>>

- 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.

<<Silicon Atom Residues>>

- 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.

[0108] Cleaning was performed using the detergent composition A, and the surface of the substrate to be processed after drying was cleaned by supplying the detergent composition B while rotating the substrate to be processed, using a wafer bonder device (manufactured by Tokyo Electron Limited, Synapse Z). The substrate to be processed after cleaning was spin-dried.

Subsequently, cleaning was performed using the detergent composition B, and the surface of the substrate to be processed after drying was rinsed by supplying the rinsing composition C while rotating the laminate D, using a wafer bonder device (manufactured by Tokyo Electron Limited, Synapse Z). The substrate to be processed was dried by heating at 100°C for 1 minute.

[0109] <Observation of Surface (Sulfur Atom Residues and Phosphorus Atom Residues)>

The surface of the substrate to be processed after performing cleaning with the detergent composition B 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 sulfur atoms and phosphorus atoms (sulfur atom residues and phosphorus atom residues) were evaluated in accordance with the following standards.

<<Sulfur Atom Residues>>

- A: Sulfur atoms exist at a ratio of less than 0.1% by mole.
- B: Sulfur atoms exist at a ratio of 0.1% by mole or more and less than 1% by mole.
- C: Sulfur atoms exist at a ratio of 1% by mole or more and less than 3% by mole.

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

<<Phosphorus Atom Residues>>

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

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

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

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

[0110] <Alleviation in Copper Discoloration>

A substrate having a copper layer with a thickness of 50 nm provided thereon was manufactured on the surface of a silicon wafer having a diameter of 12 inches in the shape of a disc by sputtering. The detergent composition A was supplied while rotating the copper layer of the silicon wafer, using a wafer bonder device (manufactured by Tokyo Electron Limited, Synapse Z). The substrate to be processed after cleaning was dried by heating at 110°C for 2 minutes. Subsequently, the substrate to be processed was cleaned by supplying the detergent composition B. Then, the substrate to be processed after cleaning was rinsed by supplying the rinsing composition C. The substrate to be processed was dried by heating at 100°C for 1 minute. A period from the start of the step of performing cleaning using the detergent composition A to the start of the step of performing cleaning using the detergent composition B was 200 seconds. A period from the start of the step of performing cleaning using the detergent composition B to the start of the step of performing cleaning using the rinsing composition C was 140 seconds. In addition, a period from the start of the step of performing cleaning using the detergent composition A to the end of the cleaning using the rinsing composition C was 460 seconds.

Thereafter, the substrate to be processed was left to stand in a clean room at room temperature of 23°C and a relative humidity of 55% for 48 hours, visually observed, and evaluated as follows.

A: Discoloration of the copper layer was not seen.

B: The copper layer was slightly discolored to pale brown.

C: The copper layer was seen to be discolored to brown.

[0111] The results are shown in Tables 7 and 8.

[Table 7]

Example	Temporary bonding material	Detergent composition A	Detergent composition B	Rinsing composition C	Carbon atom residue	Silicon atom residue	Sulfur atom residue	Phosphorous atom residue	Discoloration of copper substrate
Example 1	1	CS1	CW1	R1	A	B	A	-	A
Example 2	1	CS2	CW2	R1	A	B	A	-	A
Example 3	1	CS3	CW3	R1	A	A	A	-	A
Example 4	1	CS4	CW4	R1	A	A	A	-	A
Example 5	1	CS5	CW5	R1	A	A	A	-	A
Example 6	1	CS6	CW6	R1	A	A	A	-	A
Example 7	1	CS7	CW7	R1	A	B	-	A	A
Example 8	1	CS8	CW8	R1	A	B	-	A	A
Example 9	1	CS9	CW2	R1	A	A	A	-	A
Example 10	1	CS10	CW6	R1	A	A	A	-	A
Example 11	1	CS9	CW2	R1	A	A	A	-	A
Example 12	1	CS10	CW6	R1	A	A	A	-	A
Example 13	1	CS11	CW6	R1	A	A	A	-	A
Example 14	1	CS12	CW6	R1	A	A	A	-	A
Example 15	1	CS6	CW9	R1	A	A	A	-	A
Example 16	1	CS6	CW10	R1	A	A	A	-	A
Example 17	1	CS6	CW2	R1	A	A	A	-	A
Example 18	1	CS6	CW6	R1	A	A	A	-	A
Example 19	1	CS6	CW2	R2	A	A	A	-	A
Example 20	1	CS6	CW6	R2	A	A	A	-	A
Example 21	2	CS6	CW2	R1	A	A	A	-	A
Example 22	2	CS6	CW6	R1	A	A	A	-	A
Example 23	3	CS6	CW2	R1	A	A	A	-	A
Example 24	3	CS6	CW6	R1	A	A	A	-	A
Example 25	4	CS6	CW2	R1	A	A	A	-	A
Example 26	4	CS6	CW6	R1	A	A	A	-	A
Example 27	5	CS6	CW2	R1	A	A	A	-	A
Example 28	5	CS6	CW6	R1	A	A	A	-	A
Example 29	6	CS6	CW2	R1	A	A	A	-	A
Example 30	6	CS6	CW6	R1	A	A	A	-	A
Example 31	7	CS6	CW2	R1	A	A	A	-	A
Example 32	7	CS6	CW6	R1	A	A	A	-	A
Example 33	8	CS6	CW2	R1	A	A	A	-	A
Example 34	8	CS6	CW6	R1	A	A	A	-	A
Example 35	9	CS6	CW2	R1	A	A	A	-	A
Example 36	9	CS6	CW6	R1	A	A	A	-	A
Example 37	10	CS6	CW2	R1	A	A	A	-	A
Example 38	11	CS6	CW6	R1	A	A	A	-	A

[0112] [Table 8]

Example	Temporary bonding material	Detergent composition A	Detergent composition B	Rinsing composition C	Carbon atom residue	Silicon atom residue	Sulfur atom residue	Phosphorous atom residue	Discoloration of copper substrate
Comparative Example 1	1	CS1	None	R1	A	A	B	-	B
Comparative Example 2	1	CS2	None	R1	A	A	B	-	B
Comparative Example 3	1	CS3	None	R1	A	A	B	-	B
Comparative Example 4	1	CS4	None	R1	A	A	B	-	B
Comparative Example 5	1	CS5	None	R1	A	A	B	-	B
Comparative Example 6	1	CS6	None	R1	A	A	B	-	B
Comparative Example 7	1	CS6	None	R1	A	A	B	-	B
Comparative Example 8	1	CS6	None	R2	A	A	B	-	B
Comparative Example 9	1	CS7	None	R1	A	B	-	B	B
Comparative Example 10	1	CS8	None	R1	A	B	-	B	B
Comparative Example 11	1	CS6	None	None	A	B	B	-	B
Comparative Example 12	1	None	CW1	R1	D	C	None	-	C
Comparative Example 13	1	None	CW2	R1	D	C	None	-	C
Comparative Example 14	1	None	CW3	R1	D	C	None	-	C
Comparative Example 15	1	None	CW4	R1	D	C	None	-	C
Comparative Example 16	1	None	CW5	R1	D	C	None	-	C
Comparative Example 17	1	None	CW6	R1	D	C	None	-	C
Comparative Example 18	1	None	CW6	R1	D	C	None	-	C
Comparative Example 19	1	None	CW6	R2	D	C	None	-	C
Comparative Example 20	1	None	CW7	R1	D	C	None	-	C
Comparative Example 21	1	None	CW8	R1	D	C	None	-	C
Comparative Example 22	1	None	CW6	R1	D	C	None	-	C
Comparative Example 23	1	None	CW2	None	D	C	None	-	C
Comparative Example 24	1	CA1	CW6	R1	C	C	None	-	C
Comparative Example 25	1	CA2	CW6	R1	D	C	None	-	C
Comparative Example 26	1	CS6	CA3	R1	A	A	B	-	C
Comparative Example 27	1	CS6	CA4	None	A	A	B	-	C
Comparative Example 28	1	CS6	CA2	None	A	A	B	-	B

[0113] As is clear from the results, in a case of using the kit of the embodiment of the present invention, none of the carbon atom residue, the silicon atom residues, the sulfur atom residues, and the phosphorus atom residues was observed. In addition, discoloration of the copper layer was not observed.

Meanwhile, in the case of not using the detergent composition B (Comparative Examples 1 to 11), but the carbon atom residues and the silicon atom residues were not

observed, but the sulfur atom residues or the phosphorus atom residues were observed. In addition, some discoloration of the copper layer was observed.

On the other hand, in the case of not using the detergent composition A (Comparative Examples 12 to 23), the carbon atom residues and the silicon atom residues were observed. In addition, the copper layer was discolored to brown.

Furthermore, in a case of using other detergent compositions instead of the detergent composition A (Comparative Examples 24 and 25), any residues of the carbon atoms residues, the silicon atom residues, the sulfur atom residues, and the phosphorus atom residues were observed. In addition, discoloration of the copper layer was also observed.

Meanwhile, in a case of using other detergent compositions instead of the detergent composition B (Comparative Examples 26 to 28), the residues of the sulfur atom residues and the phosphorus atom residues were observed. In addition, some discoloration of the copper layer was observed.

[0114] The substrate obtained by the method of the present invention can be preferably used as a substrate of a semiconductor element from the viewpoint that there are none of carbon atom residues, silicon atom residues, sulfur atom residue, nor phosphorus atom residues, and there is no discoloration of the copper layer.

WHAT IS CLAIMED IS:

1. A kit comprising:

a temporary bonding material including at least one silicon-containing compound selected from the group consisting of a silicone compound and a precursor of the silicone compound;

a detergent composition A including at least one organic acid in which an acid group included in the organic acid contains a sulfur atom or a phosphorus atom, and an organic solvent; and

a detergent composition B including an organic carboxylic acid compound and at least one of water or a water-soluble solvent.

2. The kit according to claim 1,

wherein the organic acid includes at least one organic acid selected from the group consisting of an organic sulfonic acid, an organic phosphoric acid, and an organic phosphonic acid.

3. The kit according to claim 1,

wherein the silicon-containing compound includes a silicone oil.

4. The kit according to any one of claims 1 to 3,

wherein the silicon-containing compound includes a polyether-modified silicone.

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

wherein a content of the silicon-containing 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 any one of claims 1 to 7,
wherein an acid dissociation constant pK_a of the organic acid is -4 to 5.
9. The kit according to any one of claims 1 to 8,
wherein the organic acid is selected from the group consisting of an alkylsulfonic acid, an aromatic sulfonic acid, an alkylphosphoric acid, an aromatic phosphoric acid, an alkylphosphonic acid, and an aromatic phosphonic acid.
10. The kit according to any one of claims 1 to 9,
wherein the organic solvent included in the detergent composition A includes an aromatic hydrocarbon-based solvent having an alkyl group.
11. The kit according to claim 10,
wherein the aromatic hydrocarbon-based solvent having an alkyl group is a solvent having a benzene ring and 1 to 3 alkyl groups having 1 to 10 carbon atoms.
12. The kit according to any one of claims 1 to 11,
wherein a mass ratio of the organic acid to the organic solvent in the detergent composition A is 0.0001:99.9999 to 50:50.
13. The kit according to any one of claims 1 to 12,
wherein the organic carboxylic acid compound is selected from the group consisting of a saturated fatty acid, an unsaturated fatty acid, a hydroxy acid, and an aromatic carboxylic acid.
14. The kit according to any one of claims 1 to 13,
wherein a value represented by a base-10 logarithm $\log P$ of P which is a 1-octanol/water partition coefficient representing a ratio of equilibrium concentrations of the organic carboxylic acid compound in 1-octanol and water is -5 to 6.
15. The kit according to any one of claims 1 to 14,
wherein the solvent included in the detergent composition B includes water.

16. The kit according to any one of claims 1 to 15,
wherein an acid dissociation constant pK_a of the organic carboxylic acid compound is 1 to 7.
17. The kit according to any one of claims 1 to 16,
wherein a mass ratio of the organic carboxylic acid compound to the solvent in the detergent composition B is 0.0001:99.9999 to 50:50.
18. The kit according to any one of claims 1 to 17, further comprising a rinsing composition C including at least one of water or an alcohol.
19. A method for manufacturing a semiconductor element, comprising:
cleaning a substrate having a silicone compound on a surface thereof using a detergent composition A; and
further cleaning the cleaned substrate using a detergent composition B,
wherein the detergent composition A includes at least one organic acid in which an acid group included in the organic acid contains a sulfur atom or a phosphorus atom, and an organic solvent, and
the detergent composition B includes an organic carboxylic acid compound and at least one of water or a water-soluble solvent.
20. The method for manufacturing a semiconductor element according to claim 19,
wherein the organic acid includes at least one organic acid selected from the group consisting of an organic sulfonic acid, an organic phosphoric acid, and an organic phosphonic acid.
21. The method for manufacturing a semiconductor element according to claim 19 or 20,
wherein a temporary bonding layer formed from a temporary bonding material is provided on the substrate, at least a part of the temporary bonding layer is cleaned with the organic acid, and the temporary bonding material includes at least one of the silicone compound or a precursor of the silicone compound.
22. The method for manufacturing a semiconductor element according to any one of claims

19 to 21,

wherein the performing cleaning using the detergent composition A and the performing cleaning using the detergent composition B are performed by a single wafer method.

23. The method for manufacturing a semiconductor element according to any one of claims 19 to 22, further comprising a drying after each of the performing cleaning using the detergent composition A and the performing cleaning using the detergent composition B.

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

wherein a period from the start of the performing cleaning using the detergent composition A to the end of the performing cleaning using the detergent composition B for one sheet of the substrate is 30 to 300 seconds.

25. The method for manufacturing a semiconductor element according to any one of claims 19 to 24, further comprising performing a rinsing treatment using a rinsing composition C including at least one of water or an alcohol after the performing cleaning using the detergent composition B.

26. The method for manufacturing a semiconductor element according to any one of claims 19 to 25, using the kit according to any one of claims 1 to 18.

27. A method for cleaning a substrate of a semiconductor element, comprising:

cleaning a substrate having a silicone compound on a surface thereof using a detergent composition A; and

further cleaning the cleaned substrate using a detergent composition B,

wherein the detergent composition A includes at least one organic acid in which an acid group included in the organic acid contains a sulfur atom or a phosphorus atom, and an organic solvent, and

the detergent composition B includes an organic carboxylic acid compound and at least one of water or a water-soluble solvent.

28. The method for cleaning a substrate of a semiconductor element according to claim 27, further comprising performing a rinsing treatment using a rinsing composition C including at least one of water or an alcohol after the performing cleaning using the detergent composition B.
29. The method for cleaning a substrate of a semiconductor element according to claim 27 or 28, using the kit according to any one of claims 1 to 18.