

DESCRIPTION

Title of Invention:

ADHESIVE COMPOSITION, LAMINATE, AND METHOD FOR PRODUCING
PROCESSED SEMICONDUCTOR SUBSTRATE

Technical Field

[0001]

The present invention relates to an adhesive composition, a laminate, and a method for producing a processed semiconductor substrate.

Background Art

[0002]

There is a demand for semiconductor integration technology in which semiconductor wafers conventionally integrated in a two-dimensional planar direction are further integrated (laminated) also in a three-dimensional direction for the purpose of achieving even higher integration. This three-dimensional lamination is a technology of integrating multiple layers while connecting the layers by a through silicon via (TSV). At the time of multilayer integration, respective wafers to be integrated are thinned by polishing on the side opposite to the formed circuit surface (that is, the back surface), and the thinned semiconductor wafers are laminated.

[0003]

A semiconductor wafer before thinning (also referred to herein simply as a wafer) is bonded to a support in order to be polished with a polishing apparatus. The adhesion at that time needs to be easily releasable after polishing, and is therefore referred to as temporary adhesion. This temporary adhesion needs to allow easy removal from the support. Otherwise, the thinned semiconductor wafer may be cut or deformed when a large force is applied for the removal. In order to prevent such a situation, the semiconductor wafer is easily removed. On the other hand, it is not also preferable that polishing stress at the time of polishing the back surface of the semiconductor wafer causes the semiconductor wafer to be detached or displaced. Therefore, the performance required for temporary adhesion is to withstand the stress during polishing and to allow for easy removal after polishing.

[0004]

As temporary adhesives used for such temporary adhesion, an adhesive containing polydimethylsiloxane (Patent Literature 1), a temporary adhesive containing an epoxy-modified polysiloxane (Patent Literature 2), and the like have been proposed.

Citation List

Patent Literature

[0005]

Patent Literature 1: WO 2017/221772 A

Patent Literature 2: WO 2018/216732 A

Summary of Invention

Technical Problem

[0006]

An object of the present invention is to provide an adhesive composition capable of forming an adhesive layer having excellent releasability, a laminate using the adhesive composition, and a method for producing a processed semiconductor substrate or a processed electronic device layer using the laminate.

Solution to Problem

[0007]

As a result of intensive studies to solve the above problem, the present inventors have found that the above problem can be solved, and completed the present invention having the following gist.

[0008]

That is, the present invention includes the following items.

- [1] An adhesive composition containing two or more types of release agent components,

wherein one of the two or more types of release agent components is an epoxy group-containing polyorganosiloxane having an epoxy value of more than 0.02 mol/kg.

[2] The adhesive composition according to [1], wherein the epoxy group-containing polyorganosiloxane has an epoxy value of 3.0 mol/kg or less.

[3] The adhesive composition according to [1] or [2], wherein one of the two or more types of release agent components is a polyorganosiloxane other than the epoxy group-containing polyorganosiloxane.

[4] The adhesive composition according to [3], wherein a mass ratio (EPOS:POS) of the epoxy group-containing polyorganosiloxane (EPOS) to the polyorganosiloxane (POS) is 0.2:1 to 1:0.2.

[5] The adhesive composition according to any one of [1] to [4], wherein the adhesive composition contains an adhesive component.

[6] The adhesive composition according to [5], wherein the adhesive component is a component that is cured by a hydrosilylation reaction.

[7] The adhesive composition according to [6], wherein the component that is cured by a hydrosilylation reaction contains:

a component (A-1) containing an alkenyl group having 2 to 40 carbon atoms, the alkenyl group being bonded to a

silicon atom;

a component (A-2) containing a Si-H group; and

a platinum group metal-based catalyst (A-3).

[8] The adhesive composition according to [7], wherein the component (A-1) contains a polyorganosiloxane (a1) containing an alkenyl group having 2 to 40 carbon atoms, the alkenyl group being bonded to a silicon atom.

[9] The adhesive composition according to [7] or [8], wherein the component (A-2) contains a polyorganosiloxane containing a Si-H group.

[10] A laminate including:

a semiconductor substrate or an electronic device layer;

a support substrate; and

an adhesive layer provided between the semiconductor substrate or the electronic device layer and the support substrate,

wherein the adhesive layer is an adhesive layer formed from the adhesive composition according to any one of [1] to [9].

[11] A method for producing a processed semiconductor substrate or a processed electronic device layer, the method including:

a step 5A of processing the semiconductor substrate of the laminate according to [10], or a step 5B of processing

the electronic device layer of the laminate according to [10]; and

a step 6A of separating the semiconductor substrate processed in the step 5A from the support substrate, or a step 6B of separating the electronic device layer processed in the step 5B from the support substrate.

Advantageous Effects of Invention

[0009]

According to the present invention, it is possible to provide an adhesive composition capable of forming an adhesive layer having excellent releasability, a laminate using the adhesive composition, and a method for producing a processed semiconductor substrate or a processed electronic device layer using the laminate.

Brief Description of Drawings

[0010]

[Fig. 1] Fig. 1 is a schematic cross-sectional view of an example of a laminate according to a first embodiment.

[Fig. 2] Fig. 2 is a schematic cross-sectional view of another example of the laminate in the first embodiment.

[Fig. 3A] Fig. 3A is a schematic cross-sectional view for describing an example of a method for producing a laminate in the first embodiment (part 1).

[Fig. 3B] Fig. 3B is a schematic cross-sectional view for describing an example of the method for producing a laminate in the first embodiment (part 2).

[Fig. 4] Fig. 4 is a schematic cross-sectional view of an example of a laminate in a second embodiment.

[Fig. 5] Fig. 5 is a schematic cross-sectional view of another example of the laminate in the second embodiment.

[Fig. 6A] Fig. 6A is a schematic cross-sectional view for describing an example of a method for producing a laminate in the second embodiment (part 1).

[Fig. 6B] Fig. 6B is a schematic cross-sectional view for describing an example of the method for producing a laminate in the second embodiment (part 2).

[Fig. 6C] Fig. 6C is a schematic cross-sectional view for describing an example of the method for producing a laminate in the second embodiment (part 3).

[Fig. 7A] Fig. 7A is a schematic cross-sectional view for describing an example of a method for processing a laminate in the first embodiment (part 1).

[Fig. 7B] Fig. 7B is a schematic cross-sectional view for describing an example of the method for processing a laminate in the first embodiment (part 2).

[Fig. 7C] Fig. 7C is a schematic cross-sectional view for describing an example of the method for processing a laminate in the first embodiment (part 3).

[Fig. 7D] Fig. 7D is a schematic cross-sectional view for describing an example of the method for processing a laminate in the first embodiment (part 4).

[Fig. 8A] Fig. 8A is a schematic cross-sectional view for describing an example of a method for processing a laminate in the second embodiment (part 1).

[Fig. 8B] Fig. 8B is a schematic cross-sectional view for describing an example of a method for processing a laminate in the second embodiment (part 2).

[Fig. 8C] Fig. 8C is a schematic cross-sectional view for describing an example of a method for processing a laminate in the second embodiment (part 3).

[Fig. 8D] Fig. 8D is a schematic cross-sectional view for describing an example of a method for processing a laminate in the second embodiment (part 4).

[Fig. 8E] Fig. 8E is a schematic cross-sectional view for describing an example of a method for processing a laminate in the second embodiment (part 5).

[Fig. 8F] Fig. 8F is a schematic cross-sectional view for describing an example of a method for processing a laminate in the second embodiment (part 6).

Description of Embodiments

[0011]

(Adhesive Composition)

An adhesive composition of the present invention contains two or more types of release agent components.

In the adhesive composition, one of the two or more types of release agent components is an epoxy group-containing polyorganosiloxane having an epoxy value of more than 0.02 mol/kg.

Since the adhesive composition contains two or more types of release agent components, and one of the two or more types of release agent components is an epoxy group-containing polyorganosiloxane having an epoxy value of more than 0.02 mol/kg, it is possible to form an adhesive layer having excellent releasability.

Details of the release agent components will be described below.

[0012]

Examples of the adhesive composition include, but are not limited to, a polysiloxane-based adhesive, an acrylic resin-based adhesive, an epoxy resin-based adhesive, a polyamide-based adhesive, a polystyrene-based adhesive, a polyimide adhesive, and a phenolic resin-based adhesive.

Among them, a polysiloxane-based adhesive is preferable as the adhesive composition because the adhesive composition exhibits suitable adhesive performance during processing of the semiconductor substrate or the like, can be suitably released after processing, is further excellent

in heat resistance, and can be suitably removed by the cleaning agent composition.

[0013]

The adhesive composition contains, for example, an adhesive component.

[0014]

<Adhesive Component>

The adhesive component is not particularly limited, but is preferably a component that undergoes curing, and more preferably a component that is cured by a hydrosilylation reaction.

The component that is cured by a hydrosilylation reaction is not particularly limited, but preferably contains a component containing an alkenyl group having 2 to 40 carbon atoms, the alkenyl group being bonded to a silicon atom (hereinafter, also referred to as "component (A-1)" in some cases), a component containing a Si-H group (hereinafter, also referred to as "component (A-2)" in some cases), and a platinum group metal-based catalyst (A-3).

The adhesive component preferably does not contain a polyimide resin.

The adhesive component preferably does not have an imide bond.

[0015]

<<Component (A-1) and Component (A-2)>>

The adhesive composition preferably contains the component (A-1).

The adhesive composition preferably contains the component (A-2).

Hereinafter, the combination of the component (A-1), the component (A-2), and the platinum group metal-based catalyst (A-3) may be referred to as "curing component (A)" or "component (A)".

[0016]

From the viewpoint of suitably obtaining the effects of the present invention, the component (A-1) preferably contains a polyorganosiloxane (a1) containing an alkenyl group having 2 to 40 carbon atoms, the alkenyl group being bonded to a silicon atom.

From the viewpoint of suitably obtaining the effects of the present invention, the component (A-2) preferably contains a polyorganosiloxane (a2) containing a Si-H group.

Here, the alkenyl group having 2 to 40 carbon atoms may be substituted. Examples of the substituent include a halogen atom, a nitro group, a cyano group, an amino group, a hydroxy group, a carboxyl group, an aryl group, and a heteroaryl group.

[0017]

In another preferred embodiment, the adhesive composition that is cured by a hydrosilylation reaction

contains a polysiloxane (A1) containing one or two or more units selected from the group consisting of a siloxane unit (Q unit) represented by SiO_2 , a siloxane unit (M unit) represented by $\text{R}^1\text{R}^2\text{R}^3\text{SiO}_{1/2}$, a siloxane unit (D unit) represented by $\text{R}^4\text{R}^5\text{SiO}_{2/2}$, and a siloxane unit (T unit) represented by $\text{R}^6\text{SiO}_{3/2}$, and a platinum group metal-based catalyst (A-3). The polysiloxane (A1) contains a polyorganosiloxane (a1') containing one or two or more units selected from the group consisting of a siloxane unit (Q' unit) represented by SiO_2 , a siloxane unit (M' unit) represented by $\text{R}^1'\text{R}^2'\text{R}^3'\text{SiO}_{1/2}$, a siloxane unit (D' unit) represented by $\text{R}^4'\text{R}^5'\text{SiO}_{2/2}$, and a siloxane unit (T' unit) represented by $\text{R}^6'\text{SiO}_{3/2}$, and also containing at least one selected from the group consisting of M' units, D' units, and T' units; and a polyorganosiloxane (a2') containing one or two or more units selected from the group consisting of a siloxane unit (Q'' unit) represented by SiO_2 , a siloxane unit (M'' unit) represented by $\text{R}^1''\text{R}^2''\text{R}^3''\text{SiO}_{1/2}$, a siloxane unit (D'' unit) represented by $\text{R}^4''\text{R}^5''\text{SiO}_{2/2}$, and a siloxane unit (T'' unit) represented by $\text{R}^6''\text{SiO}_{3/2}$, and also containing at least one selected from the group consisting of M'' units, D'' units, and T'' units.

Note that (a1') is an example of (a1), and (a2') is an example of (a2).

[0018]

R^1 to R^6 are groups or atoms bonded to a silicon atom, and R^1 to R^6 each independently represent an alkyl group which may be substituted, an alkenyl group which may be substituted, or a hydrogen atom. Examples of the substituent include a halogen atom, a nitro group, a cyano group, an amino group, a hydroxy group, a carboxyl group, an aryl group, and a heteroaryl group.

[0019]

$R^{1'}$ to $R^{6'}$ are groups bonded to a silicon atom, and $R^{1'}$ to $R^{6'}$ each independently represent an alkyl group which may be substituted or an alkenyl group which may be substituted, provided that at least one of $R^{1'}$ to $R^{6'}$ is an alkenyl group which may be substituted. Examples of the substituent include a halogen atom, a nitro group, a cyano group, an amino group, a hydroxy group, a carboxyl group, an aryl group, and a heteroaryl group.

[0020]

$R^{1''}$ to $R^{6''}$ are groups or atoms bonded to a silicon atom, and $R^{1''}$ to $R^{6''}$ each independently represent an alkyl group which may be substituted or a hydrogen atom, provided that at least one of $R^{1''}$ to $R^{6''}$ is a hydrogen atom. Examples of the substituent include a halogen atom, a nitro group, a cyano group, an amino group, a hydroxy group, a carboxyl group, an aryl group, and a heteroaryl group.

[0021]

The alkyl group may be linear, branched, or cyclic, and is preferably a linear or branched alkyl group. The number of carbon atoms thereof is not particularly limited, and is usually 1 to 40, preferably 30 or less, more preferably 20 or less, and still more preferably 10 or less.

[0022]

Specific examples of the linear or branched alkyl group which may be substituted include, but are not limited to, a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group, an s-butyl group, a tertiary butyl group, an n-pentyl group, a 1-methyl-n-butyl group, a 2-methyl-n-butyl group, a 3-methyl-n-butyl group, a 1,1-dimethyl-n-propyl group, a 1,2-dimethyl-n-propyl group, a 2,2-dimethyl-n-propyl group, a 1-ethyl-n-propyl group, an n-hexyl group, a 1-methyl-n-pentyl group, a 2-methyl-n-pentyl group, a 3-methyl-n-pentyl group, a 4-methyl-n-pentyl group, a 1,1-dimethyl-n-butyl group, a 1,2-dimethyl-n-butyl group, a 1,3-dimethyl-n-butyl group, a 2,2-dimethyl-n-butyl group, a 2,3-dimethyl-n-butyl group, a 3,3-dimethyl-n-butyl group, a 1-ethyl-n-butyl group, a 2-ethyl-n-butyl group, a 1,1,2-trimethyl-n-propyl group, a 1,2,2-trimethyl-n-propyl group, a 1-ethyl-1-methyl-n-propyl group, and a 1-ethyl-2-methyl-n-propyl group, and the number of carbon atoms thereof is usually 1 to 14, preferably 1 to 10, and more preferably 1

to 6. Among them, a methyl group is particularly preferable.

[0023]

Specific examples of the cyclic alkyl group which may be substituted include, but are not limited to, cycloalkyl groups such as a cyclopropyl group, a cyclobutyl group, a 1-methyl-cyclopropyl group, a 2-methyl-cyclopropyl group, a cyclopentyl group, a 1-methyl-cyclobutyl group, a 2-methyl-cyclobutyl group, a 3-methyl-cyclobutyl group, a 1,2-dimethyl-cyclopropyl group, a 2,3-dimethyl-cyclopropyl group, a 1-ethyl-cyclopropyl group, a 2-ethyl-cyclopropyl group, a cyclohexyl group, a 1-methyl-cyclopentyl group, a 2-methyl-cyclopentyl group, a 3-methyl-cyclopentyl group, a 1-ethyl-cyclobutyl group, a 2-ethyl-cyclobutyl group, a 3-ethyl-cyclobutyl group, a 1,2-dimethyl-cyclobutyl group, a 1,3-dimethyl-cyclobutyl group, a 2,2-dimethyl-cyclobutyl group, a 2,3-dimethyl-cyclobutyl group, a 2,4-dimethyl-cyclobutyl group, a 3,3-dimethyl-cyclobutyl group, a 1-n-propyl-cyclopropyl group, a 2-n-propyl-cyclopropyl group, a 1-i-propyl-cyclopropyl group, a 2-i-propyl-cyclopropyl group, a 1,2,2-trimethyl-cyclopropyl group, a 1,2,3-trimethyl-cyclopropyl group, a 2,2,3-trimethyl-cyclopropyl group, a 1-ethyl-2-methyl-cyclopropyl group, a 2-ethyl-1-methyl-cyclopropyl group, a 2-ethyl-2-methyl-cyclopropyl group, and a 2-ethyl-3-methyl-cyclopropyl group; and a

bicycloalkyl group such as a bicyclobutyl group, a bicyclopentyl group, a bicyclohexyl group, a bicycloheptyl group, a bicyclooctyl group, a bicyclononyl group, and a bicyclodecyl group, and the number of carbon atoms thereof is usually 3 to 14, preferably 4 to 10, and more preferably 5 to 6.

[0024]

The alkenyl group may be linear or branched, and the number of carbon atoms thereof is not particularly limited, and is usually 2 to 40, preferably 30 or less, more preferably 20 or less, and still more preferably 10 or less.

[0025]

Specific examples of the linear or branched alkenyl group which may be substituted include, but are not limited to, a vinyl group, an allyl group, a butenyl group, and a pentenyl group, and the number of carbon atoms thereof is usually 2 to 14, preferably 2 to 10, and more preferably 1 to 6. Among them, an ethenyl group and a 2-propenyl group are particularly preferable.

Specific examples of the cyclic alkenyl group which may be substituted include, but are not limited to, cyclopentenyl and cyclohexenyl, and the number of carbon atoms thereof is usually 4 to 14, preferably 5 to 10, and more preferably 5 to 6.

[0026]

As described above, the polysiloxane (A1) contains a polyorganosiloxane (a1') and a polyorganosiloxane (a2'), and an alkenyl group contained in the polyorganosiloxane (a1') and a hydrogen atom (Si-H group) contained in the polyorganosiloxane (a2') form a crosslinked structure and cure by a hydrosilylation reaction with the platinum group metal-based catalyst (A-3). As a result, a cured film is formed.

[0027]

The polyorganosiloxane (a1') contains one or two or more units selected from the group consisting of a Q' unit, an M' unit, a D' unit, and a T' unit, and contains at least one selected from the group consisting of an M' unit, a D' unit, and a T' unit. As the polyorganosiloxane (a1'), two or more polyorganosiloxanes satisfying such conditions may be used in combination.

[0028]

Examples of preferred combinations of two or more types selected from the group consisting of a Q' unit, an M' unit, a D' unit, and a T' unit include, but are not limited to, (Q' unit and M' unit), (D' unit and M' unit), (T' unit and M' unit), and (Q' unit, T' unit, and M' unit).

[0029]

In addition, when the polyorganosiloxane (a1') contains

two or more polyorganosiloxanes, a combination of (Q' unit and M' unit) and (D' unit and M' unit), a combination of (T' unit and M' unit) and (D' unit and M' unit), and a combination of (Q' unit, T' unit, and M' unit) and (T' unit and M' unit) are preferable, but are not limited thereto.

[0030]

The polyorganosiloxane (a2') contains one or two or more units selected from the group consisting of a Q'' unit, an M'' unit, a D'' unit, and a T'' unit, and contains at least one selected from the group consisting of an M'' unit, a D'' unit, and a T'' unit. As the polyorganosiloxane (a2'), two or more polyorganosiloxanes satisfying such conditions may be used in combination.

[0031]

Examples of preferred combinations of two or more selected from the group consisting of a Q'' unit, an M'' unit, a D'' unit, and a T'' unit include, but are not limited to, (M'' unit and D'' unit), (Q'' unit and M'' unit), and (Q'' unit, T'' unit, and M'' unit).

[0032]

The polyorganosiloxane (a1') is composed of siloxane units in which alkyl groups and/or alkenyl groups are bonded to silicon atoms of the polyorganosiloxane, and the proportion of alkenyl groups in all substituents represented by R^{1'} to R^{6'} is preferably 0.1 to 50.0 mol%,

more preferably 0.5 to 30.0 mol%, and the remaining R^{1'} to R^{6'} can be alkyl groups.

[0033]

The polyorganosiloxane (a2') is composed of siloxane units in which alkyl groups and/or hydrogen atoms are bonded to silicon atoms of the polyorganosiloxane, and the proportion of hydrogen atoms in all substituents and substitutional atoms represented by R^{1''} to R^{6''} is preferably 0.1 to 50.0 mol%, more preferably 10.0 to 40.0 mol%, and the remaining R^{1''} to R^{6''} can be alkyl groups.

[0034]

When the adhesive composition contains (a1) and (a2), in a preferred embodiment of the present invention, the molar ratio of the alkenyl group contained in the polyorganosiloxane (a1) and the hydrogen atom constituting the Si-H bond contained in the polyorganosiloxane (a2) is in the range of 1.0:0.5 to 1.0:0.66.

[0035]

The weight-average molecular weight of the polysiloxane such as the polyorganosiloxane (a1) or the polyorganosiloxane (a2) is not particularly limited, and each is typically 500 to 1,000,000, and is preferably 5,000 to 50,000 from the viewpoint of achieving the effects of the present invention with good reproducibility.

In the present invention, the weight-average molecular

weight, the number-average molecular weight, and the dispersity of the polyorganosiloxanes can be measured, for example, using a GPC apparatus (EcoSEC, HLC-8320GPC, manufactured by Tosoh Corporation) and a GPC column (TSKgel SuperMultiporeHZ-N and TSKgel SuperMultiporeHZ-H, manufactured by Tosoh Corporation), at a column temperature of 40°C, using tetrahydrofuran as an eluent (elution solvent), at a flow rate of 0.35 mL/min, and using polystyrene (Shodex from Showa Denko K.K.) as a standard sample.

[0036]

The viscosities of the polyorganosiloxane (a1) and the polyorganosiloxane (a2) are not particularly limited, and are each usually 10 to 1,000,000 (mPa·s), and are preferably 50 to 10,000 (mPa·s) from the viewpoint of achieving the effects of the present invention with good reproducibility. The viscosities of the polyorganosiloxane (a1) and the polyorganosiloxane (a2) are values measured with an E-type rotational viscometer at 25°C.

[0037]

The polyorganosiloxane (a1) and the polyorganosiloxane (a2) react with each other by a hydrosilylation reaction. Accordingly, the mechanism of curing is different from, for example, that through silanol groups, and therefore, neither siloxane needs to contain a silanol group or a

functional group that forms a silanol group by hydrolysis, such as an alkyloxy group.

[0038]

<<Platinum Group Metal-Based Catalyst (A-3)>>

The platinum group metal-based catalyst is a platinum-based metal catalyst.

Such a platinum-based metal catalyst is a catalyst for promoting the hydrosilylation reaction between the alkenyl group and the Si-H group.

[0039]

As a specific example of the platinum-based metal catalyst, a catalyst known as a platinum-based compound (platinum or a compound containing platinum) can be used.

Specific examples thereof include platinum fine powder, platinum black, chloroplatinic acid, an alcohol-modified product of chloroplatinic acid, a complex of chloroplatinic acid and diolefin, a platinum-olefin complex, a platinum-carbonyl complex [platinum bis(acetoacetate), platinum bis(acetylacetonate), or the like], a chloroplatinic acid-alkenylsiloxane complex (chloroplatinic acid-divinyltetramethyldisiloxane complex, chloroplatinic acid-tetravinyltetramethylcyclotetrasiloxane complex, or the like), a platinum-alkenylsiloxane complex (platinum-divinyltetramethyldisiloxane complex, platinum-tetravinyltetramethylcyclotetrasiloxane complex, or the

like), and a complex of chloroplatinic acid and an acetylene alcohol. Among them, a platinum-alkenylsiloxane complex is particularly preferable because it has a high effect of promoting the hydrosilylation reaction.

These hydrosilylation reaction catalysts may be used alone, or two or more thereof may be used in combination.

[0040]

The alkenylsiloxane used in the platinum-alkenylsiloxane complex is not particularly limited, and examples thereof include 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane; alkenylsiloxane oligomers in which some of the methyl groups of the alkenylsiloxane are substituted with ethyl groups, phenyl groups, or the like; and alkenylsiloxane oligomers in which the vinyl groups of these alkenylsiloxanes are substituted with allyl groups, hexenyl groups, or the like. In particular, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane is preferable since the platinum-alkenylsiloxane complex to be produced has good stability.

[0041]

The content of the platinum group metal-based catalyst (A-3) in the adhesive composition is not particularly limited, and is, for example, in the range of 0.1 to 50.0 ppm based on the total mass of the component (A-1) and the

component (A-2).

[0042]

<<Polymerization Inhibitor>>

The adhesive component may contain a polymerization inhibitor for the purpose of suppressing the progress of the hydrosilylation reaction.

The polymerization inhibitor is not particularly limited as long as it is possible to suppress the progress of the hydrosilylation reaction, and specific examples thereof include alkynyl alcohols such as 1-ethynyl-1-cyclohexanol and 1,1-diphenyl-2-propyn-1-ol.

The amount of the polymerization inhibitor is not particularly limited, but is usually 1,000.0 ppm or more with respect to, for example, the total amount of the polyorganosiloxane (a1) and the polyorganosiloxane (a2) from the viewpoint of obtaining the effect, and is 10,000.0 ppm or less from the viewpoint of preventing excessive suppression of the hydrosilylation reaction.

[0043]

<Release Agent Component>

The adhesive composition contains two or more types of release agent components.

As the release agent component, a component that does not contain a fluorine atom is preferable.

In the adhesive composition, one of the two or more

types of release agent components is an epoxy group-containing polyorganosiloxane having an epoxy value of more than 0.02 mol/kg.

The epoxy value of the epoxy group-containing polyorganosiloxane is more than 0.02 mol/kg, and is preferably 0.05 mol/kg or more, more preferably 0.08 mol/kg or more, and particularly preferably 1.0 mol/kg or more. The upper limit of the epoxy value is not particularly limited, but the epoxy value is, for example, 3.0 mol/kg or less, 2.0 mol/kg or less, and 1.5 mol/kg or less.

The epoxy value can be measured, for example, by titration using an automatic titrator. Examples of the titration sample and titrant used for the titration are as follows.

A titration sample is prepared by adding 30 ml of a diluent having an acetone/acetic acid/tetraethylammonium bromide=750/750/105 (weight ratio) to 0.25 g of the epoxy group-containing polyorganosiloxane. As the titrant, a 0.1 mol/l perchloric acid-acetic acid standard solution is used.

[0044]

The two types in the two or more types of release agent components do not refer to, for example, a combination of two epoxy group-containing polyorganosiloxanes having different molecular weights, viscosities, types of epoxy

groups, or the like.

When the release agent component is a mixture of two epoxy group-containing polyorganosiloxanes (for example, two products of epoxy group-containing polyorganosiloxanes), the epoxy value refers to the epoxy value in the mixed state thereof.

The two types in the two or more types of polyorganosiloxanes mean, for example, a combination of polydimethylsiloxane and an epoxy group-containing polyorganosiloxane, and a combination of polydimethylsiloxane and a phenyl group-containing polyorganosiloxane, and do not refer to, for example, a combination of two epoxy group-containing polyorganosiloxanes having different molecular weights, viscosities, types of epoxy groups, or the like.

[0045]

As the release agent component other than the epoxy group-containing polyorganosiloxane, there is no particular limitation, but a polyorganosiloxane is preferable from the viewpoint of more suitably obtaining the effects of the present invention.

The polyorganosiloxane as the release agent component usually does not react with the adhesive component.

For example, the polyorganosiloxane as the release agent component is a component that does not undergo a

hydrosilylation reaction.

[0046]

Polyorganosiloxanes other than the epoxy group-containing polyorganosiloxane are not particularly limited, and examples thereof include polydimethylsiloxane, a phenyl group-containing polyorganosiloxane, and a carbinol-modified polyorganosiloxane.

[0047]

In the adhesive composition, the mass ratio (EPOS:POS) of the epoxy group-containing polyorganosiloxane (EPOS) to the polyorganosiloxane (POS), which is a polyorganosiloxane other than the epoxy group-containing polyorganosiloxane, is not particularly limited, but is, for example, 0.2:1 to 1:0.2, preferably 0.3:1 to 1:0.3, more preferably 0.4:1 to 1:0.4, and particularly preferably 0.5:1 to 1:0.5.

[0048]

<<Epoxy Group-Containing Polyorganosiloxane>>

As the epoxy group-containing polyorganosiloxane, one that does not have an epoxy group at a terminal is preferable.

As the epoxy group-containing polyorganosiloxane, one that has an epoxy group in a side chain is preferable.

Examples of the epoxy group-containing polyorganosiloxane include those containing a siloxane unit (D^{10} unit) represented by $R^{11}R^{12}SiO_{2/2}$.

[0049]

R¹¹ is a group bonded to a silicon atom and represents an alkyl group, and R¹² is a group bonded to a silicon atom and represents an epoxy group or an organic group containing an epoxy group. Specific examples of the alkyl group include the above-described examples.

The epoxy group in the organic group containing an epoxy group may be an independent epoxy group that is not fused to another ring, or may be an epoxy group forming a fused ring with another ring, such as a 1,2-epoxycyclohexyl group.

Specific examples of the organic group containing an epoxy group include, but are not limited to, 3-glycidoxypropyl and 2-(3,4-epoxycyclohexyl)ethyl.

In the present invention, preferred examples of the epoxy group-containing polyorganosiloxane include, but are not limited to, an epoxy group-containing polydimethylsiloxane.

[0050]

The epoxy group-containing polyorganosiloxane contains the above-described siloxane unit (D¹⁰ unit), but may contain, in addition to the D¹⁰ unit, Q units, M units, and/or T units.

In a preferred embodiment of the present invention, specific examples of the epoxy group-containing

polyorganosiloxane include a polyorganosiloxane composed only of D¹⁰ units, a polyorganosiloxane containing D¹⁰ units and Q units, a polyorganosiloxane containing D¹⁰ units and M units, a polyorganosiloxane containing D¹⁰ units and T units, a polyorganosiloxane containing D¹⁰ units, Q units, and M units, a polyorganosiloxane containing D¹⁰ units, M units, and T units, or a polyorganosiloxane containing D¹⁰ units, Q units, M units, and T units.

[0051]

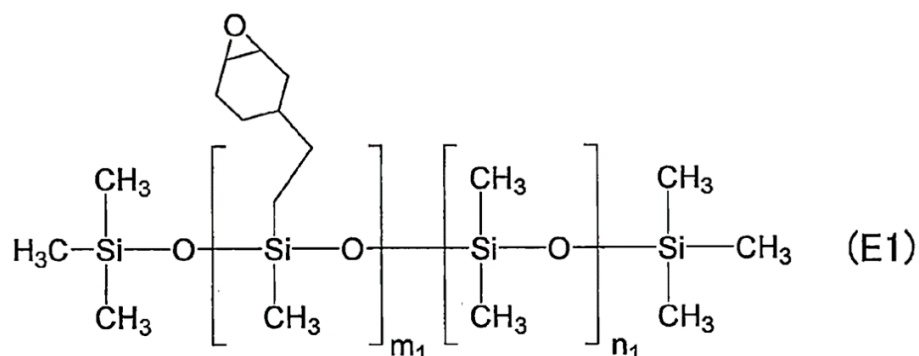
The epoxy group-containing polyorganosiloxane may have an epoxy group in a side chain, may have an epoxy group at one terminal, or may have an epoxy group at both terminals.

[0052]

Specific examples of the epoxy group-containing polyorganosiloxane include, but are not limited to, those represented by Formulas (E1) to (E3).

[0053]

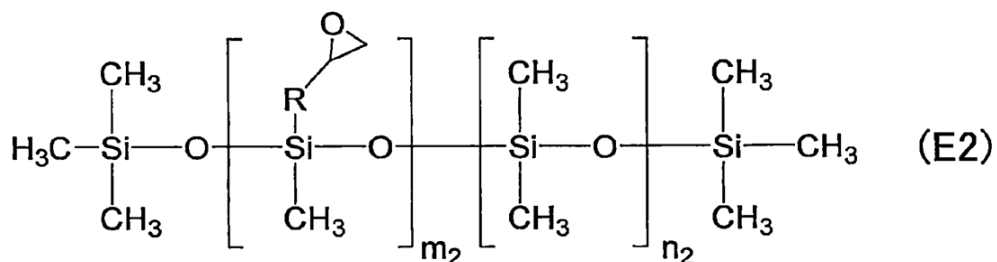
[Chem. 1]



(m_1 and n_1 represent the number of respective repeating units, and are positive integers.)

[0054]

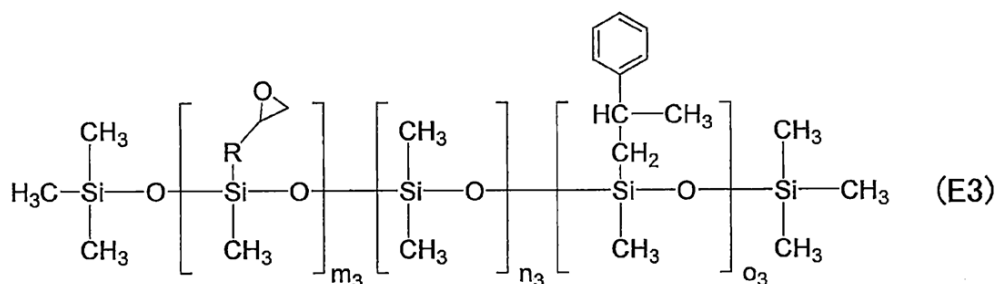
[Chem. 2]



(m_2 and n_2 represent the numbers of the respective repeating units and are positive integers, and R is an alkylene group having 1 to 10 carbon atoms which may be interrupted by at least one of an oxygen atom and an unsaturated bond (for example, a carbon-carbon double bond, a carbon-carbon triple bond, or -N=N-).)

[0055]

[Chem. 3]



(m_3 , n_3 , and o_3 represent the numbers of the respective repeating units and are positive integers, and R is an alkylene group having 1 to 10 carbon atoms which may be

interrupted by at least one of an oxygen atom and an unsaturated bond (for example, a carbon-carbon double bond, a carbon-carbon triple bond, or $-N=N-$).

[0056]

In the above general formula, when m_1 , m_2 , m_3 , and o_3 are 2 or more, these repeating units may be arranged adjacent to each other to form a block, or may be randomly arranged.

[0057]

Note that the polyorganosiloxane represented by Formula (E3) has an epoxy group and a phenyl group and is thus an epoxy group-containing polyorganosiloxane and is also a phenyl group-containing polyorganosiloxane. Note that the epoxy group-containing polyorganosiloxane may or may not have a phenyl group.

[0058]

The weight-average molecular weight of the epoxy group-containing polyorganosiloxane is not particularly limited, but is usually 100,000 to 2,000,000, and is preferably 200,000 to 1,200,000, more preferably 300,000 to 900,000 from the viewpoint of achieving the effects of the present invention with good reproducibility. In addition, the dispersity is not particularly limited, and is usually 1.0 to 10.0, and is preferably 1.5 to 5.0 and more preferably 2.0 to 3.0 from the viewpoint of achieving suitable release

with good reproducibility. The weight-average molecular weight and the dispersity can be measured by the above-described method related to the polyorganosiloxane.

The viscosity of the epoxy group-containing polyorganosiloxane is not particularly limited, but is usually 1,000 to 2,000,000 mm²/s. Note that the value of the viscosity of the epoxy group-containing polyorganosiloxane is expressed as kinematic viscosity, and centistokes (cSt)=mm²/s. The value can also be determined by dividing the viscosity (mPa·s) by the density (g/cm³). That is, the value can be determined from the viscosity measured with an E-type rotational viscometer at 25°C and the density, and can be calculated from the equation: kinematic viscosity (mm²/s)=viscosity (mPa·s)/density (g/cm³).

[0059]

<<Polydimethylsiloxane>>

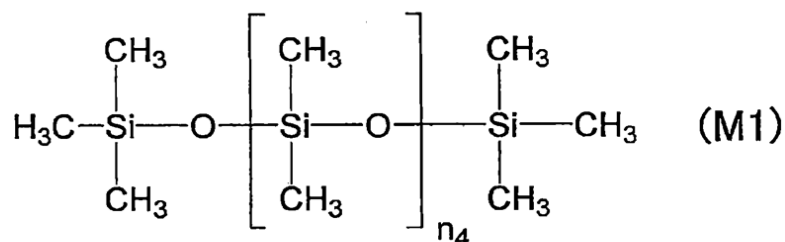
The "polydimethylsiloxane" in the present invention is an unmodified polyorganosiloxane and is a polyorganosiloxane having a methyl group as an organic group bonded to a silicon atom, unlike epoxy group-containing polydimethylsiloxane, phenyl group-containing polydimethylsiloxane, carbinol-modified polyorganosiloxane, and the like.

[0060]

Specific examples of the polydimethylsiloxane include, but are not limited to, those represented by Formula (M1).

[0061]

[Chem. 4]



(n_4 represents the number of repeating units, and is a positive integer.)

[0062]

The weight-average molecular weight of the polydimethylsiloxane is not particularly limited, but is usually 100,000 to 2,000,000, and is preferably 200,000 to 1,200,000, and more preferably 300,000 to 900,000 from the viewpoint of achieving the effects of the present invention with good reproducibility. In addition, the dispersity is not particularly limited, and is usually 1.0 to 10.0, and is preferably 1.5 to 5.0 and more preferably 2.0 to 3.0 from the viewpoint of achieving suitable release with good reproducibility. The weight-average molecular weight and the dispersity can be measured by the above-described method related to the polyorganosiloxane.

The viscosity of the polydimethylsiloxane is not

particularly limited, but is usually 1,000 to 2,000,000 mm²/s. Note that the value of the viscosity of the polydimethylsiloxane is expressed as kinematic viscosity, and centistokes (cSt)=mm²/s. The value can also be determined by dividing the viscosity (mPa·s) by the density (g/cm³). That is, the value can be determined from the viscosity measured with an E-type rotational viscometer at 25°C and the density, and can be calculated from the equation: kinematic viscosity (mm²/s)=viscosity (mPa·s)/density (g/cm³).

[0063]

<<Phenyl Group-Containing Polyorganosiloxane>>

Examples of the phenyl group-containing polyorganosiloxane include those containing a siloxane unit (D³⁰ unit) represented by R³¹R³²SiO_{2/2}.

[0064]

R³¹ is a group bonded to a silicon atom and represents a phenyl group or an alkyl group, and R³² is a group bonded to a silicon atom and represents a phenyl group. Specific examples of the alkyl group include the above-described examples, but a methyl group is preferable.

[0065]

The phenyl group-containing polyorganosiloxane contains the above-described siloxane unit (D³⁰ unit), but may contain, in addition to the D³⁰ unit, Q units, M units,

and/or T units.

[0066]

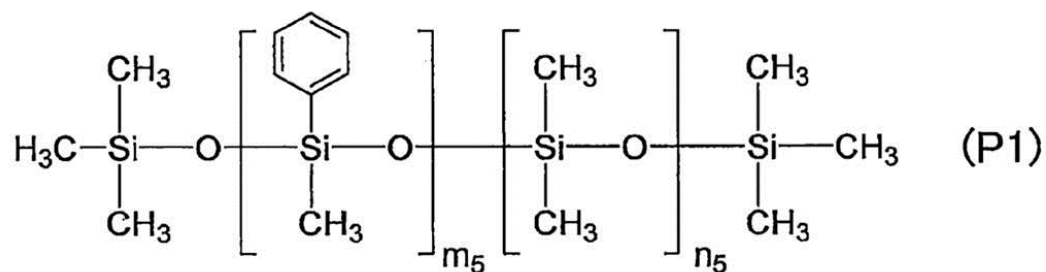
In a preferred embodiment, specific examples of the phenyl group-containing polyorganosiloxane include a polyorganosiloxane composed only of D³⁰ units, a polyorganosiloxane containing D³⁰ units and Q units, a polyorganosiloxane containing D³⁰ units and M units, a polyorganosiloxane containing D³⁰ units and T units, a polyorganosiloxane containing D³⁰ units, Q units, and M units, a polyorganosiloxane containing D³⁰ units, M units, and T units, or a polyorganosiloxane containing D³⁰ units, Q units, M units, and T units.

[0067]

Specific examples of the phenyl group-containing polyorganosiloxane include, but are not limited to, those represented by Formula (P1) or (P2).

[0068]

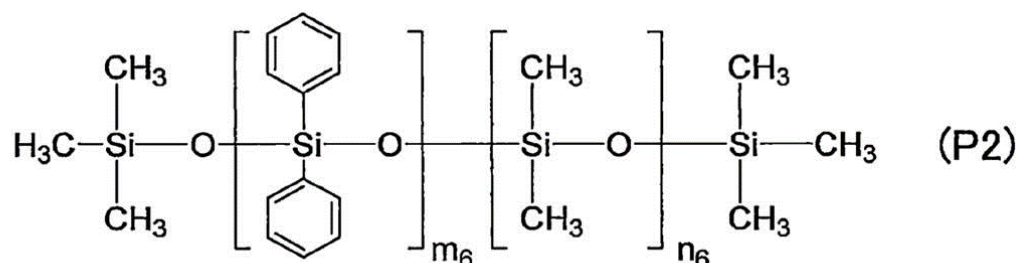
[Chem. 5]



(m5 and n5 represent the number of respective repeating units, and are positive integers.)

[0069]

[Chem. 6]



(m₆ and n₆ represent the number of respective repeating units, and are positive integers.)

[0070]

In the above general formula, when m₅ and m₆ are 2 or more, these repeating units may be arranged adjacent to each other to form a block, or may be randomly arranged.

[0071]

<<Carbinol-Modified Polyorganosiloxane>>

The carbinol-modified polyorganosiloxane is not particularly limited.

The carbinol-modified polyorganosiloxane is a polyorganosiloxane having a hydroxy group directly bonded to a carbon atom. As described above, the carbinol in the "carbinol-modified polyorganosiloxane" is not limited to methanol in a narrow sense, and includes methanol derivatives.

[0072]

The carbinol-modified polyorganosiloxane is, for

example, a carbinol-modified polydimethylsiloxane.

[0073]

The number of hydroxy groups directly bonded to a carbon atom in the carbinol-modified polyorganosiloxane is not particularly limited, and may be one or two or more.

[0074]

The carbinol-modified polyorganosiloxane may have a hydroxy group directly bonded to a carbon atom in a side chain, may have a hydroxy group directly bonded to a carbon atom at one end, or may have hydroxy groups directly bonded to a carbon atom at both terminals.

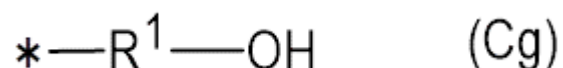
The carbinol-modified polyorganosiloxane preferably has a hydroxy group directly bonded to a carbon atom in a side chain. In this case, even when the content of the carbinol-modified polyorganosiloxane is small, it is possible to impart good releasability to the adhesive layer formed from the adhesive composition.

[0075]

The carbinol-modified polyorganosiloxane has, for example, a group represented by the following Formula (Cg) as a group directly bonded to a silicon atom.

[0076]

[Chem. 7]



(In Formula (Cg), R^1 represents a group having one or more carbon atoms. * represents a bond bonded to a silicon atom. However, the hydroxy group in Formula (Cg) is directly bonded to a carbon atom.)

[0077]

The number of hydroxy groups directly bonded to a carbon atom in the group represented by Formula (Cg) may be one or two or more. Examples of the two or more include two, three, four, and the like.

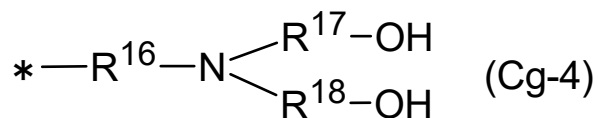
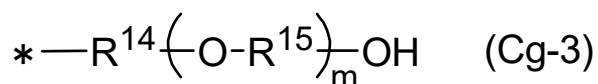
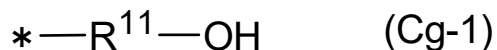
[0078]

The number of carbon atoms in R^1 is not particularly limited, and may be, for example, 1 to 30, 1 to 20, or 1 to 10.

[0079]

Examples of the group represented by Formula (Cg) include groups represented by the following Formulas (Cg-1) to (Cg-4).

[Chem. 8]



(In Formula (Cg-1), R^{11} represents an alkylene group having 1 to 6 carbon atoms which may be substituted with an alkoxy group having 1 to 3 carbon atoms.

In Formula (Cg-2), R^{12} represents an alkylene group having 1 to 6 carbon atoms. R^{13} represents an alkylene group having 1 to 6 carbon atoms which may be substituted with an alkoxy group having 1 to 3 carbon atoms or a hydroxy group.

In Formula (Cg-3), R^{14} represents an alkylene group having 1 to 6 carbon atoms. R^{15} represents an alkylene group having 1 to 3 carbon atoms. m represents an integer of 1 to 10.

In Formula (Cg-4), R^{16} to R^{18} each independently represent an alkylene group having 1 to 6 carbon atoms.

In Formula (Cg-1) to Formula (Cg-4), $*$ represents a bond bonded to a silicon atom.)

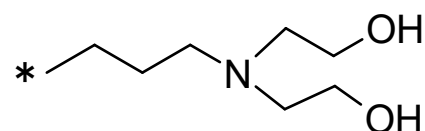
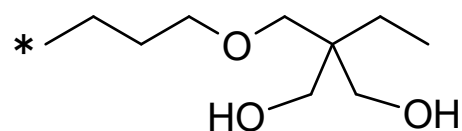
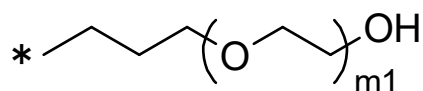
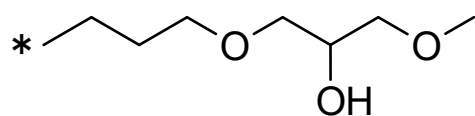
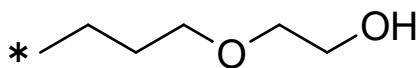
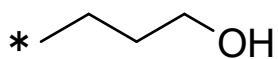
[0080]

The alkylene groups of R^{11} to R^{18} may be linear, branched, or cyclic.

[0081]

Examples of the group represented by Formula (Cg) include the following groups.

[Chem. 9]



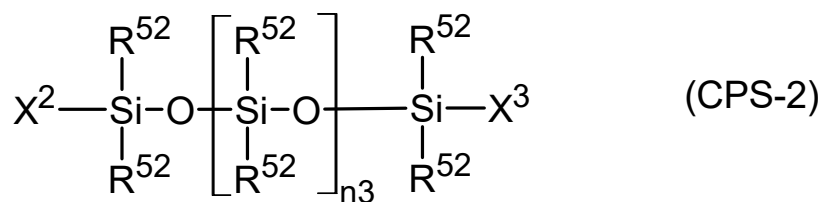
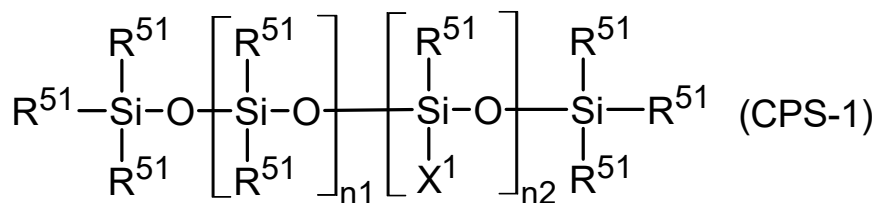
(In the formula, m1 represents an integer of 2 to 10.

* represents a bond bonded to a silicon atom.)

[0082]

The carbinol-modified polyorganosiloxane is represented by, for example, the following Formula (CPS-1) or (CPS-2).

[Chem. 10]



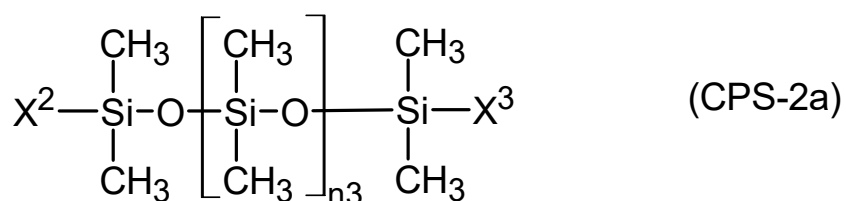
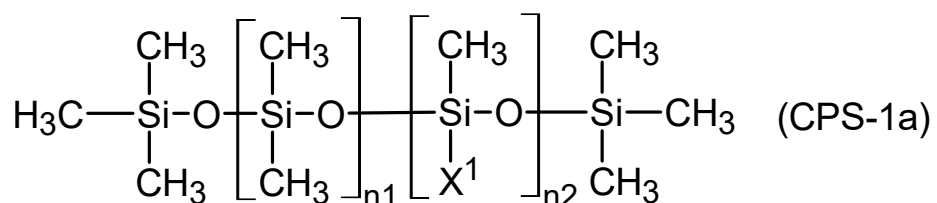
(In Formula (CPS-1), each R⁵¹ independently represents a hydrocarbon group. X¹ represents the group represented by Formula (Cg). n₁ represents an integer of 0 or more. n₂ represents an integer of 1 or more.

In Formula (CPS-2), each R⁵² independently represents a hydrocarbon group. X² represents the group represented by Formula (Cg). X³ represents a hydrocarbon group or the group represented by Formula (Cg). n₃ represents an integer of 0 or more.)

[0083]

Examples of the hydrocarbon groups in R⁵¹, R⁵², and X³ include alkyl groups having 1 to 8 carbon atoms. As the alkyl group having 1 to 8 carbon atoms, a methyl group is preferable. That is, the carbinol-modified polyorganosiloxane is preferably polydimethylsiloxane represented by the following Formula (CPS-1a) or (CPS-2a).

[Chem. 11]



(In Formula (CPS-1a), X¹ represents the group

represented by Formula (Cg). n1 represents an integer of 0 or more. n2 represents an integer of 1 or more.

In Formula (CPS-2a), X² represents the group represented by Formula (Cg). X³ represents a methyl group or the group represented by Formula (Cg). n3 represents an integer of 0 or more.)

[0084]

Note that the carbinol-modified polyorganosiloxane represented by Formula (CPS-1) and the carbinol-modified polydimethylsiloxane represented by Formula (CPS-1a) have a hydroxy group directly bonded to a carbon atom in a side chain.

The carbinol-modified polyorganosiloxane represented by Formula (CPS-2) and the carbinol-modified polydimethylsiloxane represented by Formula (CPS-2a) have a hydroxy group(s) directly bonded to a carbon atom at one terminal or both terminals.

[0085]

Note that when n2 is 2 or more in the carbinol-modified polyorganosiloxane represented by Formula (CPS-1), siloxane units represented by -Si(R⁵¹)(X¹)-O- may be arranged adjacent to each other to form a block, or may be randomly arranged.

In addition, when n2 is 2 or more in the carbinol-modified polydimethylsiloxane represented by Formula (CPS-

1a), siloxane units represented by $-\text{Si}(\text{CH}_3)(\text{X}^1)-\text{O}-$ may be arranged adjacent to each other to form a block, or may be randomly arranged.

[0086]

The weight-average molecular weight of the carbinol-modified polyorganosiloxane is not particularly limited, but is usually 500 to 1,000,000, and is preferably 5,000 to 50,000 from the viewpoint of achieving the effects of the present invention with good reproducibility. In addition, the dispersity is not particularly limited, and is usually 1.0 to 10.0, and is preferably 1.5 to 5.0 and more preferably 2.0 to 3.0 from the viewpoint of achieving suitable release with good reproducibility.

The viscosity of the carbinol-modified polyorganosiloxane is not particularly limited, but is usually 100 to 200,000 mm^2/s . Note that the value of the viscosity of the polydimethylsiloxane is expressed as kinematic viscosity, and centistokes (cSt)= mm^2/s . The value can also be determined by dividing the viscosity ($\text{mPa}\cdot\text{s}$) by the density (g/cm^3). That is, the value can be determined from the viscosity measured with an E-type rotational viscometer at 25°C and the density, and can be calculated from the equation: kinematic viscosity (mm^2/s)= $\text{viscosity} (\text{mPa}\cdot\text{s})/\text{density} (\text{g}/\text{cm}^3)$.

[0087]

The polyorganosiloxane as the release agent component (B) may be a commercially available product or a synthesized product.

Examples of commercially available polyorganosiloxanes include, but are not limited to, Wacker Silicone Fluid AK series (AK 50, AK 350, AK 1000, AK 10000, AK 1000000) and GENIOPLAST GUM, which are products manufactured by Wacker Chemie AG, dimethyl silicone oil (KF-96L, KF-96A, KF-96, KF-96H, KF-69, KF-965, KF-968) and cyclic dimethyl silicone oil (KF-995), manufactured by Shin-Etsu Chemical Co., Ltd.; epoxy group-containing polyorganosiloxane manufactured by Gelest, Inc. (trade names: CMS-227, ECMS-327, EMS-622), epoxy group-containing polyorganosiloxane manufactured by Shin-Etsu Chemical Co., Ltd. (KF-101, KF-1001, KF-1005, X-22-343), epoxy group-containing polyorganosiloxane (DOWSIL BY16-839, DOWSIL8413, DOWSIL8411) manufactured by Dow Toray Co., Ltd.; and phenyl group-containing polyorganosiloxane (PMM-1043, PMM-1025, PDM-0421, PDM-0821) manufactured by Gelest, Inc., phenyl group-containing polyorganosiloxane (KF50-3000CS) manufactured by Shin-Etsu Chemical Co., Ltd., and phenyl group-containing polyorganosiloxane (TSF431, TSF433) manufactured by Momentive Performance Materials, Inc.

[0088]

In addition, examples of commercially available

carbinol-modified polyorganosiloxanes include KF6000, KF6001, KF6002, KF6003, X-22-4039, and X-22-4015 manufactured by Shin-Etsu Chemical Co., Ltd.; DMS-C15, DMS-C16, DMS-C21, DMS-C23, DBE-C25, DBE-C22, DMS-CA21, DMS-CS26, CMS-221, CMS-222, CMS-832, CMS-626, MCR-C12, MCR-C18, MCR-C22, MCS-C11, MCS-C13, MCR-C61, MCR-C62, and MCR-C63 manufactured by Gelest, Inc.; and DOWSIL BY 16-201, DOWSIL SF 8427 Fluid, and DOWSIL SF 8428 Fluid manufactured by Dow Toray Co., Ltd.

[0089]

The content of the release agent component in the adhesive composition is not particularly limited, but is preferably 0.01 mass% or more, more preferably 0.05 mass% or more, and particularly preferably 0.10 mass% or more based on the nonvolatile matter of the adhesive composition from the viewpoint of suitably obtaining the effects of the present invention. The upper limit is not particularly limited, but is, for example, preferably 30 mass% or less, more preferably 25 mass% or less, and particularly preferably 20 mass% or less.

The nonvolatile matter in the adhesive composition refers to a component other than the solvent in the adhesive composition.

[0090]

<Solvent>

The adhesive composition may contain a solvent for the purpose of adjusting the viscosity. Specific examples thereof include aliphatic hydrocarbons, aromatic hydrocarbons, and ketones, but are not limited thereto.

More specific examples of the solvent include, but are not limited to, hexane, heptane, octane, nonane, isononane, decane, undecane, dodecane, isododecane, menthane, limonene, toluene, xylene, mesitylene, cumene, MIBK (methyl isobutyl ketone), butyl acetate, diisobutyl ketone, 2-octanone, 2-nonanone, 5-nonanone, cyclohexanone, propylene glycol monomethyl ether acetate, and propylene glycol monomethyl ether. Such solvents can be used alone or in combination with two or more thereof.

[0091]

When the adhesive composition contains a solvent, the content thereof is appropriately determined in consideration of the desired viscosity of the composition, the coating method to be employed, the thickness of the film to be produced, and the like, and is, for example, in a range of about 10 to 90 mass% with respect to the entire composition.

[0092]

The viscosity of the adhesive composition used in the present invention is not particularly limited, and is usually 500 to 20,000 mPa·s, and preferably 1,000 to 10,000

mPa·s at 25°C.

[0093]

An example of the adhesive composition used in the present invention can be manufactured by mixing the component (A), the release agent component (B), and the solvent.

The mixing order is not particularly limited, and examples of the method capable of producing the adhesive composition easily with good reproducibility include, but are not limited to, a method in which the component (A) and the release agent component (B) are dissolved in the solvent, and a method in which the component (A) and the release agent component (B) are partially dissolved in the solvent, the remainder is dissolved in a solvent, and the resulting solutions are mixed. Note that when the adhesive composition is prepared, the components may be heated, if appropriate, as long as the components are not decomposed or altered.

In the present invention, for the purpose of removing foreign matter, a solvent, a solution, or the like to be used may be filtered using a filter or the like during the production of the adhesive composition or after mixing all the components.

[0094]

(Laminate)

The laminate according to the present invention includes a semiconductor substrate or an electronic device layer, a support substrate, and an adhesive layer.

The laminate according to the present invention may further include a release agent layer, and in this case, includes a semiconductor substrate or an electronic device layer, a support substrate, a release agent layer, and an adhesive layer.

[0095]

The adhesive layer is provided between the semiconductor substrate or the electronic device layer and the support substrate.

[0096]

The laminate of the present invention is used for temporary adhesion for processing the semiconductor substrate or the electronic device layer, and can be suitably used for processing such as thinning of the semiconductor substrate or the electronic device layer.

While the semiconductor substrate is subjected to processing such as thinning, the semiconductor substrate is supported by the support substrate. On the other hand, after the processing of the semiconductor substrate, the support substrate and the semiconductor substrate are separated from each other.

In addition, while the electronic device layer is

subjected to processing such as thinning, the electronic device layer is supported by the support substrate.

Meanwhile, after the processing of the electronic device layer, the support substrate and the electronic device layer are separated from each other.

Furthermore, after the semiconductor substrate or the electronic device layer is separated from the support substrate, the residue of the release agent layer or the adhesive layer remaining on the semiconductor substrate, the electronic device layer, or the support substrate can be removed by, for example, a cleaning agent composition for cleaning the semiconductor substrate and the like.

[0097]

Hereinafter, a case where the laminate includes a semiconductor substrate and a case where the laminate includes an electronic device layer will be described in detail separately.

The case where the laminate includes a semiconductor substrate will be described in the following <First Embodiment>, and the case where the laminate includes an electronic device layer will be described in the following <Second Embodiment>.

[0098]

<First Embodiment>

The laminate having a semiconductor substrate is used

for processing the semiconductor substrate. While the semiconductor substrate is processed, the semiconductor substrate is bonded to the support substrate. After the processing of the semiconductor substrate, the semiconductor substrate is separated from the support substrate.

[0099]

<<Semiconductor Substrate>>

The main material constituting the entire semiconductor substrate is not particularly limited as long as the material is used for this type of application, and examples thereof include silicon, silicon carbide, a compound semiconductor, and an organic resin-attached glass substrate.

The shape of the semiconductor substrate is not particularly limited, and is, for example, a disk shape. The disk-shaped semiconductor substrate does not need to have a completely circular surface, and for example, the outer periphery of the semiconductor substrate may have a linear portion called an orientation flat or may have a cut called a notch.

The thickness of the disk-shaped semiconductor substrate may be appropriately determined depending on the purpose of use of the semiconductor substrate and the like, and is not particularly limited, and is, for example, 500

to 1,000 μm .

The diameter of the disk-shaped semiconductor substrate may be appropriately determined depending on the purpose of use of the semiconductor substrate and the like, and is not particularly limited, and is, for example, 100 to 1,000 mm. [0100]

The semiconductor substrate may have a bump. The bump is a protruding terminal. The bump is, for example, an electrode.

In the laminate, when the semiconductor substrate has a bump, the semiconductor substrate has the bump on the support substrate side.

In the semiconductor substrate, the bump is usually formed on a surface on which a circuit is formed. The circuit may be a single layer or a multilayer. The shape of the circuit is not particularly limited.

In the semiconductor substrate, a surface (back surface) opposite to the surface having the bump is a surface to be processed.

The material, size, shape, structure, and density of the bump of the semiconductor substrate are not particularly limited.

Examples of the bump include a ball bump, a print bump, a stud bump, and a plating bump.

Usually, the height, radius, and pitch of the bump are

appropriately determined from the conditions of a bump height of approximately 1 to 200 μm , a bump radius of 1 to 200 μm , and a bump pitch of 1 to 500 μm .

Examples of the material of the bump include low melting point solder, high melting point solder, tin, indium, gold, silver, and copper. The bump may contain only a single component or may contain a plurality of components. More specific examples thereof include Sn-based alloy plating, such as SnAg bumps, SnBi bumps, Sn bumps, and AuSn bumps.

In addition, the bump may have a laminated structure including a metal layer made of at least one of these components.

[0101]

An example of the semiconductor substrate is a silicon wafer having a diameter of about 300 mm and a thickness of about 770 μm .

[0102]

<<Support Substrate>>

The support substrate is not particularly limited as long as it is a member capable of supporting the semiconductor substrate when the semiconductor substrate is processed. Examples thereof include a glass support substrate and a silicon support substrate.

[0103]

The shape of the support substrate is not particularly limited, and examples thereof include a disk shape. The disk-shaped support substrate does not need to have a completely circular surface shape, and for example, the outer periphery of the support substrate may have a straight portion called an orientation flat or may have a cut called a notch.

The thickness of the disk-shaped support substrate may be appropriately determined depending on the size of the semiconductor substrate and the like, and is not particularly limited, and is, for example, 500 to 1,000 μm .

The diameter of the disk-shaped support substrate may be appropriately determined depending on the size of the semiconductor substrate and the like, and is not particularly limited, and is, for example, 100 to 1,000 mm.

[0104]

An example of the support substrate is a glass wafer having a diameter of about 300 mm and a thickness of about 700 μm .

[0105]

When peeling is performed by light irradiation in the laminate, a substrate that is light-transmissive to the light used is used as the support substrate, for example.

[0106]

<<Adhesive Layer>>

The adhesive layer is provided between the support substrate and the semiconductor substrate.

The adhesive layer is in contact with, for example, the semiconductor substrate. The adhesive layer may be in contact with, for example, the support substrate.

The adhesive layer is an adhesive layer formed from an adhesive composition.

[0107]

The thickness of the adhesive layer included in the laminate of the present invention is not particularly limited, and is usually 5 to 500 μm , preferably 10 μm or more, more preferably 20 μm or more, and still more preferably 30 μm or more from the viewpoint of maintaining the film strength, and is preferably 200 μm or less, more preferably 150 μm or less, still more preferably 120 μm or less, and even still more preferably 100 μm or less from the viewpoint of avoiding nonuniformity caused by a thick film.

[0108]

The method for forming the adhesive layer from the adhesive composition will be described in detail in the description of <<Method for Producing One Example of Laminate in First Embodiment>> described below.

[0109]

<<Release Agent Layer>>

The laminate may include a release agent layer.

In the laminate having the release agent layer, the semiconductor substrate and the support substrate are separated by, for example, irradiating the release agent layer with light.

The release agent layer is formed from, for example, a release agent composition.

[0110]

<<<Release Agent Composition>>>

The release agent composition contains, for example, at least an organic resin or a polynuclear phenol derivative, and further contains other components as necessary.

The organic resin is preferably one that can exhibit a suitable releasing ability. When the semiconductor substrate and the support substrate are separated from each other by irradiating the release agent layer with light, the organic resin absorbs light and suitably undergoes alteration that is necessary to improve releasing ability, for example, decomposition.

[0111]

In the laminate having a release agent layer formed from a release agent composition, peeling can be performed, for example, by irradiating the release agent layer with a laser, without applying an excessive load for peeling.

The release agent layer included in the laminate has,

for example, an adhesive strength that is lower after laser irradiation than before laser irradiation. That is, in the laminate, for example, while the semiconductor substrate is subjected to processing such as thinning, the semiconductor substrate is suitably supported on a support substrate that transmits a laser via the adhesive layer and the release agent layer, and after the processing is completed, by irradiating the laminate with the laser from the support substrate side, the laser transmitted through the support substrate is absorbed by the release agent layer, and alteration of the release agent layer (for example, separation) occurs at the interface between the release agent layer and the adhesive layer, at the interface between the release agent layer and the support substrate, or inside the release agent layer. As a result, suitable peeling (separation) can be achieved without applying an excessive load for peeling.

[0112]

Examples of the organic resin include novolac resin bodies. Details thereof will be described below.

[0113]

As a preferred embodiment, the release agent composition contains at least a novolac resin, and further contains other components such as a crosslinking agent, an acid generator, an acid, a surfactant, and a solvent as

necessary.

As another preferred embodiment, the release agent composition contains at least a polynuclear phenol derivative and a crosslinking agent, and further contains other components such as an acid generator, an acid, a surfactant, and a solvent as necessary.

As still another preferred embodiment, the release agent composition contains at least an organic resin and a branched polysilane, and further contains other components such as a crosslinking agent, an acid generator, an acid, a surfactant, and a solvent as necessary.

[0114]

<<<<Novolac Resin>>>>

The novolac resin is, for example, a resin obtained by condensation reaction of at least one of a phenolic compound, a carbazole compound, and an aromatic amine compound with at least one of an aldehyde compound, a ketone compound, and a divinyl compound under an acid catalyst.

[0115]

Examples of the phenolic compound include phenols, naphthols, anthrols, and hydroxypyrenes. Examples of the phenols include phenol, cresol, xylenol, resorcinol, bisphenol A, p-tert-butylphenol, p-octylphenol, 9,9-bis(4-hydroxyphenyl)fluorene, and 1,1,2,2-tetrakis(4-

hydroxyphenyl)ethane. Examples of the naphthols include 1-naphthol, 2-naphthol, 1,5-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, and 9,9-bis(6-hydroxynaphthyl)fluorene. Examples of the anthrols include 9-anthrol. Examples of the hydroxypyrenes include 1-hydroxypyrene and 2-hydroxypyrene.

Examples of the carbazole compound include carbazole, 1,3,6,8-tetranitrocarbazole, 3,6-diaminocarbazole, 3,6-dibromo-9-ethylcarbazole, 3,6-dibromo-9-phenylcarbazole, 3,6-dibromocarbazole, 3,6-dichlorocarbazole, 3-amino-9-ethylcarbazole, 3-bromo-9-ethylcarbazole, 4,4'-bis(9H-carbazole-9-yl)biphenyl, 4-glycidylcarbazole, 4-hydroxycarbazole, 9-(1H-benzotriazole-1-ylmethyl)-9H-carbazole, 9-acetyl-3,6-diiodocarbazole, 9-benzoylcarbazole, 9-benzoylcarbazole-6-dicarboxaldehyde, 9-benzylcarbazole-3-carboxaldehyde, 9-methylcarbazole, 9-phenylcarbazole, 9-vinylcarbazole, carbazole potassium, carbazole-N-carbonyl chloride, N-ethylcarbazole-3-carboxaldehyde, and N-((9-ethylcarbazole-3-yl)methylene)-2-methyl-1-indolinylamine.

Examples of the aromatic amine compound include diphenylamine and N-phenyl-1-naphthylamine.

These can be used alone or in combination with two or more thereof.

These may have a substituent. For example, these may

have a substituent on an aromatic ring.

[0116]

Examples of the aldehyde compound include saturated aliphatic aldehydes such as formaldehyde, paraformaldehyde, acetaldehyde, propylaldehyde, butyraldehyde, isobutyraldehyde, valeraldehyde, caproaldehyde, 2-methylbutyraldehyde, hexylaldehyde, undecane aldehyde, 7-methoxy-3,7-dimethyloctylaldehyde, cyclohexanealdehyde, 3-methyl-2-butyraldehyde, glyoxal, malonaldehyde, succinaldehyde, glutaraldehyde, and adipaldehyde; unsaturated aliphatic aldehydes such as acrolein and methacrolein; heterocyclic aldehydes such as furfural and pyridinealdehyde; and aromatic aldehydes such as benzaldehyde, naphthylaldehyde, anthrylaldehyde, phenanthrylaldehyde, salicylaldehyde, phenylacetaldehyde, 3-phenylpropionaldehyde, tolylaldehyde, (N,N-dimethylamino)benzaldehyde, and acetoxybenzaldehyde. Among them, aromatic aldehydes are preferable.

Examples of the ketone compound include diaryl ketone compounds such as diphenyl ketone, phenyl naphthyl ketone, dinaphthyl ketone, phenyl tolyl ketone, and ditolyl ketone.

Examples of the divinyl compound include divinylbenzene, dicyclopentadiene, tetrahydroindene, 4-vinylcyclohexene, 5-vinylnorborn-2-ene, divinylpyrene, limonene, and 5-vinylnorbornadiene.

These can be used alone or in combination with two or more thereof.

[0117]

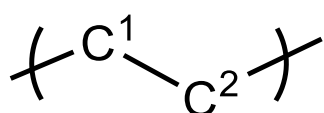
The novolac resin is, for example, a novolac resin that absorbs light radiated from the support substrate side and alters. The alteration is, for example, photolysis.

[0118]

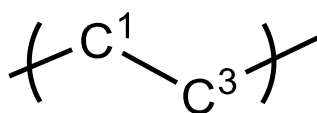
The novolac resin contains, for example, at least one of a structural unit represented by the following Formula (C1-1), a structural unit represented by the following Formula (C1-2), and a structural unit represented by the following Formula (C1-3).

[0119]

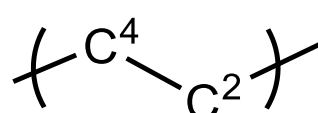
[Chem. 12]



(C1-1)



(C1-2)



(C1-3)

[0120]

In the formula, C¹ represents a group derived from an aromatic compound containing a nitrogen atom, C² represents a group containing a tertiary carbon atom having, as a side chain, at least one selected from the group consisting of secondary carbon atoms, quaternary carbon atoms, and aromatic rings, C³ represents a group derived from an

aliphatic polycyclic compound, and C⁴ represents a group derived from phenol, a group derived from bisphenol, a group derived from naphthol, a group derived from biphenyl, or a group derived from biphenol.

[0121]

That is, the novolac resin contains, for example, one or two or more of the following structural units.

- Structural unit (Formula (C1-1)) having a bond between a group derived from an aromatic compound containing a nitrogen atom and a group containing a tertiary carbon atom having, as a side chain, at least one selected from the group consisting of a secondary carbon atom, a quaternary carbon atom, and an aromatic ring

- Structural unit (Formula (C1-2)) having a bond between a group derived from an aromatic compound containing a nitrogen atom and a group derived from an aliphatic polycyclic compound

- Structural unit (Formula (C1-3)) having a bond between a group derived from phenol, a group derived from bisphenol, a group derived from naphthol, a group derived from biphenyl, or a group derived from biphenol, and a group containing a tertiary carbon atom having, as a side chain, at least one selected from the group consisting of a quaternary carbon atom and an aromatic ring

[0122]

In a preferred embodiment, the novolac resin contains either one or both of a structural unit (Formula (C1-1)) having a bond between a group derived from an aromatic compound containing a nitrogen atom and a group containing a tertiary carbon atom having, as a side chain, at least one selected from the group consisting of a secondary carbon atom, a quaternary carbon atom, and an aromatic ring, and a structural unit (Formula (C1-2)) having a bond between a group derived from an aromatic compound containing a nitrogen atom and a group derived from an aliphatic polycyclic compound.

[0123]

The group derived from the aromatic compound containing the nitrogen atom of C¹ can be, for example, a group derived from carbazole, a group derived from N-phenyl-1-naphthylamine, a group derived from N-phenyl-2-naphthylamine, or the like, but is not limited thereto.

The group containing a tertiary carbon atom having, as a side chain, at least one selected from the group consisting of a secondary carbon atom, a quaternary carbon atom, and an aromatic ring of C² can be, for example, a group derived from 1-naphthaldehyde, a group derived from 1-pyrenecarboxaldehyde, a group derived from 4-(trifluoromethyl)benzaldehyde, a group derived from acetaldehyde, or the like, but is not limited thereto.

The group derived from the aliphatic polycyclic compound of C³ can be, but is not limited to, a group derived from dicyclopentadiene.

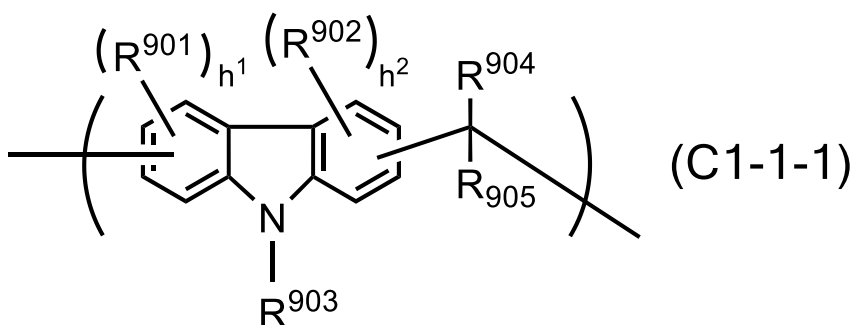
C⁴ is a group derived from phenol, a group derived from bisphenol, a group derived from naphthol, a group derived from biphenyl, or a group derived from biphenol.

[0124]

In a preferred embodiment, the novolac resin contains, for example, a structural unit represented by the following Formula (C1-1-1) as the structural unit represented by Formula (C1-1).

[0125]

[Chem. 13]



[0126]

In Formula (C1-1-1), R⁹⁰¹ and R⁹⁰² represent substituents on a ring, and R⁹⁰¹ and R⁹⁰² each independently represent a halogen atom, a nitro group, a cyano group, an amino group, a hydroxy group, a carboxy group, an alkyl group which may be substituted, an alkenyl group which may be substituted, or an aryl group which may be substituted.

R^{903} represents a hydrogen atom, an alkyl group which may be substituted, an alkenyl group which may be substituted, or an aryl group which may be substituted.

R^{904} represents a hydrogen atom, an aryl group which may be substituted, or a heteroaryl group which may be substituted.

R^{905} represents an alkyl group which may be substituted, an aryl group which may be substituted, or a heteroaryl group which may be substituted.

The group of R^{904} and the group of R^{905} may be bonded to each other to form a divalent group.

Examples of the substituent of the alkyl group and the alkenyl group include a halogen atom, a nitro group, a cyano group, an amino group, a hydroxy group, a carboxy group, an aryl group, and a heteroaryl group.

Examples of the substituent of the aryl group and the heteroaryl group include a halogen atom, a nitro group, a cyano group, an amino group, a hydroxy group, a carboxy group, an alkyl group, and an alkenyl group.

h^1 and h^2 each independently represent an integer of 0 to 3.

[0127]

The number of carbon atoms of the alkyl group which may be substituted and the alkenyl group which may be substituted is usually 40 or less, and from the viewpoint

of solubility, the number of carbon atoms is preferably 30 or less, and more preferably 20 or less.

The number of carbon atoms of the aryl group which may be substituted and the heteroaryl group which may be substituted is usually 40 or less, and from the viewpoint of solubility, the number of carbon atoms is preferably 30 or less, and more preferably 20 or less.

[0128]

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

[0129]

Specific examples of the alkyl group which may be substituted include, but are not limited to, a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group, an s-butyl group, a t-butyl group, an n-pentyl group, a 1-methyl-n-butyl group, a 2-methyl-n-butyl group, a 3-methyl-n-butyl group, a 1,1-dimethyl-n-propyl group, a 1,2-dimethyl-n-propyl group, a 2,2-dimethyl-n-propyl group, a 1-ethyl-n-propyl group, n-hexyl, a 1-methyl-n-pentyl group, a 2-methyl-n-pentyl group, a 3-methyl-n-pentyl group, a 4-methyl-n-pentyl group, a 1,1-dimethyl-n-butyl group, a 1,2-dimethyl-n-butyl group, a 1,3-dimethyl-n-butyl group, a 2,2-dimethyl-n-butyl group, a 2,3-dimethyl-n-butyl group, a 3,3-dimethyl-n-butyl group, a 1-ethyl-n-butyl group, a 2-

ethyl-n-butyl group, a 1,1,2-trimethyl-n-propyl group, a 1,2,2-trimethyl-n-propyl group, a 1-ethyl-1-methyl-n-propyl group, and a 1-ethyl-2-methyl-n-propyl group.

[0130]

Specific examples of the alkenyl group which may be substituted include, but are not limited to, an ethenyl group, a 1-propenyl group, a 2-propenyl group, a 1-methyl-1-ethenyl group, a 1-butenyl group, a 2-butenyl group, a 3-butenyl group, a 2-methyl-1-propenyl group, a 2-methyl-2-propenyl group, a 1-ethylethenyl group, a 1-methyl-1-propenyl group, a 1-methyl-2-propenyl group, a 1-pentenyl group, a 2-pentenyl group, a 3-pentenyl group, a 4-pentenyl group, a 1-n-propylethenyl group, a 1-methyl-1-butenyl group, a 1-methyl-2-butenyl group, a 1-methyl-3-butenyl group, a 2-ethyl-2-propenyl group, a 2-methyl-1-butenyl group, a 2-methyl-2-butenyl group, a 2-methyl-3-butenyl group, a 3-methyl-1-butenyl group, a 3-methyl-2-butenyl group, a 3-methyl-3-butenyl group, a 1,1-dimethyl-2-propenyl group, a 1-i-propylethenyl group, a 1,2-dimethyl-1-propenyl group, a 1,2-dimethyl-2-propenyl group, a 1-cyclopentenyl group, a 2-cyclopentenyl group, a 3-cyclopentenyl group, a 1-hexenyl group, a 2-hexenyl group, a 3-hexenyl group, a 4-hexenyl group, a 5-hexenyl group, a 1-methyl-1-pentenyl group, a 1-methyl-2-pentenyl group, a 1-methyl-3-pentenyl group, a 1-methyl-4-pentenyl group, a

1-n-butylethenyl group, a 2-methyl-1-pentenyl group, a 2-methyl-2-pentenyl group, a 2-methyl-3-pentenyl group, a 2-methyl-4-pentenyl group, a 2-n-propyl-2-propenyl group, a 3-methyl-1-pentenyl group, a 3-methyl-2-pentenyl group, a 3-methyl-3-pentenyl group, a 3-methyl-4-pentenyl group, a 3-ethyl-3-butenyl group, a 4-methyl-1-pentenyl group, a 4-methyl-2-pentenyl group, a 4-methyl-3-pentenyl group, a 4-methyl-4-pentenyl group, a 1,1-dimethyl-2-butenyl group, a 1,1-dimethyl-3-butenyl group, a 1,2-dimethyl-1-butenyl group, a 1,2-dimethyl-2-butenyl group, a 1,2-dimethyl-3-butenyl group, a 1-methyl-2-ethyl-2-propenyl group, a 1-s-butylethenyl group, a 1,3-dimethyl-1-butenyl group, a 1,3-dimethyl-2-butenyl group, a 1,3-dimethyl-3-butenyl group, a 1-i-butylethenyl group, a 2,2-dimethyl-3-butenyl group, a 2,3-dimethyl-1-butenyl group, a 2,3-dimethyl-2-butenyl group, a 2,3-dimethyl-3-butenyl group, a 2-i-propyl-2-propenyl group, a 3,3-dimethyl-1-butenyl group, a 1-ethyl-1-butenyl group, a 1-ethyl-2-butenyl group, a 1-ethyl-3-butenyl group, a 1-n-propyl-1-propenyl group, a 1-n-propyl-2-propenyl group, a 2-ethyl-1-butenyl group, a 2-ethyl-2-butenyl group, a 2-ethyl-3-butenyl group, a 1,1,2-trimethyl-2-propenyl group, a 1-tertiary butylethenyl group, a 1-methyl-1-ethyl-2-propenyl group, a 1-ethyl-2-methyl-1-propenyl group, a 1-ethyl-2-methyl-2-propenyl group, a 1-i-propyl-1-propenyl group, a 1-i-propyl-2-

propenyl group, a 1-methyl-2-cyclopentenyl group, a 1-methyl-3-cyclopentenyl group, a 2-methyl-1-cyclopentenyl group, a 2-methyl-2-cyclopentenyl group, a 2-methyl-3-cyclopentenyl group, a 2-methyl-4-cyclopentenyl group, a 2-methyl-5-cyclopentenyl group, a 2-methylene-cyclopentyl group, a 3-methyl-1-cyclopentenyl group, a 3-methyl-2-cyclopentenyl group, a 3-methyl-3-cyclopentenyl group, a 3-methyl-4-cyclopentenyl group, a 3-methyl-5-cyclopentenyl group, a 3-methylene-cyclopentyl group, a 1-cyclohexenyl group, a 2-cyclohexenyl group, and a 3-cyclohexenyl group.

[0131]

Specific examples of the aryl group which may be substituted include, but are not limited to, a phenyl group, a 2-methylphenyl group, a 3-methylphenyl group, a 4-methylphenyl group, a 2-chlorophenyl group, a 3-chlorophenyl group, a 4-chlorophenyl group, a 2-fluorophenyl group, a 3-fluorophenyl group, a 4-fluorophenyl group, a 4-methoxyphenyl group, a 4-ethoxyphenyl group, a 4-nitrophenyl group, a 4-cyanophenyl group, a 1-naphthyl group, a 2-naphthyl group, a biphenyl-4-yl group, a biphenyl-3-yl group, a biphenyl-2-yl group, a 1-anthryl group, a 2-anthryl group, a 9-anthryl group, a 1-phenanthryl group, a 2-phenanthryl group, a 3-phenanthryl group, a 4-phenanthryl group, and a 9-phenanthryl group.

[0132]

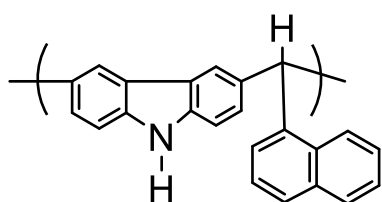
Specific examples of the heteroaryl group which may be substituted include, but are not limited to, a 2-thienyl group, a 3-thienyl group, a 2-furanyl group, a 3-furanyl group, a 2-oxazolyl group, a 4-oxazolyl group, a 5-oxazolyl group, a 3-isoxazolyl group, a 4-isoxazolyl group, a 5-isoxazolyl group, a 2-thiazolyl group, a 4-thiazolyl group, a 5-thiazolyl group, a 3-isothiazolyl group, a 4-isothiazolyl group, and a 5-isothiazolyl group.

[0133]

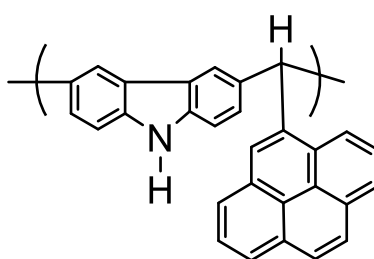
Hereinafter, specific examples of the structural unit represented by Formula (C1-1-1) will be given, but these are not limited thereto.

[0134]

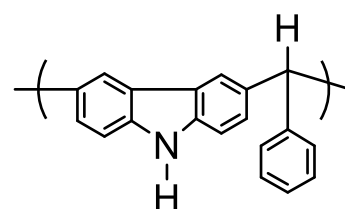
[Chem. 14]



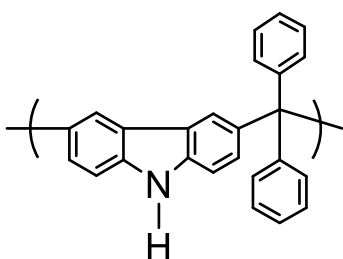
(C1-1-1-1)



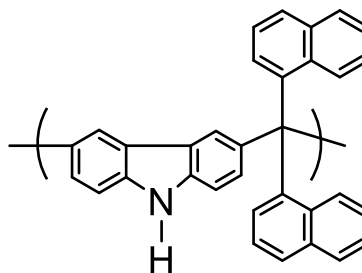
(C1-1-1-2)



(C1-1-1-3)



(C1-1-1-4)



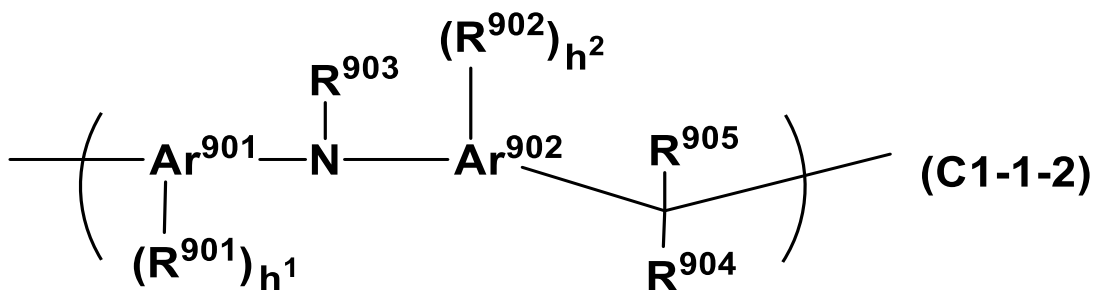
(C1-1-1-5)

[0135]

In a preferred embodiment, the novolac resin contains, for example, a structural unit represented by the following Formula (C1-1-2) as the structural unit represented by Formula (C1-1).

[0136]

[Chem. 15]



[0137]

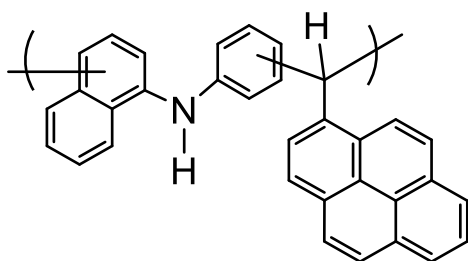
In Formula (C1-1-2), Ar^{901} and Ar^{902} each independently represent an aromatic ring such as a benzene ring or a naphthalene ring, and R^{901} to R^{905} , h^1 , and h^2 have the same meanings as described above.

[0138]

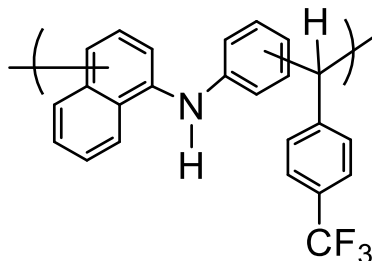
Hereinafter, specific examples of the structural unit represented by Formula (C1-1-2) will be given, but these are not limited thereto.

[0139]

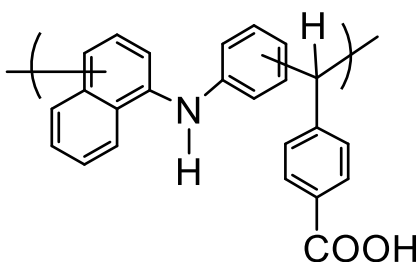
[Chem. 16]



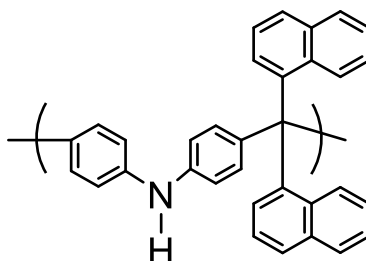
(C1-1-2-1)



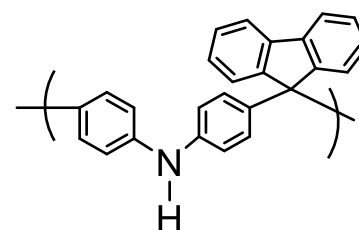
(C1-1-2-2)



(C1-1-2-3)



(C1-1-2-4)



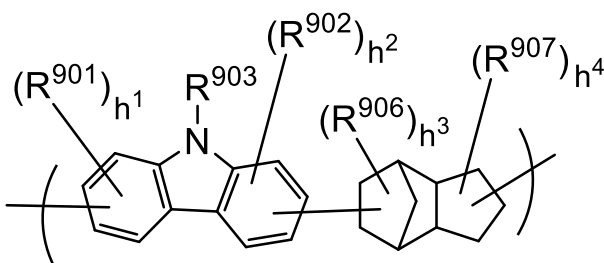
(C1-1-2-5)

[0140]

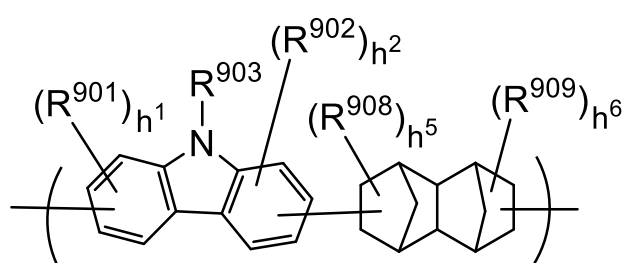
In a preferred embodiment, the novolac resin contains, for example, a structural unit represented by the following Formula (C1-2-1) or (C1-2-2) as the structural unit represented by Formula (C1-2).

[0141]

[Chem. 17]



(C1-2-1)



(C1-2-2)

[0142]

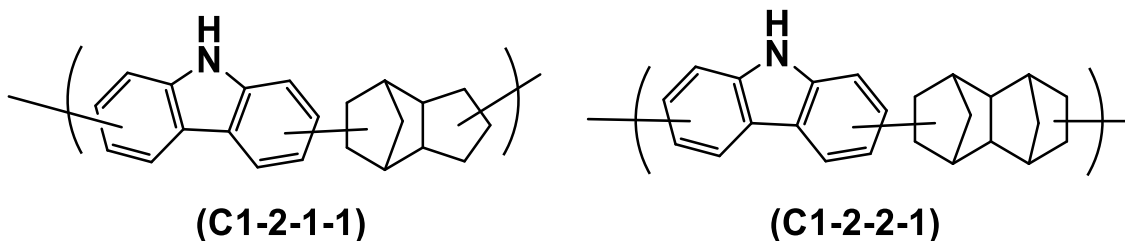
In the above formula, R^{906} to R^{909} are substituents bonded to a ring, and R^{906} to R^{909} each independently represent a halogen atom, a nitro group, a cyano group, an amino group, a hydroxy group, a carboxy group, an alkyl group which may be substituted, an alkenyl group which may be substituted, or an aryl group which may be substituted. Specific examples and suitable numbers of carbon atoms of the halogen atom, the alkyl group which may be substituted, the alkenyl group which may be substituted, and the aryl group which may be substituted are the same as those described above, h^3 to h^6 each independently represent an integer of 0 to 3, and R^{901} to R^{903} and h^1 and h^2 have the same meanings as described above.

[0143]

Hereinafter, specific examples of the structural units represented by Formulas (C1-2-1) and (C1-2-2) will be given, but these are not limited thereto.

[0144]

[Chem. 18]



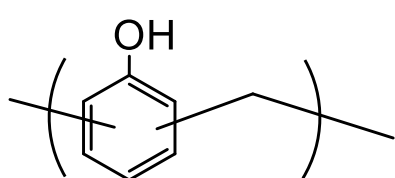
[0145]

Hereinafter, specific examples of the structural unit

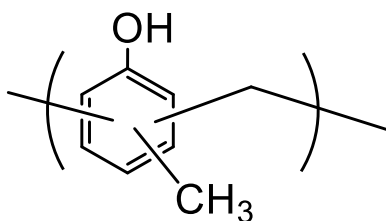
represented by Formula (C1-3) will be given, but these are not limited thereto.

[0146]

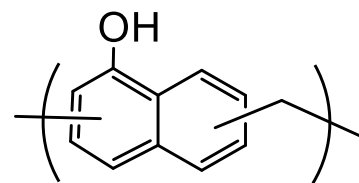
[Chem. 19]



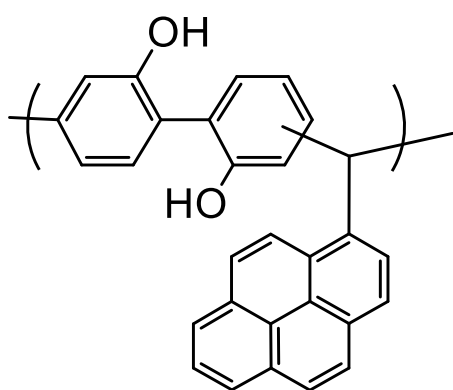
(C1-3-1-1)



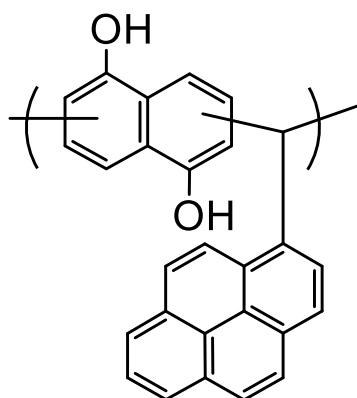
(C1-3-1-2)



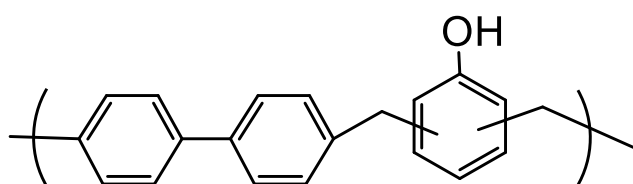
(C1-3-1-3)



(C1-3-1-4)



(C1-3-1-5)



(C1-3-1-6)

[0147]

As described above, the novolac resin is, for example, a resin obtained by a condensation reaction of at least one of a phenolic compound, a carbazole compound, and an aromatic amine compound with at least one of an aldehyde

compound, a ketone compound, and a divinyl compound under an acid catalyst.

In this condensation reaction, for example, an aldehyde compound or a ketone compound is usually used in a ratio of 0.1 to 10 equivalents to 1 equivalent of a benzene ring constituting a ring of a carbazole compound.

[0148]

In the condensation reaction, an acid catalyst is usually used.

Examples of the acid catalyst include, but are not limited to, mineral acids such as sulfuric acid, phosphoric acid, and perchloric acid, organic sulfonic acids such as p-toluenesulfonic acid and p-toluenesulfonic acid monohydrate, and carboxylic acids such as formic acid and oxalic acid.

The amount of the acid catalyst is appropriately determined depending on the type of the acid to be used and the like, and thus cannot be generally defined, and is usually appropriately determined from the range of 0.001 to 10,000 parts by mass with respect to 100 parts by mass of the carbazole compound.

[0149]

When either the raw material compound or the acid catalyst to be used is a liquid, the condensation reaction can be performed without using a solvent in some cases, but

is usually performed using a solvent.

Such a solvent is not particularly limited as long as the reaction is not inhibited, and typically includes ether compounds such as cyclic ether compounds such as tetrahydrofuran and dioxane.

[0150]

The reaction temperature is usually appropriately determined from the range of 40°C to 200°C, and the reaction time cannot be generally specified because the reaction time varies depending on the reaction temperature, and is usually appropriately determined from the range of 30 minutes to 50 hours.

[0151]

After completion of the reaction, as necessary, purification and isolation are performed according to a conventional method, and the obtained novolac resin is used for preparation of a release agent composition.

Those skilled in the art can determine the production conditions of the novolac resin without an excessive burden based on the above description and the common general technical knowledge, and therefore can produce the novolac resin.

[0152]

The weight-average molecular weight of the organic resin such as the novolac resin is usually 500 to 200,000,

and is preferably 100,000 or less, more preferably 50,000 or less, still more preferably 10,000 or less, even more preferably 5,000 or less, and even still more preferably 3,000 or less from the viewpoint of securing solubility in a solvent, the viewpoint of favorably mixing with a branched polysilane when the organic resin has been made into a film and obtaining a uniform film and the like, and is preferably 600 or more, more preferably 700 or more, still more preferably 800 or more, even still more preferably 900 or more, and even still more preferably 1,000 or more from the viewpoint of improving the strength of the film and the like.

In the present invention, the weight-average molecular weight, the number-average molecular weight, and the dispersity of the organic resin such as the novolac resin, which is a polymer, can be measured, for example, using a GPC device (EcoSEC, HLC-8320GPC, manufactured by Tosoh Corporation) and a GPC column (TSKgel SuperMultiporeHZ-N and TSKgel SuperMultiporeHZ-H manufactured by Tosoh Corporation), at a column temperature of 40°C, using tetrahydrofuran as an eluent (elution solvent), at a flow rate of 0.35 mL/min, and using polystyrene (manufactured by Sigma-Aldrich) as a standard sample.

[0153]

As the organic resin contained in the release agent

composition, a novolac resin is preferable, and the release agent composition thus preferably contains a novolac resin alone as the organic resin, but may contain other polymers together with the novolac resin for the purpose of adjusting film physical properties and the like.

Examples of such other polymers include polyacrylic acid ester compounds, polymethacrylic acid ester compounds, polyacrylamide compounds, polymethacrylamide compounds, polyvinyl compounds, polystyrene compounds, polymaleimide compounds, polymaleic anhydrides, and polyacrylonitrile compounds.

[0154]

The content of the novolac resin in the release agent composition is not particularly limited, and is preferably 70 mass% or more with respect to the total amount of the polymer contained in the release agent composition.

The content of the novolac resin in the release agent composition is not particularly limited, and is preferably 50 to 100 mass% with respect to the film constituent components. In the present invention, the film constituent component means a component other than the solvent contained in the composition.

[0155]

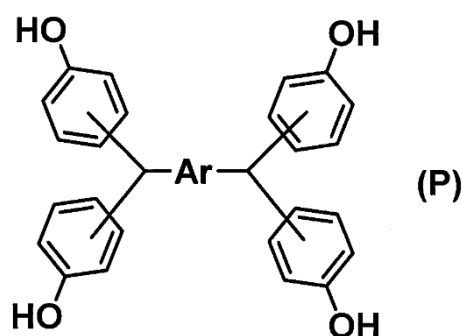
<<<<Polynuclear Phenol Derivative>>>>

The polynuclear phenol derivative is represented by,

for example, the following Formula (P).

[0156]

[Chem. 20]



In Formula (P), Ar represents an arylene group, and the number of carbon atoms therein is not particularly limited, and is usually 6 to 60, preferably 30 or less, more preferably 20 or less, still more preferably 18 or less, and even still more preferably 12 or less from the viewpoint of preparing a release agent composition having excellent uniformity and obtaining a release agent layer having higher flatness with good reproducibility.

[0157]

Specific examples of such an arylene group include, but are not limited to, 1,2-phenylene, 1,3-phenylene, and 1,4-phenylene; groups derived by removing two hydrogen atoms on an aromatic ring of a condensed ring aromatic hydrocarbon compound such as 1,5-naphthalenediyl, 1,8-naphthalenediyl, 2,6-naphthalenediyl, 2,7-naphthalenediyl, 1,2-anthracenediyl, 1,3-anthracenediyl, 1,4-anthracenediyl,

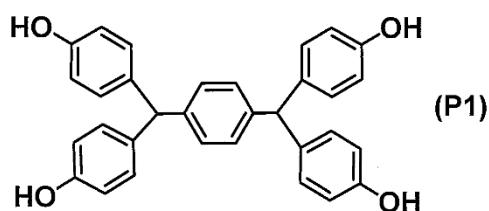
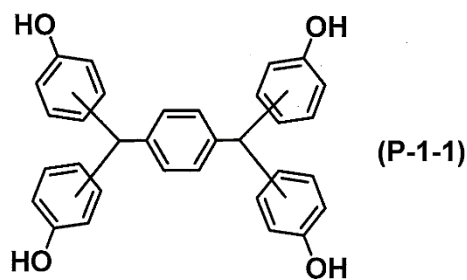
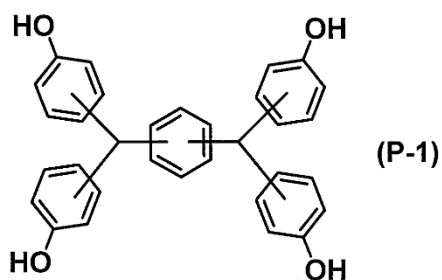
1,5-anthracenediyl, 1,6-anthracenediyl, 1,7-anthracenediyl, 1,8-anthracenediyl, 2,3-anthracenediyl, 2,6-anthracenediyl, 2,7-anthracenediyl, 2,9-anthracenediyl, 2,10-anthracenediyl, and a 9,10-anthracenediyl group; and groups derived by removing two hydrogen atoms on an aromatic ring of a ring-linked aromatic hydrocarbon compound such as a biphenyl-4,4'-diyl group or a paraterphenyl-4,4''-diyl group.

[0158]

The polynuclear phenol derivative represented by Formula (P) is preferably a polynuclear phenol derivative represented by Formula (P-1), more preferably a polynuclear phenol derivative represented by Formula (P-1-1), and still more preferably a polynuclear phenol derivative represented by Formula (P1) from the viewpoint of obtaining a laminate in which the release agent layer exhibits good releasability and a support substrate can be favorably separated with good reproducibility.

[0159]

[Chem. 21]



[0160]

The content of the polynuclear phenol derivative in the release agent composition is not particularly limited, and is preferably 50 to 100 mass% with respect to the film constituent component.

[0161]

<<<<Branched Polysilane>>>>

The above-described release agent composition may contain a branched polysilane.

The branched polysilane has a Si-Si bond and a branched structure. When the branched polysilane is contained in the release agent composition, the release agent layer formed of the obtained film cannot be suitably removed with any of an organic solvent, an acid, and a chemical solution used in the production of a semiconductor element (an alkali developer, hydrogen peroxide water, or the like),

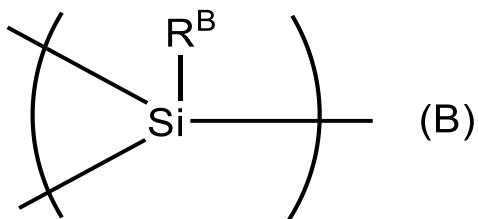
but can be suitably removed with a cleaning agent composition, and as a result, the residues of the release agent layer on the substrate can be suitably removed by separating the semiconductor substrate and the support substrate of the laminate and then cleaning each substrate with the cleaning agent composition. Although the reason therefor is not clear, it is presumed that depending on the type of the terminal group (terminal substituent (atom)) of the polysilane, the polysilane can react with the organic resin and crosslink, the branched polysilane has more terminal groups (terminal substituents (atoms)) than linear polysilanes, and it is thus considered that the branched polysilane has more crosslinking points than linear polysilanes, and both a property of not being suitably removed with an organic solvent, an acid, and a chemical solution used in the production of a semiconductor element (an alkali developer, hydrogen peroxide water, or the like) and a property of being suitably removed with a cleaning agent composition can be achieved by appropriate and suitable curing through such more crosslinking points in the branched polysilane.

[0162]

The branched polysilane preferably includes a structural unit represented by Formula (B).

[0163]

[Chem. 22]



[0164]

In Formula (B), R^B represents a hydrogen atom, a hydroxy group, a silyl group, or an organic group, and specific examples of such an organic group include hydrocarbon groups (an alkyl group which may be substituted, an alkenyl group which may be substituted, an aryl group which may be substituted, and an aralkyl group which may be substituted) and ether groups corresponding to these hydrocarbon groups (an alkoxy group which may be substituted, an aryloxy group which may be substituted, an aralkyloxy group which may be substituted, and the like), and the organic group is usually a hydrocarbon group such as an alkyl group, an alkenyl group, an aryl group, or an aralkyl group in many cases. In addition, a hydrogen atom, a hydroxy group, an alkoxy group, a silyl group, or the like is often substituted at the terminal.

[0165]

The alkyl group which may be substituted may be linear, branched, or cyclic.

Specific examples of the linear or branched alkyl group

which may be substituted include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group, an s-butyl group, a tertiary butyl group, an n-pentyl group, a 1-methyl-n-butyl group, a 2-methyl-n-butyl group, a 3-methyl-n-butyl group, a 1,1-dimethyl-n-propyl group, a 1,2-dimethyl-n-propyl group, a 2,2-dimethyl-n-propyl group, a 1-ethyl-n-propyl group, an n-hexyl group, a 1-methyl-n-pentyl group, a 2-methyl-n-pentyl group, a 3-methyl-n-pentyl group, a 4-methyl-n-pentyl group, a 1,1-dimethyl-n-butyl group, a 1,2-dimethyl-n-butyl group, a 1,3-dimethyl-n-butyl group, a 2,2-dimethyl-n-butyl group, a 2,3-dimethyl-n-butyl group, a 3,3-dimethyl-n-butyl group, a 1-ethyl-n-butyl group, a 2-ethyl-n-butyl group, a 1,1,2-trimethyl-n-propyl group, a 1,2,2-trimethyl-n-propyl group, a 1-ethyl-1-methyl-n-propyl group, and a 1-ethyl-2-methyl-n-propyl group, but are not limited thereto, and the number of carbon atoms thereof is usually 1 to 14, preferably 1 to 10, and more preferably 1 to 6.

Specific examples of the cyclic alkyl group which may be substituted include a cycloalkyl group such as a cyclopropyl group, a cyclobutyl group, a 1-methyl-cyclopropyl group, a 2-methyl-cyclopropyl group, a cyclopentyl group, a 1-methyl-cyclobutyl group, a 2-methyl-cyclobutyl group, a 3-methyl-cyclobutyl group, a 1,2-

dimethyl-cyclopropyl group, a 2,3-dimethyl-cyclopropyl group, a 1-ethyl-cyclopropyl group, a 2-ethyl-cyclopropyl group, a cyclohexyl group, a 1-methyl-cyclopentyl group, a 2-methyl-cyclopentyl group, a 3-methyl-cyclopentyl group, a 1-ethyl-cyclobutyl group, a 2-ethyl-cyclobutyl group, a 3-ethyl-cyclobutyl group, a 1,2-dimethyl-cyclobutyl group, a 1,3-dimethyl-cyclobutyl group, a 2,2-dimethyl-cyclobutyl group, a 2,3-dimethyl-cyclobutyl group, a 2,4-dimethyl-cyclobutyl group, a 3,3-dimethyl-cyclobutyl group, a 1-n-propyl-cyclopropyl group, a 2-n-propyl-cyclopropyl group, a 1-i-propyl-cyclopropyl group, a 2-i-propyl-cyclopropyl group, a 1,2,2-trimethyl-cyclopropyl group, a 1,2,3-trimethyl-cyclopropyl group, a 2,2,3-trimethyl-cyclopropyl group, a 1-ethyl-2-methyl-cyclopropyl group, a 2-ethyl-1-methyl-cyclopropyl group, a 2-ethyl-2-methyl-cyclopropyl group, and a 2-ethyl-3-methyl-cyclopropyl group; and a bicycloalkyl group such as a bicyclobutyl group, a bicyclopentyl group, a bicyclohexyl group, a bicycloheptyl group, a bicyclooctyl group, a bicyclononyl group, and a bicyclodecyl group, but are not limited thereto, and the number of carbon atoms thereof is usually 3 to 14, preferably 4 to 10, and more preferably 5 to 6.

[0166]

The alkenyl group may be linear, branched, or cyclic.

Specific examples of the linear or branched alkenyl

group which may be substituted include, but are not limited to, a vinyl group, an allyl group, a butenyl group, and a pentenyl group, and the number of carbon atoms thereof is usually 2 to 14, preferably 2 to 10, and more preferably 1 to 6.

Specific examples of the cyclic alkenyl group which may be substituted include, but are not limited to, cyclopentenyl and cyclohexenyl, and the number of carbon atoms thereof is usually 4 to 14, preferably 5 to 10, and more preferably 5 to 6.

[0167]

Specific examples of the aryl group which may be substituted include, but are not limited to, a phenyl group, a 4-methylphenyl group, a 3-methylphenyl group, a 2-methylphenyl group, a 3,5-dimethylphenyl group, a 1-naphthyl group, and a 2-naphthyl group, and the number of carbon atoms therein is usually 6 to 20, preferably 6 to 14, and more preferably 6 to 12.

[0168]

Specific examples of the aralkyl group which may be substituted include, but are not limited to, a benzyl group, a phenethyl group, and a phenylpropyl group. The aralkyl group which may be substituted is preferably a group in which one hydrogen atom of an alkyl group having 1 to 4 carbon atoms has been substituted with an aryl group

having 6 to 20 carbon atoms.

[0169]

The alkoxy group which may be substituted may be linear, branched, or cyclic in an alkyl moiety thereof.

Specific examples of the linear or branched alkoxy group which may be substituted include, but are not limited to, a methoxy group, an ethoxy group, a propoxy group, an isopropoxy group, a butoxy group, a t-butoxy group, and a pentyloxy group, and the number of carbon atoms therein is usually 1 to 14, preferably 1 to 10, and more preferably 1 to 6.

Specific examples of the cyclic alkoxy group which may be substituted include, but are not limited to, cyclopentyloxy and cyclohexyloxy, and the number of carbon atoms thereof is usually 3 to 14, preferably 4 to 10, and more preferably 5 to 6.

[0170]

Specific examples of the aryloxy group which may be substituted include, but are not limited to, phenoxy, 1-naphthyloxy, and 2-naphthyloxy, and the number of carbon atoms thereof is usually 6 to 20, preferably 6 to 14, and more preferably 6 to 10.

[0171]

Specific examples of the aralkyloxy group which may be substituted include, but are not limited to, benzyloxy,

phenethyloxy, and phenylpropyloxy. The aralkyloxy group which may be substituted is preferably a group in which one hydrogen atom of an alkyloxy group having 1 to 4 carbon atoms has been substituted with an aryl group having 6 to 20 carbon atoms.

[0172]

Specific examples of the silyl group include, but are not limited to, a silyl group, a disilanyl group, and a trisilanyl group, and the number of silicon atoms thereof is usually 1 to 10 and preferably 1 to 6.

[0173]

When R^B is the organic group or the silyl group, at least one of the hydrogen atoms may be substituted with a substituent. Specific examples of such a substituent include a hydroxy group, an alkyl group, an aryl group, and an alkoxy group.

[0174]

R^B is preferably an alkyl group or an aryl group, more preferably an aryl group, still more preferably a phenyl group, a 1-naphthyl group, or a 2-naphthyl group, and even still more preferably a phenyl group from the viewpoint of suppressing unintentional release when the laminate is brought into contact with any of an organic solvent, an acid, and a chemical solution used in the production of a semiconductor element (an alkali developer, hydrogen

peroxide water, or the like), the viewpoint of suitably removing the residue of the release agent layer on the substrate when the semiconductor substrate and the support substrate of the laminate have been separated and each substrate has then been cleaned with a cleaning agent composition, and the like.

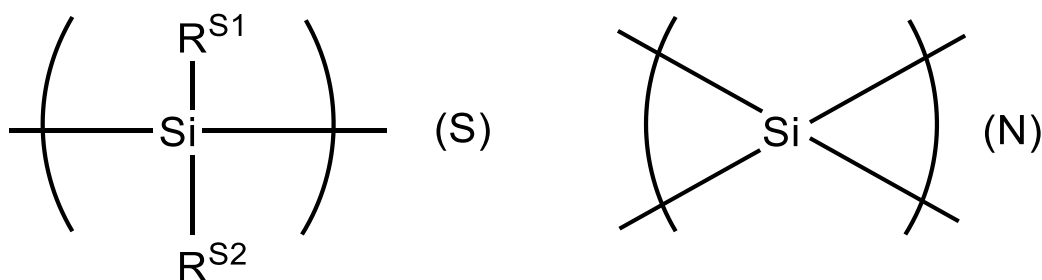
[0175]

The branched polysilane may contain a structural unit represented by the following Formula (S) or a structural unit represented by the following Formula (N) together with the structural unit represented by Formula (B), and the content of the structural unit represented by Formula (B) in the branched polysilane is usually 50 mol% or more, preferably 60 mol% or more, more preferably 70 mol% or more, still more preferably 80 mol% or more, even still more preferably 90 mol% or more, and even still more preferably 95 mol% or more based on the total structural units from the viewpoint of suppressing unintentional release when the laminate is brought into contact with any of an organic solvent, an acid, and a chemical solution used in the production of a semiconductor element (an alkali developer, hydrogen peroxide water, or the like), the viewpoint of suitably removing the residue of the release agent layer on the substrate when the semiconductor substrate and the support substrate of the laminate have

been separated and each substrate has then been cleaned with a cleaning agent composition, and the like.

[0176]

[Chem. 23]



(R^{S1} and R^{S2} represent the same meanings as R^B.)

[0177]

The terminal group (terminal substituent (atom)) of the branched polysilane may be usually a hydrogen atom, a hydroxy group, a halogen atom (a chlorine atom or the like), an alkyl group, an aryl group, an alkoxy group, a silyl group, or the like. Among them, the terminal group is often a hydroxy group, a methyl group, or a phenyl group, and among them, a methyl group is preferable, and the terminal group may be a trimethylsilyl group.

[0178]

In an embodiment, the average degree of polymerization of the branched polysilane is usually 2 to 100, preferably 3 to 80, more preferably 5 to 50, and still more preferably 10 to 30 in terms of silicon atoms (that is, the average number of silicon atoms per molecule).

In an embodiment, the upper limit of the weight-average molecular weight of the branched polysilane is usually 30,000, preferably 20,000, more preferably 10,000, still more preferably 5,000, even more preferably 2,000, and even still more preferably 1,500, and the lower limit thereof is usually 50, preferably 100, more preferably 150, still more preferably 200, even still more preferably 300, and even more preferably 500.

The average degree of polymerization and weight-average molecular weight of the branched polysilane can be measured using, for example, a GPC device (EcoSEC, HLC-8220GPC, manufactured by Tosoh Corporation) and a GPC column (Shodex KF-803L, KF-802, and KF-801, manufactured by Showa Denko K.K., used in this order), at a column temperature of 40°C, using tetrahydrofuran as an eluent (elution solvent), at a flow rate of 1.00 mL/min, and using polystyrene (manufactured by Sigma-Aldrich) as a standard sample.

When the degree of polymerization and weight-average molecular weight of the branched polysilane being used are too small, there is a possibility that the branched polysilane may vaporize by heating when a film that is the release agent layer is formed or when the laminate including the obtained release agent layer is processed, or a disadvantage due to a poor strength of the film may be generated, and when the degree of polymerization and

molecular weight of the branched polysilane being used are too large, there is a possibility that sufficient solubility cannot be secured depending on the type of a solvent to be used for the preparation of the release agent composition, precipitation may occur in the composition, or mixing with a resin may become insufficient, which makes it impossible to obtain a highly uniform film with high reproducibility.

Therefore, it is desirable that the degree of polymerization and weight-average molecular weight of the branched polysilane satisfy the above-described ranges from the viewpoint of obtaining a laminate including a release agent layer contributing to suitable production of a semiconductor element with better reproducibility.

[0179]

The 5% weight loss temperature of the branched polysilane is usually 300°C or higher, preferably 350°C or higher, more preferably 365°C or higher, still more preferably 380°C or higher, even still more preferably 395°C or higher, and even more preferably 400°C or higher from the viewpoint of reproducibly obtaining a release agent layer excellent in heat resistance.

The 5% weight loss temperature of the branched polysilane can be measured by, for example, raising the temperature from normal temperature (25°C) to 400°C at

10°C/min under air using a 2010SR manufactured by NETZSCH Group.

[0180]

When the semiconductor substrate and the support substrate of the laminate are separated from each other, and each substrate is then cleaned with a cleaning agent composition, the branched polysilane is preferably soluble in at least one of an ether compound such as tetrahydrofuran, an aromatic compound such as toluene, a glycol ether ester compound such as propylene glycol monomethyl ether acetate, a ketone compound such as cyclohexanone or methyl ethyl ketone, and a glycol ether compound such as propylene glycol monomethyl ether from the viewpoint of suitably removing the residue of the release agent layer on the substrate, from the viewpoint of preparing a release agent composition having excellent uniformity with good reproducibility, and the like. The dissolution in this case means that, when dissolution is attempted using a shaker at normal temperature (25°C) to prepare a 10 mass% solution, dissolution is visually confirmed within 1 hour.

[0181]

The branched polysilane may be either solid or liquid at normal temperature.

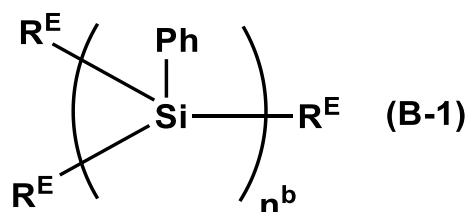
[0182]

The branched polysilane can be produced with reference to known methods described in, for example, JP 2011-208054 A, JP 2007-106894 A, JP 2007-145879 A, and WO 2005/113648 A, or can also be obtained as a commercially available product. Specific examples of the commercially available product include, but are not limited to, silicon materials Polysilane OGSOL SI-20-10 and SI-20-14 manufactured by Osaka Gas Chemicals Co., Ltd.

[0183]

Suitable examples of the branched polysilane include, but are not limited to, the following.

[Chem. 24]



(Ph represents a phenyl group, each R^E independently represents a terminal substituent and represents an atom or a group, and n^b indicates the number of repeating units.)

[0184]

The content of the branched polysilane in the release agent composition is usually 10 to 90 mass% with respect to the film constituent component, and is preferably 15 to 80 mass%, more preferably 20 to 70 mass%, still more preferably 25 to 60 mass%, and even still more preferably

30 to 50 mass% from the viewpoint of achieving with good reproducibility a film that cannot be suitably removed with an organic solvent, an acid, or a chemical solution used in the production of a semiconductor element (an alkali developer, hydrogen peroxide water, or the like) but can be suitably removed with a cleaning agent composition.

[0185]

<<<<Crosslinking Agent>>>>

The release agent composition may contain a crosslinking agent.

The crosslinking agent may cause a crosslinking reaction by self-condensation, but when crosslinkable substituents are present in the novolac resin, the crosslinking agent can cause a crosslinking reaction with these crosslinkable substituents.

[0186]

Specific examples of the crosslinking agent are not particularly limited, but typically include phenol-based crosslinking agents, melamine-based crosslinking agents, urea-based crosslinking agents, thiourea-based crosslinking agents, and the like, each of which has a crosslinking-forming group in the molecule, such as an alkoxymethyl group (for example, a hydroxymethyl group, a methoxymethyl group, or a butoxymethyl group), and these may be low molecular weight compounds or high molecular weight

compounds.

The crosslinking agent contained in the release agent composition usually has two or more crosslinking-forming groups, and the number of crosslinking-forming groups contained in a compound as the crosslinking agent is preferably 2 to 10, and more preferably 2 to 6 from the viewpoint of achieving more suitable curing with good reproducibility.

The crosslinking agent contained in the release agent composition preferably has an aromatic ring (for example, a benzene ring or a naphthalene ring) in the molecule from the viewpoint of achieving higher heat resistance, and typical examples of such a crosslinking agent include, but are not limited to, a phenol-based crosslinking agent.

[0187]

The phenol-based crosslinking agent having a crosslinking-forming group is a compound having a crosslinking-forming group bonded to an aromatic ring and having at least one of a phenolic hydroxy group and an alkoxy group derived from a phenolic hydroxy group, and examples of such an alkoxy group derived from a phenolic hydroxy group include, but are not limited to, a methoxy group and a butoxy group.

Each of the aromatic ring to which the crosslinking-forming group is bonded and the aromatic ring to which the

phenolic hydroxy group and/or the alkoxy group derived from a phenolic hydroxy group is bonded is not limited to a non-condensed ring type aromatic ring such as a benzene ring, and may be a condensed ring type aromatic ring such as a naphthalene ring or anthracene.

When a plurality of aromatic rings are present in the molecule of the phenol-based crosslinking agent, the crosslinking-forming group and the phenolic hydroxy group and the alkoxy group derived from a phenolic hydroxy group may be bonded to the same aromatic ring in the molecule or may be bonded to different aromatic rings.

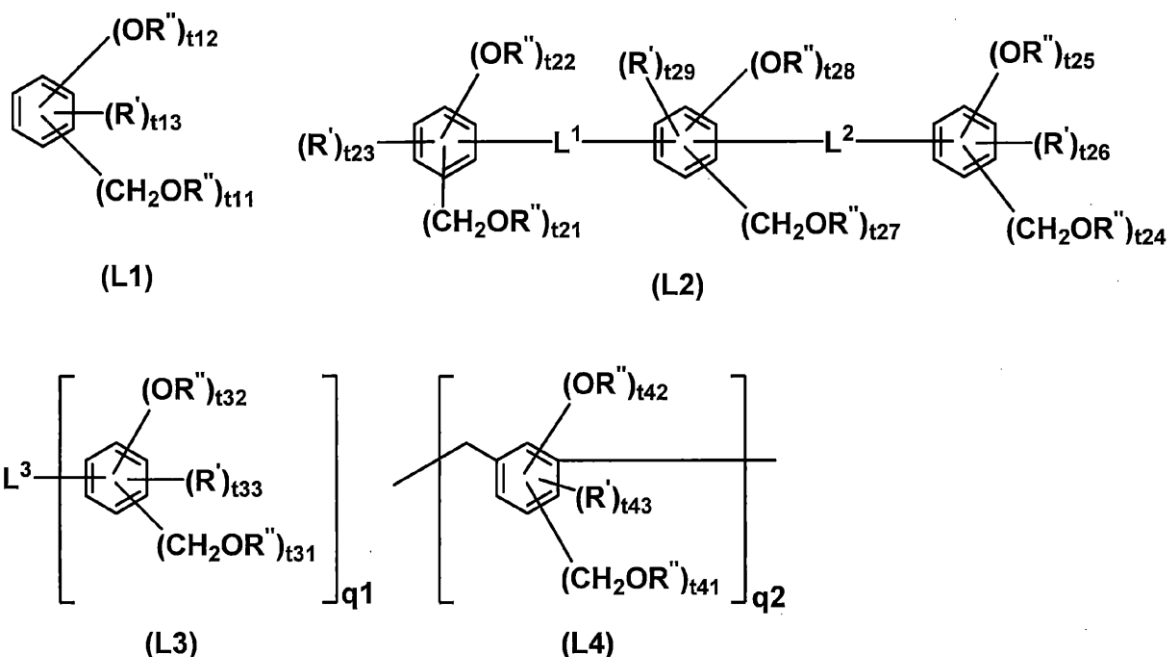
The aromatic ring to which the crosslinking-forming group, the phenolic hydroxy group, and the alkoxy group derived from a phenolic hydroxy group are bonded may be further substituted with an alkyl group such as a methyl group, an ethyl group, or a butyl group, a hydrocarbon group such as an aryl group (for example, a phenyl group), a halogen atom such as a fluorine atom, or the like.

[0188]

For example, specific examples of the phenol-based crosslinking agent having a crosslinking-forming group include compounds represented by any of Formulas (L1) to (L4).

[0189]

[Chem. 25]



[0190]

In each formula, each R' independently represents a fluorine atom, an aryl group, or an alkyl group, each R'' independently represents a hydrogen atom or an alkyl group, L^1 and L^2 each independently represent a single bond, a methylene group, or a propane-2,2-diyl group, L^3 is determined depending on $q1$ and represents a single bond, a methylene group, a propane-2,2-diyl group, a methantriyl group, or an ethane-1,1,1-triyl group, $t11$, $t12$, and $t13$ are integers satisfying $2 \leq t11 \leq 5$, $1 \leq t12 \leq 4$, $0 \leq t13 \leq 3$, and $t11 + t12 + t13 \leq 6$, $t21$, $t22$, and $t23$ are integers satisfying $2 \leq t21 \leq 4$, $1 \leq t22 \leq 3$, $0 \leq t23 \leq 2$, and $t21 + t22 + t23 \leq 5$, $t24$, $t25$, and $t26$ are integers satisfying $2 \leq t24 \leq 4$, $1 \leq t25 \leq 3$, $0 \leq t26 \leq 2$, and $t24 + t25 + t26 \leq 5$, $t27$, $t28$, and $t29$ are integers satisfying $0 \leq t27 \leq 4$, 0

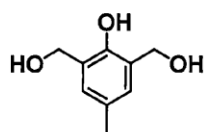
$\leq t_{28} \leq 4$, $0 \leq t_{29} \leq 4$, and $t_{27} + t_{28} + t_{29} \leq 4$, t_{31} , t_{32} , and t_{33} are integers satisfying $2 \leq t_{31} \leq 4$, $1 \leq t_{32} \leq 3$, $0 \leq t_{33} \leq 2$, and $t_{31} + t_{32} + t_{33} \leq 5$, t_{41} , t_{42} , and t_{43} are integers satisfying $2 \leq t_{41} \leq 3$, $1 \leq t_{42} \leq 2$, $0 \leq t_{43} \leq 1$, and $t_{41} + t_{42} + t_{43} \leq 4$, q_1 is 2 or 3, q_2 represents the number of repetitions and is an integer of 0 or more, and specific examples of the aryl group and the alkyl group include those the same as the following specific examples, but the aryl group is preferably a phenyl group, and the alkyl group is preferably a methyl group or a t-butyl group.

[0191]

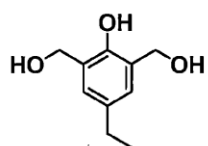
Hereinafter, specific examples of the compounds represented by Formulas (L1) to (L4) will be given, but these are not limited thereto. These compounds may be synthesized by a known method, and can also be obtained, for example, as products of Asahi Organic Chemical Industry Co., Ltd. or Honshu Chemical Industry Co., Ltd.

[0192]

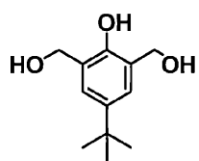
[Chem. 26]



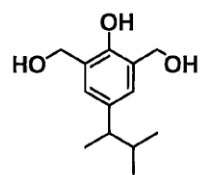
(L1)



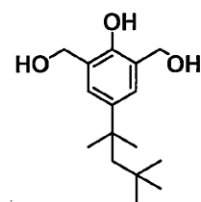
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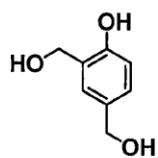
(L3)



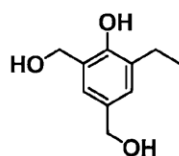
(L4)



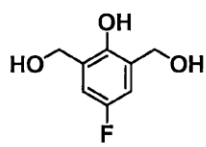
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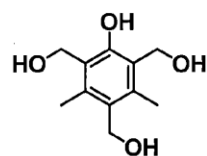
(L6)



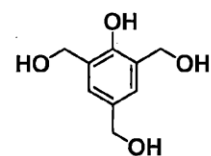
(L7)



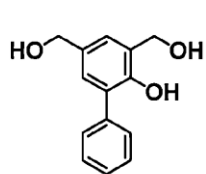
(L8)



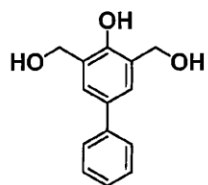
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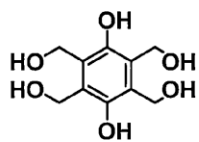
(L10)



(L11)



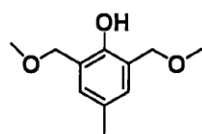
(L12)



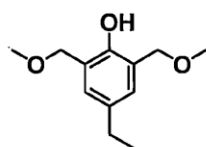
(L13)

[0193]

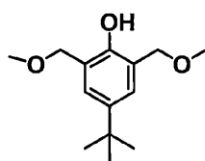
[Chem. 27]



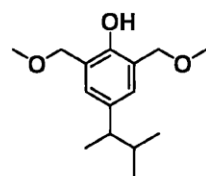
(L1M)



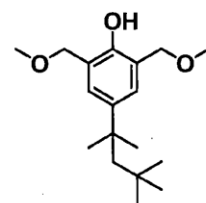
(L2M)



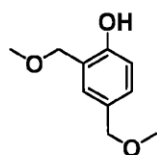
(L3M)



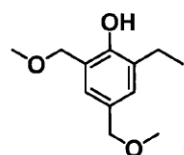
(L4M)



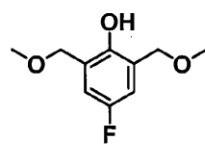
(L5M)



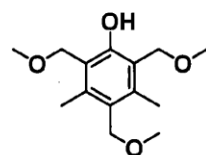
(L6M)



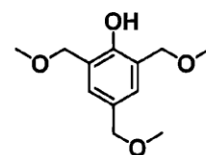
(L7M)



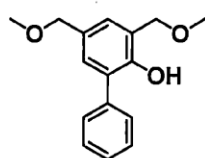
(L8M)



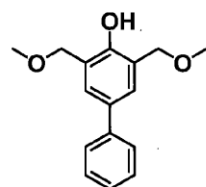
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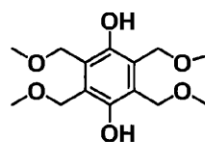
(L10M)



(L11M)



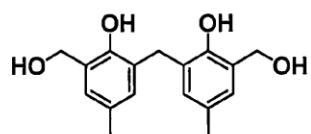
(L12M)



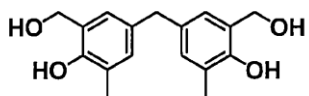
(L13M)

[0194]

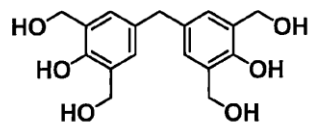
[Chem. 28]



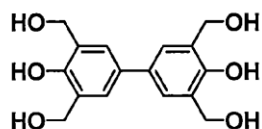
(L14)



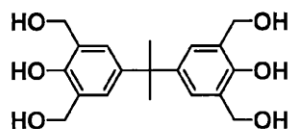
(L15)



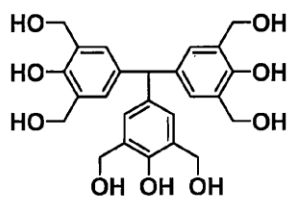
(L16)



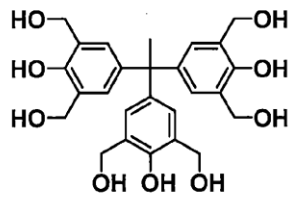
(L17)



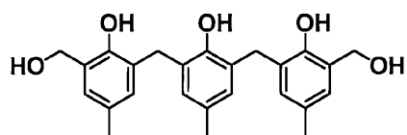
(L18)



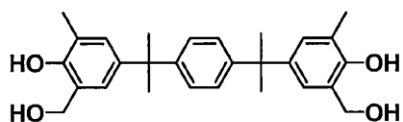
(L19)



(L20)



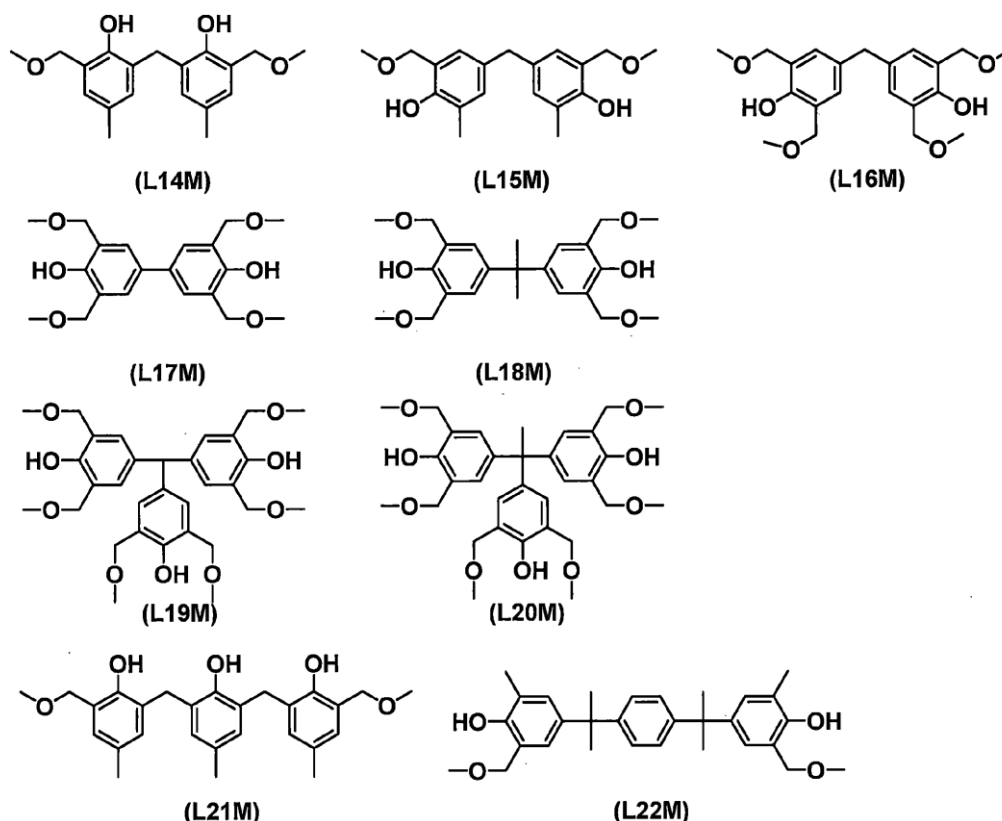
(L21)



(L22)

[0195]

[Chem. 29]



[0196]

The melamine-based crosslinking agent having a crosslinking-forming group is a melamine derivative, a 2,4-diamino-1,3,5-triazine derivative, or a 2-amino-1,3,5-triazine derivative in which at least one of the hydrogen atoms of an amino group bonded to the triazine ring is substituted with a crosslinking-forming group, and the triazine ring may further have a substituent such as an aryl group such as a phenyl group.

Specific examples of the melamine-based crosslinking agent having a crosslinking-forming group include, but are not limited to, mono-, bis-, tris-, tetrakis-, pentakis- or

hexakisalkoxymethylmelamines such as N,N,N',N',N'',N''-hexakis(methoxymethyl)melamine and N,N,N',N',N'',N''-hexakis(butoxymethyl)melamine; and mono-, bis-, tris- or tetrakisalkoxymethylbenzoguanamines such as N,N,N',N'-tetrakis(methoxymethyl)benzoguanamine and N,N,N',N'-tetrakis(butoxymethyl)benzoguanamine.

[0197]

The urea-based crosslinking agent having a crosslinking-forming group is a derivative of a urea bond-containing compound, and has a structure in which at least one of the hydrogen atoms of an NH group constituting a urea bond is substituted with a crosslinking-forming group.

Specific examples of the urea-based crosslinking agent having a crosslinking-forming group include, but are not limited to, mono-, bis-, tris-, or tetrakisalkoxymethylglycolurils such as 1,3,4,6-tetrakis(methoxymethyl)glycoluril and 1,3,4,6-tetrakis(butoxymethyl)glycoluril; and mono-, bis-, tris-, or tetrakisalkoxymethylureas such as 1,3-bis(methoxymethyl)urea and 1,1,3,3-tetrakis(methoxymethyl)urea.

[0198]

The thiourea-based crosslinking agent having a crosslinking-forming group is a derivative of a thiourea bond-containing compound, and has a structure in which at

least one of the hydrogen atoms of an NH group constituting a thiourea bond is substituted with a crosslinking-forming group.

Specific examples of the thiourea-based crosslinking agent having a crosslinking-forming group include, but are not limited to, mono-, bis-, tris-, or tetrakisalkoxymethylthioureas such as 1,3-bis(methoxymethyl)thiourea and 1,1,3,3-tetrakis(methoxymethyl)thiourea.

[0199]

The amount of the crosslinking agent contained in the release agent composition varies depending on the coating method to be employed, the desired film thickness, and the like, and thus cannot be generally determined, but is usually 0.01 to 50 mass% with respect to the organic resin or the polynuclear phenol derivative, and is preferably 0.1 mass% or more, more preferably 1 mass% or more, still more preferably 3 mass% or more, and further preferably 5 mass% or more, and preferably 45 mass% or less, more preferably 40 mass% or less, still more preferably 35 mass% or less, and further preferably 30 mass% or less from the viewpoint of achieving suitable curing and obtaining a laminate in which a semiconductor substrate and a support substrate can be satisfactorily separated from each other with high reproducibility.

[0200]

<<<<Acid Generator and Acid>>>>

For the purpose of, for example, promoting the crosslinking reaction, the release agent composition may contain an acid generator or an acid.

[0201]

Examples of the acid generator include a thermal acid generator and a photoacid generator.

The thermal acid generator is not particularly limited as long as an acid is generated by heat, and specific examples thereof include, but are not limited to, 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, 2-nitrobenzyl tosylate, K-PURE [registered trademark] CXC-1612, CXC-1614, TAG-2172, TAG-2179, TAG-2678, TAG2689, and TAG2700 (manufactured by King Industries, Inc.), SI-45, SI-60, SI-80, SI-100, SI-110, and SI-150 (manufactured by Sanshin Chemical Industry Co., Ltd.), and other organic sulfonic acid alkyl esters.

[0202]

Examples of the photoacid generator include an onium salt compound, a sulfonimide compound, and a disulfonyldiazomethane compound.

[0203]

Specific examples of the onium salt compound include, but are not limited to, iodonium salt compounds such as

diphenyliodonium hexafluorophosphate, diphenyliodonium trifluoromethanesulfonate, diphenyliodonium nonafluoronormal butanesulfonate, diphenyliodonium perfluoronormal octanesulfonate, diphenyliodonium camphor sulfonate, bis(4-tert-butylphenyl)iodonium camphorsulfonate, and bis(4-tert-butylphenyl)iodonium trifluoromethanesulfonate; and sulfonium salt compounds such as triphenylsulfonium nitrate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium nonafluoro-normal butanesulfonate, triphenylsulfonium camphorsulfonate, and triphenylsulfonium trifluoromethanesulfonate.

[0204]

Specific examples of the sulfonimide compound include, but are not limited to, N-(trifluoromethanesulfonyloxy)succinimide, N-(nonafluoro normal butane sulfonyloxy)succinimide, N-(camphorsulfonyloxy)succinimide, and N-(trifluoromethanesulfonyloxy)naphthalimide.

[0205]

Specific examples of the disulfonyl diazomethane compound include, but are not limited to, bis(trifluoromethylsulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane, bis(phenylsulfonyl)diazomethane, bis(p-toluenesulfonyl)diazomethane, bis(2,4-

dimethylbenzenesulfonyl)diazomethane, and methylsulfonyl-p-toluenesulfonyldiazomethane.

[0206]

Specific examples of the acid include, but are not limited to, arylsulfonic acids and pyridinium salts such as p-toluenesulfonic acid, pyridinium p-toluenesulfonate(pyridinium paratoluenesulfonate), pyridinium trifluoromethanesulfonate, pyridinium phenolsulfonic acid, 5-sulfosalicylic acid, 4-phenolsulfonic acid, 4-chlorobenzenesulfonic acid, benzenedisulfonic acid, and 1-naphthalenesulfonic acid, and salts thereof; arylcarboxylic acids such as salicylic acid, benzoic acid, hydroxybenzoic acid, and naphthalenecarboxylic acid, and salts thereof; linear or cyclic alkylsulfonic acids such as trifluoromethanesulfonic acid and camphorsulfonic acid, and salts thereof; and linear or cyclic alkylcarboxylic acids such as citric acid, and salts thereof.

[0207]

The amounts of the acid generating agent and the acid contained in the release agent composition cannot be generally determined because the amounts vary depending on the type of the crosslinking agent to be used together, the heating temperature at the time of forming the film, and the like, but are usually 0.01 to 5 mass% with respect to

the film constituent component.

[0208]

<<<<Surfactant>>>>

The release agent composition may contain a surfactant for the purpose of, for example, adjusting the liquid properties of the composition itself or the film properties of the obtained film, or preparing a highly uniform release agent composition with high reproducibility.

Examples of the surfactant include nonionic surfactants such as polyoxyethylene alkyl ethers (for example, polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene cetyl ether, and polyoxyethylene oleyl ether), polyoxyethylene alkyl aryl ethers (for example, polyoxyethylene octylphenol ether and polyoxyethylene nonylphenol ether), polyoxyethylene/polyoxypropylene block copolymers, sorbitan fatty acid esters (for example, sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan monooleate, sorbitan trioleate, and sorbitan tristearate), and polyoxyethylene sorbitan fatty acid esters such as polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan trioleate, and polyoxyethylene sorbitan tristearate; fluorine surfactants such as EFTOP EF301, EF303, and EF352 (manufactured by

Token Products, trade name), MEGAFACE F171, F173, R-30, and R-30N (manufactured by DIC Corporation, trade name), FLUORAD FC430 and FC431 (manufactured by Sumitomo 3M Ltd., trade name), ASAHIGUARD AG710, SURFLON S-382, SC101, SC102, SC103, SC104, SC105, and SC106 (manufactured by Asahi Glass Co., Ltd., trade name); and organosiloxane polymer KP341 (manufactured by Shin-Etsu Chemical Co., Ltd.).

Surfactants can be used alone or in combination with two or more thereof.

The amount of the surfactant is usually 2 mass% or less with respect to the film constituent components of the release agent composition.

[0209]

<<<<Solvent>>>>

The release agent composition preferably contains a solvent.

As such a solvent, it is possible to use, for example, a high-polarity solvent capable of satisfactorily dissolving film constituent components such as the organic resin, the polynuclear phenol derivative, the branched polysilane and the crosslinking agent, and as necessary, a low-polarity solvent may also be used for purposes such as adjusting viscosity and surface tension. In the present invention, the low-polarity solvent is defined as a solvent having a relative permittivity of less than 7 at a

frequency of 100 kHz, and the high-polarity solvent is defined as a solvent having a relative permittivity of 7 or more at a frequency of 100 kHz. The solvents can be used alone or in combination with two or more thereof.

[0210]

In addition, examples of the high-polarity solvent include amide-based solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N,N-dimethylisobutyramide, N-methylpyrrolidone, and 1,3-dimethyl-2-imidazolidinone; ketone-based solvents such as ethyl methyl ketone, isophorone, and cyclohexanone; cyano-based solvents such as acetonitrile and 3-methoxypropionitrile; polyhydric alcohol-based solvents such as ethylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, 1,3-butanediol, and 2,3-butanediol; monohydric alcohol-based solvents other than aliphatic alcohols, such as propylene glycol monomethyl ether, diethylene glycol monomethyl ether, diethylene glycol monophenyl ether, triethylene glycol monomethyl ether, dipropylene glycol monomethyl ether, benzyl alcohol, 2-phenoxyethanol, 2-benzyloxyethanol, 3-phenoxybenzyl alcohol, and tetrahydrofurfuryl alcohol; and sulfoxide-based solvents such as dimethyl sulfoxide.

[0211]

Examples of the low-polarity solvent include chlorine-

based solvents such as chloroform and chlorobenzene; aromatic hydrocarbon-based solvents such as alkylbenzenes (for example, toluene, xylene, tetralin, cyclohexylbenzene, and decylbenzene); aliphatic alcohol-based solvents such as 1-octanol, 1-nonanol, and 1-decanol; ether-based solvents such as tetrahydrofuran, dioxane, anisole, 4-methoxytoluene, 3-phenoxytoluene, dibenzyl ether, diethylene glycol dimethyl ether, diethylene glycol butyl methyl ether, triethylene glycol dimethyl ether, and triethylene glycol butyl methyl ether; and ester-based solvents such as methyl benzoate, ethyl benzoate, butyl benzoate, isoamyl benzoate, bis(2-ethylhexyl)phthalate, dibutyl maleate, dibutyl oxalate, hexyl acetate, propylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, and diethylene glycol monobutyl ether acetate.

[0212]

The content of the solvent is appropriately determined in consideration of the viscosity of the desired composition, the coating method to be adopted, the thickness of the film to be prepared, and the like, but is 99 mass% or less of the entire composition, preferably 70 to 99 mass% with respect to the entire composition, that is, the amount of the film constituent component in that case is 1 to 30 mass% with respect to the entire

composition.

[0213]

The viscosity and surface tension of the release agent composition are appropriately adjusted by changing the type of the solvent to be used, the ratio thereof, the concentration of the film constituent components, and the like in consideration of various factors such as the coating method to be used and the desired film thickness.

[0214]

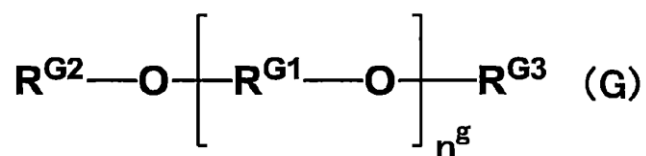
In an embodiment of the present invention, the release agent composition contains a glycol-based solvent from the viewpoint of obtaining a highly uniform composition with good reproducibility, from the viewpoint of obtaining a highly storage-stable composition with good reproducibility, from the viewpoint of obtaining a composition that provides a highly uniform film with good reproducibility, and the like. The "glycol-based solvent" as used herein is a generic term for glycols, glycol monoethers, glycol diethers, glycol monoesters, glycol diesters, and glycol ester ethers.

[0215]

An example of a preferred glycol-based solvent is represented by Formula (G).

[0216]

[Chem. 30]



[0217]

In Formula (G), each $\text{R}^{\text{G}1}$ independently represents a linear or branched alkylene group having 2 to 4 carbon atoms, $\text{R}^{\text{G}2}$ and $\text{R}^{\text{G}3}$ each independently represent a hydrogen atom, a linear or branched alkyl group having 1 to 8 carbon atoms, or an alkylacyl group in which the alkyl moiety is a linear or branched alkyl group having 1 to 8 carbon atoms, and n^{g} is an integer of 1 to 6.

[0218]

Specific examples of the linear or branched alkylene group having 2 to 4 carbon atoms include, but are not limited to, an ethylene group, a trimethylene group, a 1-methylethylene group, a tetramethylene group, a 2-methylpropane-1,3-diyl group, a pentamethylene group, and a hexamethylene group.

Among them, a linear or branched alkylene group having 2 to 3 carbon atoms is preferable, and a linear or branched alkylene group having 3 carbon atoms is more preferable from the viewpoint of obtaining a highly uniform composition with good reproducibility, from the viewpoint of obtaining a highly storage-stable composition with good reproducibility, from the viewpoint of obtaining a

composition that provides a highly uniform film with good reproducibility, and the like.

[0219]

Specific examples of the linear or branched alkyl group having 1 to 8 carbon atoms include, but are not limited to, a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group, an s-butyl group, a tertiary butyl group, an n-pentyl group, a 1-methyl-n-butyl group, a 2-methyl-n-butyl group, a 3-methyl-n-butyl group, a 1,1-dimethyl-n-propyl group, a 1,2-dimethyl-n-propyl group, a 2,2-dimethyl-n-propyl group, a 1-ethyl-n-propyl group, n-hexyl, a 1-methyl-n-pentyl group, a 2-methyl-n-pentyl group, a 3-methyl-n-pentyl group, a 4-methyl-n-pentyl group, a 1,1-dimethyl-n-butyl group, a 1,2-dimethyl-n-butyl group, a 1,3-dimethyl-n-butyl group, a 2,2-dimethyl-n-butyl group, a 2,3-dimethyl-n-butyl group, a 3,3-dimethyl-n-butyl group, a 1-ethyl-n-butyl group, a 2-ethyl-n-butyl group, a 1,1,2-trimethyl-n-propyl group, a 1,2,2-trimethyl-n-propyl group, a 1-ethyl-1-methyl-n-propyl group, and a 1-ethyl-2-methyl-n-propyl group.

Among them, a methyl group and an ethyl group are preferable, and a methyl group is more preferable from the viewpoint of obtaining a highly uniform composition with good reproducibility, from the viewpoint of obtaining a highly storage-stable composition with good

reproducibility, from the viewpoint of obtaining a composition that provides a highly uniform film with good reproducibility, and the like.

[0220]

Specific examples of the linear or branched alkyl group having 1 to 8 carbon atoms in the alkylacyl group in which the alkyl moiety is a linear or branched alkyl group having 1 to 8 carbon atoms include those same as the specific examples described above.

Among them, a methylcarbonyl group and an ethylcarbonyl group are preferable, and a methylcarbonyl group is more preferable from the viewpoint of obtaining a highly uniform composition with good reproducibility, from the viewpoint of obtaining a highly storage-stable composition with good reproducibility, from the viewpoint of obtaining a composition that provides a highly uniform film with good reproducibility, and the like.

[0221]

n^g is preferably 4 or less, more preferably 3 or less, still more preferably 2 or less, and most preferably 1 from the viewpoint of obtaining a highly uniform composition with good reproducibility, from the viewpoint of obtaining a highly storage-stable composition with good reproducibility, from the viewpoint of obtaining a composition that provides a highly uniform film with good

reproducibility, and the like.

[0222]

In Formula (G), preferably, at least one of R^{G2} or R^{G3} is a linear or branched alkyl group having 1 to 8 carbon atoms, more preferably, one of R^{G2} and R^{G3} is a linear or branched alkyl group having 1 to 8 carbon atoms, and the other is a hydrogen atom or an alkylacyl group in which the alkyl moiety is a linear or branched alkyl group having 1 to 8 carbon atoms from the viewpoint of obtaining a highly uniform composition with good reproducibility, from the viewpoint of obtaining a highly storage-stable composition with good reproducibility, from the viewpoint of obtaining a composition that provides a highly uniform film with good reproducibility, and the like.

[0223]

The content of the glycol-based solvent is preferably 50 mass% or more, more preferably 70 mass% or more, still more preferably 80 mass% or more, further preferably 90 mass% or more, and even more preferably 95 mass% or more with respect to the solvent contained in the release agent composition from the viewpoint of obtaining a highly uniform composition with good reproducibility, from the viewpoint of obtaining a highly storage-stable composition with good reproducibility, from the viewpoint of obtaining a composition that provides a highly uniform film with good

reproducibility, and the like.

In the release agent composition, the film constituent components are uniformly dispersed or dissolved, preferably dissolved in the solvent from the viewpoint of obtaining a highly uniform composition with good reproducibility, from the viewpoint of obtaining a highly storage-stable composition with good reproducibility, from the viewpoint of obtaining a composition that provides a highly uniform film with good reproducibility, and the like.

[0224]

The release agent composition can be produced by, for example, mixing the organic resin or the polynuclear phenol derivative, the solvent, and the crosslinking agent as necessary.

The mixing order is not particularly limited, and examples of a method capable of easily producing the release agent composition with good reproducibility include, but are not limited to, a method in which the organic resin or the polynuclear phenol derivative and the crosslinking agent are dissolved in the solvent at once and a method in which the organic resin or the polynuclear phenol derivative and a part of the crosslinking agent are dissolved in the solvent, the residue is separately dissolved in the solvent, and each of the obtained solutions is mixed together. When the release agent

composition is prepared, the components may be heated, as appropriate, as long as the components are not decomposed or altered.

In the present invention, for the purpose of removing foreign matter, a solvent, a solution, or the like to be used may be filtered using a filter or the like during the production of the release agent composition or after mixing all the components.

[0225]

The thickness of the release agent layer is not particularly limited and is usually 5 nm to 100 μm , 10 nm to 10 μm in an embodiment, 50 nm to 1 μm in another embodiment, and 100 nm to 700 nm in still another embodiment.

[0226]

A method for forming the release agent layer from the release agent composition is not particularly limited, and examples thereof include a method in which the release agent layer is formed by applying the release agent composition.

The coating method for the release agent composition is not particularly limited, but is usually a spin coating method.

The heating temperature of the applied release agent composition varies depending on the type and amount of the

release agent component contained in the release agent composition, the desired thickness of the release agent layer, and the like, and thus cannot be generally determined, but from the viewpoint of achieving a suitable release agent layer with good reproducibility, the heating temperature is 80°C or higher and 300°C or lower, and the heating time is appropriately determined usually in the range of 10 seconds to 10 minutes depending on the heating temperature. The heating temperature is preferably 100°C or higher and 280°C or lower, and more preferably 150°C or higher and 250°C or lower. The heating time is preferably 30 seconds or more and 8 minutes or less, and more preferably 1 minute or more and 5 minutes or less.

The heating can be performed using a hot plate, an oven, or the like.

[0227]

Hereinafter, an example of the configuration of the laminate of the first embodiment will be described with reference to the drawings.

Fig. 1 illustrates a schematic cross-sectional view of an example of a laminate of the first embodiment.

The laminate of Fig. 1 includes a semiconductor substrate 1, an adhesive layer 2, and a support substrate 4 in this order. That is, the adhesive layer 2 is provided between the semiconductor substrate 1 and the support

substrate 4. The adhesive layer 2 is in contact with the semiconductor substrate 1 and the support substrate 4.

[0228]

Hereinafter, another example of the configuration of the laminate of the first embodiment will be described with reference to the drawings.

Fig. 2 illustrates a schematic cross-sectional view of another example of the laminate of the first embodiment.

The laminate of Fig. 2 includes the semiconductor substrate 1, the adhesive layer 2, a release agent layer 3, and the support substrate 4 in this order.

The adhesive layer 2 and the release agent layer 3 are provided between the semiconductor substrate 1 and the support substrate 4. The adhesive layer 2 is in contact with the semiconductor substrate 1. The release agent layer 3 is in contact with the adhesive layer 2 and the support substrate 4.

[0229]

<<Method for Producing One Example of Laminate in First Embodiment>>

A method for producing a laminate will be described below with the laminate illustrated in Fig. 1 as an example of the laminate in the first embodiment.

An example of the laminate of the present invention can be produced, for example, by a method including the

following first step and second step.

First step: Step of applying an adhesive composition onto a semiconductor substrate to form an adhesive coating layer

Second step: Step of heating the adhesive coating layer to form an adhesive layer

[0230]

The coating method for the adhesive composition is not particularly limited, and is usually a spin coating method. A method for separately forming a coating film by a spin coating method or the like, forming a sheet-like coating film, and attaching the sheet-like coating film as an adhesive coating layer can be adopted.

The heating temperature of the applied adhesive composition varies depending on the type and amount of the adhesive component contained in the adhesive composition, whether or not a solvent is contained, the boiling point of the solvent to be used, the desired thickness of the adhesive layer, and the like, and thus cannot be generally determined, but the heating temperature is usually 80 to 150°C, and the heating time is usually 30 seconds to 5 minutes.

When the adhesive composition contains a solvent, the applied adhesive composition is usually heated.

The film thickness of an adhesive coating layer

obtained by applying an adhesive composition and heating the adhesive composition, as necessary, is usually about 5 to 500 μm , and finally, is appropriately determined to fall within the above-described range of the thickness of the adhesive layer.

[0231]

In the present invention, the laminate of the present invention can be obtained by applying a load in the thickness direction of the semiconductor substrate and the support substrate while performing heat treatment or decompression treatment or both thereof, and then performing post-heat treatment. The treatment conditions to be adopted, whether heat treatment, decompression treatment, or a combination of both, are appropriately determined taking into consideration various factors such as the type of adhesive composition, the film thickness, and the desired adhesive strength.

[0232]

The heat treatment is appropriately determined from the range of usually 20 to 160°C from the viewpoint of removing the solvent from the composition. In particular, from the viewpoint of suppressing or avoiding excessive curing and unnecessary alteration of the adhesive component (A), the heating temperature is preferably 150°C or lower, and more preferably 130°C or lower, and the heating time is

appropriately determined depending on the heating temperature and the type of the adhesive. However, from the viewpoint of reliably exhibiting suitable adhesion, the heating time is usually 30 seconds or longer, and preferably 1 minute or longer. From the viewpoint of suppressing alteration of the adhesive layer and other members, the heating time is usually 10 minutes or shorter, preferably 5 minutes or shorter.

[0233]

In the decompression treatment, the adhesive coating layers in contact with each other may be exposed to an atmospheric pressure of 10 to 10,000 Pa. The time for the decompression treatment is usually 1 to 30 minutes.

[0234]

The load in the thickness direction of the semiconductor substrate and the support substrate is not particularly limited as long as the load does not adversely affect the semiconductor substrate, the support substrate, and those layers therebetween, and can bring them into close contact with each other, but is usually within the range of 10 to 50,000 N.

[0235]

The temperature of the post-heating is preferably 120°C or higher from the viewpoint of achieving a sufficient curing rate and the like, and is preferably 260°C or lower

from the viewpoint of preventing alteration of the substrate and each layer, and the like.

The post-heating time is usually 1 minute or more, and preferably 5 minutes or more from the viewpoint of achieving suitable bonding of the substrate and the layer constituting the laminate, and is usually 180 minutes or less, and preferably 120 minutes or less from the viewpoint of suppressing or avoiding an adverse effect on each layer due to excessive heating, and the like.

The heating can be performed using a hot plate, an oven, or the like. When post-heating is performed using a hot plate, heating may be performed with either the semiconductor substrate or the support substrate of the laminate facing downward. Preferably, the post-heating is performed with the semiconductor substrate facing downward from the viewpoint of achieving suitable release with excellent reproducibility.

One object of the post-heat treatment is to achieve an adhesive layer as a more preferable self-standing film, and to suitably achieve, particularly, curing by a hydrosilylation reaction.

[0236]

Figs. 3A to 3C are views for describing an embodiment of production of the laminate.

First, a laminate in which an adhesive coating layer 2a

is formed on the semiconductor substrate 1 is prepared (Fig. 3A). This laminate can be obtained, for example, by applying the adhesive composition onto the semiconductor substrate 1, followed by heating.

Next, the laminate shown in Fig. 3A and the support substrate 4 are bonded to each other such that the adhesive coating layer 2a and the support substrate 4 are in contact with each other. Then, after a load is applied in the thickness direction between the semiconductor substrate 1 and the support substrate 4 under reduced pressure, a heating device (not shown; a hot plate) is disposed on the surface opposite to a surface of the semiconductor substrate 1 with which the adhesive coating layer 2a is in contact, and the adhesive coating layer 2a is heated and cured by the heating device to be converted into the adhesive layer 2 (Fig. 3B).

The laminate shown in Fig. 1 is obtained by the steps shown in Figs. 3A and 3B.

[0237]

<Second Embodiment>

The laminate including an electronic device layer is used for processing of the electronic device layer. While the electronic device layer is being processed, the electronic device layer is bonded to the support substrate. After the electronic device layer is processed, the

electronic device layer is separated from the support substrate.

[0238]

<<Electronic Device Layer>>

The electronic device layer refers to a layer having an electronic device, and in the present invention, the electronic device layer refers to a layer in which a plurality of semiconductor chip substrates are embedded in a sealing resin, that is, a layer including a plurality of semiconductor chip substrates and a sealing resin disposed between the semiconductor chip substrates.

Here, the "electronic device" means a member constituting at least a part of an electronic component. The electronic device is not particularly limited, and can be one in which various mechanical structures and circuits are formed on the surface of a semiconductor substrate. The electronic device is preferably a composite of a member made of metal or a semiconductor and a resin that seals or insulates the member. The electronic device may be one in which a rewiring layer, which will be described below, and/or a semiconductor element or other elements are sealed or insulated with a sealing material or an insulating material, and has a single-layer or multi-layer structure.

[0239]

<<Support Substrate>>

As the support substrate, those similar to those described in the section of <<Support Substrate>> above of <First Embodiment> above are exemplified.

[0240]

<<Release Agent Layer>>

The release agent layer is formed using the release agent composition for release by irradiation with light of the present invention described above.

The detailed description of the release agent layer is as described in the section of <<Release Agent Layer>> above of <First Embodiment> above.

[0241]

<<Adhesive Layer>>

The adhesive layer is formed using the adhesive composition described above.

The detailed description of the adhesive layer is as described in the section of <<Adhesive Layer>> above of <First Embodiment> above.

[0242]

Hereinafter, an example of the configuration of the laminate of the second embodiment will be described with reference to the drawings.

The laminate in Fig. 4 includes a support substrate 24, an adhesive layer 22, and an electronic device layer 26 in this order.

The electronic device layer 26 includes a plurality of semiconductor chip substrates 21 and a sealing resin 25 which is a sealing material disposed between the semiconductor chip substrates 21.

The adhesive layer 22 is provided between the electronic device layer 26 and the support substrate 24. The adhesive layer 22 is in contact with the electronic device layer 26 and the support substrate 24.

[0243]

Fig. 5 shows a schematic cross-sectional view of another example of the laminate of the second embodiment.

The laminate of Fig. 5 includes the support substrate 24, a release agent layer 23, the adhesive layer 22, and the electronic device layer 26 in this order.

The electronic device layer 26 includes a plurality of semiconductor chip substrates 21 and a sealing resin 25 which is a sealing material disposed between the semiconductor chip substrates 21.

The adhesive layer 22 and the release agent layer 23 are provided between the electronic device layer 26 and the support substrate 24. The adhesive layer 22 is in contact with the electronic device layer 26. The release agent layer 23 is in contact with the adhesive layer 22 and the support substrate 24.

[0244]

<<Method for Producing One Example of Laminate in
Second Embodiment>>

A method for producing a laminate will be described below with the laminate shown in Fig. 4 as an example of the laminate in the second embodiment.

The laminate of the present invention can be produced, for example, by a method including the following Steps 1 to 4.

Step 1: Step of coating a surface of the support substrate with the adhesive composition to form an adhesive coating layer (as necessary, further heating is performed to form an adhesive layer)

Step 2: Step of placing a semiconductor chip substrate on the adhesive coating layer or the adhesive layer, and bonding the semiconductor chip substrate to the adhesive coating layer or the adhesive layer while performing at least one of heat treatment or decompression treatment

Step 3: Step of curing the adhesive coating layer by post-heat treatment to form an adhesive layer

Step 4: Step of encapsulating the semiconductor chip substrate fixed onto the adhesive layer using an encapsulating resin

To describe step 2 in more detail, for example, there is the following step (i) of the embodiment.

(i) The semiconductor chip substrate is placed on the

adhesive coating layer or the adhesive layer, and while at least one of the heat treatment and the decompression treatment is performed, a load is applied in the thickness direction of the semiconductor chip substrate and the support substrate to bring the semiconductor chip substrate and the support substrate into close contact with each other, and the semiconductor chip substrate is bonded to the adhesive coating layer or the adhesive layer.

[0245]

Step 3 may be performed after the semiconductor chip substrate in step 2 is bonded to the adhesive coating layer, or may be performed in combination with step 2. For example, by placing the semiconductor chip substrate on the adhesive coating layer and heating and curing the adhesive coating layer while applying a load in the thickness direction of the semiconductor chip substrate and the support substrate, adhesion between the semiconductor chip substrate and the adhesive coating layer and curing from the adhesive coating layer to the adhesive layer may be performed together, and the adhesive layer and the semiconductor chip substrate may be bonded to each other.

In addition, step 3 may be performed before step 2, and the semiconductor chip substrate may be placed on the adhesive layer, and while a load is applied in the thickness direction of the semiconductor chip substrate and

the support substrate, the adhesive layer and the semiconductor chip substrate may be bonded to each other.

[0246]

The coating method, the heating temperature of the applied adhesive composition, the heating means and the like are as described in <<Method for Producing One Example of Laminate in First Embodiment>> above of <First Embodiment> above.

[0247]

Hereinafter, the procedure of the method for producing a laminate of the second embodiment will be described in more detail with reference to the drawings. In this production method, the laminate shown in Fig. 4 is produced.

As shown in Fig. 6A, an adhesive coating layer 22' made of the adhesive composition is formed on the support substrate 24. At that time, the adhesive coating layer 22' may be heated to form an adhesive layer 22.

Next, as shown in Fig. 6B, the semiconductor chip substrate 21 is placed on the adhesive layer 22 or the adhesive coating layer 22', and while at least one of the heat treatment and the decompression treatment is performed, a load is applied in the thickness direction of the semiconductor chip substrate 21 and the support substrate 24 to bring the semiconductor chip substrate 21

and the support substrate 24 into close contact with each other, and the semiconductor chip substrate 21 is bonded to the adhesive layer 22 or the adhesive coating layer 22'. When the semiconductor chip substrate 21 is bonded to the adhesive coating layer 22', the adhesive coating layer 22' is cured by post-heat treatment to form the adhesive layer 22, and the semiconductor chip substrate 21 is fixed to the adhesive layer 22.

Next, as shown in Fig. 6C, the semiconductor chip substrate 21 fixed onto the adhesive layer 22 is sealed using the sealing resin 25. In Fig. 6C, the plurality of semiconductor chip substrates 21 temporarily bonded onto the support substrate 24 via the adhesive layer 22 are sealed with the sealing resin 25. The electronic device layer 26, which includes the semiconductor chip substrate 21 and the sealing resin 25 between the semiconductor chip substrates 21, is formed on the adhesive layer 22, and as described above, the electronic device layer 26 is a base material layer in which the plurality of semiconductor chip substrates are embedded in the sealing resin.

[0248]

<<<Sealing Step>>>

The semiconductor chip substrate 21 is sealed using a sealing material.

As the sealing material for sealing the semiconductor

chip substrate 21, a member capable of insulating or sealing a member made of metal or a semiconductor is used.

In the present invention, for example, a resin composition (sealing resin) is used as the sealing material. The type of the sealing resin is not particularly limited as long as the sealing resin can seal and/or insulate metal or a semiconductor, and for example, an epoxy-based resin or a silicone-based resin is preferably used.

The sealing material may contain, in addition to the resin component, other components such as a filler. Examples of the filler include spherical silica particles.

In the sealing step, for example, the sealing resin heated to 130 to 170°C is supplied onto the adhesive layer 22 to cover the semiconductor chip substrate 21 while maintaining a high viscosity state, and is compression-molded to form a layer containing the sealing resin 25 on the adhesive layer 22. At this time, the temperature condition is, for example, 130 to 170°C. In addition, the pressure applied to the semiconductor chip substrate 21 is, for example, 50 to 500 N/cm².

[0249]

(Method for Producing Processed Semiconductor Substrate or Processed Electronic Device Layer)

When the laminate according to the present invention is

used, a method for producing a processed semiconductor substrate or a method for producing a processed electronic device layer can be provided.

In the "method for producing a processed semiconductor substrate", the laminate described in the section of <First Embodiment> above of the (Laminate) above is used. In addition, in the "method for producing a processed electronic device layer", the laminate described in the section of <Second Embodiment> above of the (Laminate) above is used.

The "method for producing a processed semiconductor substrate" will be described in <Third Embodiment> below, and the "method for producing a processed electronic device layer" will be described in <Fourth Embodiment> below.

[0250]

<Third Embodiment>

The method for producing a processed semiconductor substrate of the present invention includes the following step 5A and the following step 6A. The method for producing a processed electronic device layer may further include the following step 7A.

Here, the step 5A is a step of processing the semiconductor substrate in the laminate described in the section of <First Embodiment> above.

In addition, the step 6A is a step of separating the

processed semiconductor substrate in the step 5A and the support substrate from each other.

In addition, the step 7A is a step of cleaning the processed semiconductor substrate after step 6A.

[0251]

The processing performed on the semiconductor substrate in the step 5A is, for example, processing on the side opposite to the circuit surface of the wafer, and includes thinning of the wafer by polishing the back surface of the wafer. Thereafter, for example, a through-silicon via (TSV) or the like is formed, and the thinned wafer is then released from the support substrate to form a laminate of wafers which are three-dimensionally mounted. In addition, for example, before and after that, a wafer back surface electrode and the like are also formed. Heat of approximately 250 to 350°C is applied to thinning of a wafer and a TSV process in a state of being bonded to the support substrate. The laminate of the present invention ordinarily includes the adhesive layer to provide heat resistance to the load.

The processing is not limited to the above-described processing, and includes, for example, implementation of a process of mounting a semiconductor component in a case where the support substrate is temporarily bonded in order to support a base material for mounting the semiconductor

component.

[0252]

A method for separating (releasing) the semiconductor substrate and the support substrate from each other in the step 6A is not particularly limited.

Examples thereof include a method in which the semiconductor substrate and the support substrate are mechanically released with a tool having a sharp portion (so-called debonder). Specifically, for example, the sharp portion is inserted between the semiconductor substrate and the support substrate, and the semiconductor substrate and the support substrate are then separated from each other.

In addition, when the laminate includes the release agent layer, the method for separating (releasing) the semiconductor substrate and the support substrate from each other in the step 6A may be releasing or the like in which the release agent layer is irradiated with light, and the semiconductor substrate and the support substrate are then torn off.

By irradiating the release agent layer with light from the support substrate side, the release agent layer is altered (for example, the release agent layer is separated or decomposed) as described above, and thereafter, for example, one of the substrates is pulled up, and the semiconductor substrate and the support substrate can be

easily separated from each other.

[0253]

The release agent layer is not necessarily irradiated with light over the entire region of the release agent layer. Even when the region irradiated with light and the region not irradiated with light are mixed, the semiconductor substrate and the support substrate can be separated from each other by a slight external force such as pulling up of the support substrate as long as the release agent layer as a whole has sufficiently improved releasing ability. The ratio and positional relationship between the region irradiated with light and the region not irradiated with light vary depending on the type and specific composition of the adhesive to be used, the thickness of the adhesive layer, the thickness of the adhesive layer, the thickness of the release agent layer, the intensity of light to be emitted, and the like, but those skilled in the art can appropriately set conditions without requiring an excessive test. For such circumstances, according to the method for producing a processed semiconductor substrate of the present invention, for example, in a case where the support substrate of the laminate to be used is light-transmissive, it is possible to shorten the irradiation time with light when release is performed by irradiation with light from the support

substrate side, and as a result, not only improvement in throughput can be expected, but also physical stress and the like required for release can be avoided, and the semiconductor substrate and the support substrate can be easily and efficiently separated from each other only by irradiation with light.

The irradiation amount of light required for release is usually 50 to 3,000 mJ/cm². The irradiation time is appropriately determined depending on the wavelength and the irradiation amount.

[0254]

The wavelength of light used for release is preferably, for example, a wavelength of 250 to 600 nm, and more preferably a wavelength of 250 to 370 nm. A more suitable wavelength is 308 nm, 343 nm, 355 nm, 365 nm, or 532 nm. The irradiation amount of light required for release is an irradiation amount that can cause suitable alteration, for example, decomposition of the specific compound and polymer.

The light used for release may be laser light or non-laser light emitted from a light source such as an ultraviolet lamp.

[0255]

The substrate can be cleaned by spraying a cleaning agent composition onto the surface of at least one of the

separated semiconductor substrate and the support substrate, or immersing the separated semiconductor substrate or the support substrate in a cleaning agent composition.

In addition, the surface of the processed semiconductor substrate or the like may be cleaned using a removal tape or the like.

As an example of cleaning the substrate, the step 7A of cleaning the processed semiconductor substrate may be performed after the step 6A.

Examples of the cleaning agent composition to be used for cleaning include the following.

[0256]

The cleaning agent composition usually contains a solvent.

Examples of the solvent include lactones, ketones, polyhydric alcohols, compounds having an ester bond, derivatives of polyhydric alcohols, cyclic ethers, esters, and aromatic organic solvents.

Examples of the lactones include γ -butyrolactone.

Examples of the ketones include acetone, methyl ethyl ketone, cyclohexanone, methyl-n-pentyl ketone, methyl isopentyl ketone, and 2-heptanone.

Examples of the polyhydric alcohols include ethylene glycol, diethylene glycol, propylene glycol, and

dipropylene glycol.

Examples of the compound having an ester bond include ethylene glycol monoacetate, diethylene glycol monoacetate, propylene glycol monoacetate, and dipropylene glycol monoacetate.

Examples of the derivatives of polyhydric alcohols include monoalkyl ethers such as monomethyl ether, monoethyl ether, monopropyl ether, and monobutyl ether of the polyhydric alcohols or the compounds having an ester bond, or compounds having an ether bond such as monophenyl ether. Among them, propylene glycol monomethyl ether acetate (PGMEA) and propylene glycol monomethyl ether (PGME) are preferable.

Examples of the cyclic ethers include dioxane.

Examples of the esters include methyl lactate, ethyl lactate (EL), methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate, and ethyl ethoxypropionate.

Examples of the aromatic organic solvents include anisole, ethyl benzyl ether, cresyl methyl ether, diphenyl ether, dibenzyl ether, phenetol, butyl phenyl ether, ethylbenzene, diethylbenzene, pentylbenzene, isopropylbenzene, toluene, xylene, cymene, and mesitylene.

These can be used alone or in combination with two or more thereof.

Among them, propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monomethyl ether (PGME), cyclohexanone, and ethyl lactate (EL) are preferable.

[0257]

In addition, a mixed solvent obtained by mixing PGMEA and a polar solvent is also preferable. The blending ratio (mass ratio) may be appropriately determined in consideration of compatibility between PGMEA and the polar solvent or the like, and is preferably in the range of 1:9 to 9:1, more preferably 2:8 to 8:2.

For example, when EL is blended as the polar solvent, the mass ratio of PGMEA:EL is preferably 1:9 to 9:1, more preferably 2:8 to 8:2. In addition, when PGME is blended as the polar solvent, the mass ratio of PGMEA:PGME is preferably 1:9 to 9:1, more preferably 2:8 to 8:2, still more preferably 3:7 to 7:3. In addition, when PGME and cyclohexanone are blended as the polar solvent, the mass ratio of PGMEA:(PGME + cyclohexanone) is preferably 1:9 to 9:1, more preferably 2:8 to 8:2, still more preferably 3:7 to 7:3.

[0258]

The cleaning agent composition may contain or may not contain a salt, but it is preferable that the cleaning agent composition does not contain a salt from the viewpoint of enhancing versatility in processing a

semiconductor substrate using a laminate, and suppressing cost.

[0259]

An example of the case where the cleaning agent composition contains a salt includes a cleaning agent composition containing a quaternary ammonium salt and a solvent.

The quaternary ammonium salt is composed of a quaternary ammonium cation and an anion, and is not particularly limited as long as the quaternary ammonium salt is used for this type of application.

Such quaternary ammonium cations typically include tetra(hydrocarbon)ammonium cations. On the other hand, examples of an anion paired therewith include, but are not limited to, a hydroxide ion (OH^-); a halogen ion such as a fluorine ion (F^-), a chlorine ion (Cl^-), a bromine ion (Br^-), and an iodine ion (I^-); a tetrafluoroborate ion (BF_4^-); or a hexafluorophosphate ion (PF_6^-).

[0260]

The quaternary ammonium salt is preferably a halogen-containing quaternary ammonium salt, and more preferably a fluorine-containing quaternary ammonium salt.

In the quaternary ammonium salt, the halogen atom may be contained in the cation or the anion, and is preferably contained in the anion.

[0261]

In a preferred embodiment, the fluorine-containing quaternary ammonium salt is tetra(hydrocarbon)ammonium fluoride.

Specific examples of the hydrocarbon group in tetra(hydrocarbon)ammonium fluoride include an alkyl group having 1 to 20 carbon atoms, an alkenyl group having 2 to 20 carbon atoms, an alkynyl group having 2 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms.

In a more preferred embodiment, the tetra(hydrocarbon)ammonium fluoride includes tetraalkylammonium fluoride.

Specific examples of tetraalkylammonium fluoride include, but are not limited to, tetramethylammonium fluoride, tetraethylammonium fluoride, tetrapropylammonium fluoride, and tetrabutylammonium fluoride. Among them, tetrabutylammonium fluoride is preferable.

[0262]

As the quaternary ammonium salt such as tetra(hydrocarbon)ammonium fluoride, a hydrate may be used. In addition, the quaternary ammonium salts such as tetra(hydrocarbon)ammonium fluoride may be used alone or in combination of two or more thereof.

The amount of the quaternary ammonium salt is not particularly limited as long as the quaternary ammonium

salt dissolves in the solvent contained in the cleaning agent composition, but is usually 0.1 to 30 mass% with respect to the cleaning agent composition.

[0263]

When the cleaning agent composition contains a salt, the solvent to be used in combination is not particularly limited as long as the solvent is used for this type of application and dissolves a salt such as a quaternary ammonium salt, but from the viewpoint of obtaining a cleaning agent composition having excellent cleanability with good reproducibility, the viewpoint of obtaining a cleaning agent composition having excellent uniformity by dissolving a salt such as a quaternary ammonium salt well, and the like, the cleaning agent composition preferably contains one or two or more amide-based solvents.

[0264]

Suitable examples of the amide-based solvents include an acid amide derivative represented by Formula (Z).

[Chem. 31]



[0265]

In the formula, R^0 represents an ethyl group, a propyl group or an isopropyl group, and is preferably an ethyl group or an isopropyl group, and more preferably an ethyl group. R^A and R^B each independently represent an alkyl group having 1 to 4 carbon atoms. The alkyl group having 1 to 4 carbon atoms may be linear, branched, or cyclic, and specific examples thereof include a methyl group, an ethyl group, a propyl group, an isopropyl group, a cyclopropyl group, a n-butyl group, an isobutyl group, a s-butyl group, a t-butyl group, and a cyclobutyl group. Among them, R^A and R^B are preferably a methyl group or an ethyl group, more preferably both are a methyl group or an ethyl group, and still more preferably both are a methyl group.

[0266]

Examples of the acid amide derivative represented by Formula (Z) include N,N-dimethylpropionamide, N,N-diethylpropionamide, N-ethyl-N-methylpropionamide, N,N-dimethylbutyramide, N,N-diethylbutyramide, N-ethyl-N-methylbutyramide, N,N-dimethylisobutyramide, N,N-diethylisobutyramide, or N-ethyl-N-methylisobutyramide. Among them, N,N-dimethylpropionamide and N,N-dimethylisobutyramide are particularly preferable, and N,N-dimethylpropionamide is more preferable.

[0267]

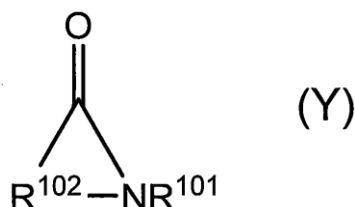
The acid amide derivative represented by Formula (Z)

may be synthesized by a substitution reaction between a corresponding carboxylic acid ester and an amine, or a commercially available product may be used.

[0268]

Another example of the preferable amide-based solvents includes a lactam compound represented by Formula (Y).

[Chem. 32]



[0269]

In Formula (Y), R^{101} represents a hydrogen atom or an alkyl group having 1 to 6 carbon atoms, and R^{102} represents an alkylene group having 1 to 6 carbon atoms. Specific examples of the alkyl group having 1 to 6 carbon atoms include a methyl group, an ethyl group, an n-propyl group, and an n-butyl group, and specific examples of the alkylene group having 1 to 6 carbon atoms include, but are not limited to, a methylene group, an ethylene group, a trimethylene group, a tetramethylene group, a pentamethylene group, and a hexamethylene group.

[0270]

Specific examples of the lactam compound represented by Formula (Y) include an α -lactam compound, a β -lactam

compound, a γ -lactam compound, and a δ -lactam compound, and these compounds can be used alone or in combination of two or more thereof.

[0271]

In a preferred embodiment, the lactam compound represented by Formula (Y) contains 1-alkyl-2-pyrrolidone (N-alkyl- γ -butyrolactam), in a more preferred embodiment, contains N-methylpyrrolidone (NMP) or N-ethylpyrrolidone (NEP), and in a still more preferred embodiment, contains N-methylpyrrolidone (NMP).

[0272]

The cleaning agent composition used in the present invention may contain water as the solvent, but usually, only an organic solvent is intended to be used as the solvent, for example, from the viewpoint of avoiding corrosion of the substrates and the like. In this case, it is not denied that hydrated water of the salt or trace amounts of water contained in the organic solvent is contained in the cleaning agent composition. The water content of the cleaning agent composition used in the present invention is usually 5 mass% or less.

[0273]

The constituent elements and method elements related to the above-described steps of the method for producing a processed semiconductor substrate of the present invention

may be variously changed without departing from the gist of the present invention.

The method for producing a processed semiconductor substrate of the present invention may include steps other than the above-described steps.

[0274]

In one example of the releasing method of the present invention, when the semiconductor substrate or the support substrate of the laminate of the present invention is light-transmissive, the semiconductor substrate and the support substrate of the laminate are separated from each other by irradiating the release agent layer with light from the semiconductor substrate side or the support substrate side.

In an example of the laminate of the present invention, since the semiconductor substrate and the support substrate are temporarily bonded to each other by the adhesive layer and the release agent layer to be suitably releasable, for example, when the support substrate is light-transmissive, the semiconductor substrate and the support substrate can be easily separated from each other by irradiating the release agent layer with light from the support substrate side of the laminate. Usually, release is performed after the semiconductor substrate of the laminate is processed.

[0275]

An example of the third embodiment will be described with reference to Figs. 7A to 7D. This example is an example of production of a thinned semiconductor substrate.

First, a laminate is prepared (Fig. 7A). This laminate is the same laminate as the laminate shown in Figs. 1 and 3B.

Next, the surface of the semiconductor substrate 1 opposite to a surface in contact with the adhesive layer 2 is polished using a polishing apparatus (not shown) to thin the semiconductor substrate 1 (Fig. 7B). Note that a through electrode may be formed on the thinned semiconductor substrate 1.

Next, the thinned semiconductor substrate 1 and the support substrate 4 are separated from each other using a peeling apparatus (not shown) (Fig. 7C).

Then, the thinned semiconductor substrate 1 is obtained (Fig. 7D).

Here, the residue of the adhesive layer 2 may remain on the thinned semiconductor substrate 1. Accordingly, it is preferable to clean the thinned semiconductor substrate 1 using the cleaning agent composition to remove the residue of the adhesive layer 2 from the semiconductor substrate 1.

[0276]

<Fourth Embodiment>

The method for producing a processed electronic device

layer of the present invention includes the following step 5B and the following step 6B. The method for producing a processed electronic device layer may further include the following step 7B.

Here, the step 5B is a step of processing the electronic device layer in the laminate described in the section of <Second Embodiment> above.

In addition, the step 6B is a step of separating the electronic device layer processed in the step 5B from the support substrate.

In addition, the step 7B is a step of cleaning the processed electronic device layer after the step 6B.

Hereinafter, a specific example of the fourth embodiment will be described with reference to Figs. 8A to 8F.

[0277]

Examples of the processing performed on the electronic device layer in the step 5B include a grinding step and a wiring layer formation step.

[0278]

<<Grinding Step>>

The grinding step is a step of grinding the resin part of the layer of the sealing resin 25 in the electronic device layer 26 such that a part of the semiconductor chip substrate 21 is exposed.

For example, as shown in Fig. 8B, the sealing resin part is ground by grinding the layer of the sealing resin 25 of the laminate shown in Fig. 8A until the layer has a thickness substantially equal to that of the semiconductor chip substrate 21. Note that the laminate shown in Fig. 8A is the same laminate as the laminate shown in Fig. 4 and Fig. 6C.

[0279]

<<Wiring Layer Formation Step>>

The wiring layer formation step is a step of forming a wiring layer on the exposed semiconductor chip substrate 21 after the grinding step.

In Fig. 8C, a wiring layer 28 is formed on the electronic device layer 26 including a layer of the semiconductor chip substrate 21 and the sealing resin 25.

The wiring layer 28 is also called a redistribution layer (RDL), and is a thin-film wiring body constituting wiring connected to a substrate, and may have a single-layer or multi-layer structure. The wiring layer may be, but is not limited to, one in which wiring is formed of a conductor (for example, metals such as aluminum, copper, titanium, nickel, gold, and silver, and alloys such as a silver-tin alloy) between dielectrics (for example, silicon oxide (SiO_x) or a photosensitive resin such as photosensitive epoxy).

Examples of the method for forming the wiring layer 28 include the following methods.

First, a dielectric layer of silicon oxide (SiO_x), a photosensitive resin, or the like is formed on the layer of the sealing resin 25. The dielectric layer made of silicon oxide can be formed by, for example, a sputtering method, a vacuum vapor deposition method, or the like. The dielectric layer made of a photosensitive resin can be formed by coating the layer of the sealing resin 25 with a photosensitive resin by a method such as spin coating, dipping, roller blade, spray coating, or slit coating.

Subsequently, wiring is formed on the dielectric layer with a conductor such as metal. As a method for forming the wiring, for example, known semiconductor process techniques such as lithography processing such as photolithography (resist lithography) or etching processing can be used. Examples of such lithography processing include lithography processing using a positive resist material and lithography processing using a negative resist material.

In the method for producing a laminate according to a fourth embodiment, a bump can be further formed or an element can be mounted on the wiring layer 28. The element can be mounted on the wiring layer 28 using, for example, a chip mounter or the like.

The laminate according to the fourth embodiment may be a laminate prepared in a process based on a fan-out-type technology in which a terminal provided on a semiconductor chip substrate is mounted on a wiring layer extending outside a chip area.

[0280]

In the step 6B, examples of the method for separating (releasing) the electronic device layer and the support substrate include, but are not limited to, a method for mechanical releasing with a tool having a sharp portion, a method for releasing by pulling apart between the support and the electronic device layer, and the like.

When the laminate includes the release agent layer, the release agent layer is altered (for example, the release agent layer is separated or decomposed) as described above by, for example, irradiating the release agent layer with light from the support substrate side, and thereafter, for example, one of the substrates is pulled up, and the electronic device layer and the support substrate can be easily separated from each other.

[0281]

Figs. 8D and 8E are schematic cross-sectional views for describing a separation method for the laminate, and Fig. 8F is a schematic cross-sectional view for describing a cleaning method after separation of the laminate. One

embodiment of the method for producing a semiconductor package (electronic component) can be described with reference to Figs. 8D to 8F.

The step of separating the laminate is a step of separating the electronic device layer 26 and the support substrate 24 using a peeling apparatus (not shown) as shown in Figs. 8D and 8E.

[0282]

The substrate can be cleaned by spraying the cleaning agent composition onto the surface of at least one of the separated electronic device layer and the support substrate, or immersing the separated electronic device layer or the support substrate in the cleaning agent composition.

In addition, the surface of the processed electronic device layer or the like may be cleaned using a removal tape or the like.

For example, in Fig. 8E, the adhesive layer 22 is bonded to the electronic device layer 26 after the separation step, but the adhesive layer 22 can be removed by decomposing the adhesive layer 22 using a cleaning agent composition such as an acid or an alkali. By removing the adhesive layer, a processed electronic device layer (electronic component) as shown in Fig. 8F can be suitably obtained.

[0283]

The constituent elements and method elements related to the above-described steps of the method for producing a processed electronic device layer of the present invention may be variously changed without departing from the gist of the present invention.

The method for producing a processed electronic device layer of the present invention may include steps other than the above-described steps.

Examples

[0284]

Hereinafter, the present invention will be more specifically described with reference to Examples, but the present invention is not limited to the following Examples. The apparatus used is as follows.

[0285]

[Apparatus]

(1) Planetary centrifugal mixer: ARE-500, manufactured by Thinky Corporation

(2) Viscometer: TV-35H, manufactured by Toki Sangyo Co., Ltd.

(3) Automatic titrator: GT-200, manufactured by Mitsubishi Chemical Analytech Co., Ltd.

(4) Vacuum bonding apparatus: XBS-300 manufactured by

SUSS MicroTec SE

(5) Peeling apparatus: Manual debonder manufactured by
SUSS MicroTec SE
[0286]

[1] Preparation of Adhesive Composition

[Example 1]

Into a 600 mL stirring container dedicated to a stirrer, 61.29 g of an MQ resin (manufactured by Wacker Chemie AG) containing a polysiloxane and a vinyl group as the polyorganosiloxane (a1), 10.40 g of a SiH group-containing linear polydimethylsiloxane having a viscosity of 100 mPa·s (manufactured by Wacker Chemie AG) as the polyorganosiloxane (a2), 6.48 g of a vinyl group-containing linear polydimethylsiloxane having a viscosity of 70 mPa·s (manufactured by Wacker Chemie AG) as the polyorganosiloxane (a3), 0.09 g of 1-ethynylcyclohexanol (manufactured by Wacker Chemie AG) as the polymerization inhibitor (a4), 0.09 g of 1,1-diphenyl-2-propyn-1-ol (manufactured by Tokyo Chemical Industry Co., Ltd.) as the polymerization inhibitor (a5), 0.01 g of a platinum catalyst (manufactured by Wacker Chemie AG) as the platinum group metal-based catalyst (a6), 13.98 g of p-menthane (manufactured by Tokyo Chemical Industry Co., Ltd.) as a solvent, and 3.83 g of SF-8411 (manufactured by Dow Toray Co., Ltd.) and 3.83 g of PMM-1043 (manufactured by Gelest,

Inc.) as the component (B) were added, and the mixture was stirred with a stirrer for 5 minutes. Finally, the obtained mixture was filtered through a 300-mesh nylon filter to produce an adhesive composition 1.

[0287]

[Examples 2 to 4 and Comparative Example 1]

Adhesive compositions 2 to 5 were prepared in the same manner as in Example 1. The compositional ratios of the respective adhesive compositions are shown in Table 1. Since different materials may be used depending on the composition with respect to the component (B), the names and added amounts thereof are shown. In addition, the two types of the component (B) are described as (B)-1 and (B)-2, respectively.

[0288]

[Table 1]

	Adhesive composition	(a1)	(a2)	(a3)	(a4)	(a5)	(a6)	p-Menthane	Component (B)-1		Component (B)-2	
		(g)	(g)	(g)	(g)	(g)	(g)		Name	(g)	Name	(g)
Example 1	1	61.29	10.40	6.48	0.09	0.09	0.01	13.98	SF-8411	3.83	PMM-1043	3.83
Example 2	2	61.29	10.40	6.48	0.09	0.09	0.01	13.98	X-22-343	3.83	PMM-1043	3.83
Example 3	3	61.29	10.40	6.48	0.09	0.09	0.01	13.98	KF-1001	3.83	PMM-1043	3.83
Example 4	4	61.29	10.40	6.48	0.09	0.09	0.01	13.98	EMS-622	3.83	PMM-1043	3.83
Comparative Example 1	5	61.29	10.40	6.48	0.09	0.09	0.01	13.98	TSF-4730	3.83	PMM-1043	3.83

[0289]

The details of the component (B)-1 and the component

(B)-2 in Table 1 are as follows.

*1 SF-8411: Epoxy group-containing polyorganosiloxane, manufactured by Dow Toray Co., Ltd.

*2 X-22-343: Epoxy group-containing polyorganosiloxane, manufactured by Shin-Etsu Chemical Co., Ltd.

*3 KF-1001: Epoxy group-containing polyorganosiloxane, manufactured by Shin-Etsu Chemical Co., Ltd.

*4 EMS-622: Epoxy group-containing polyorganosiloxane, manufactured by Gelest Inc.

*5 TSF4730: Epoxy group-containing polyorganosiloxane, manufactured by Momentive Performance Materials Inc.

*6 PMM-1043: Phenyl group-containing polyorganosiloxane having a viscosity of 30,000 mPa·s, manufactured by Gelest Inc.

[0290]

[2] Measurement of Physical Properties of Release Agent Component

With respect to the epoxy group-containing polyorganosiloxane of the release agent component (B) used for preparation of the adhesive composition, the viscosity at 25°C was measured using a viscometer. In addition, the epoxy value was measured using an automatic titrator. Specifically, the epoxy value was measured as follows.

A titration sample was prepared by adding 30 ml of a diluent having an acetone/acetic acid/tetraethylammonium

bromide=750/750/105 (weight ratio) to 0.25 g of the epoxy group-containing polyorganosiloxane. As the titrant, a 0.1 mol/l perchloric acid-acetic acid standard solution was used.

The results are shown in Table 2.

[0291]

[Table 2]

	Adhesive composition	Epoxy Group-Containing Polyorganosiloxane		
		Type	Viscosity (mPa)	Epoxy value (mol/kg)
Example 1	1	SF-8411	8000	0.15
Example 2	2	X-22-343	25	1.90
Example 3	3	KF-1001	13000	0.11
Example 4	4	EMS-622	200	0.35
Comparative Example 1	5	TSF-4730	15000	0.02

[0292]

[3] Preparation of Laminate and Confirmation of Releasability

Each obtained adhesive composition was spin-coated onto a 300 mm silicon wafer (thickness: 775 μm) as a substrate on the device side so that the film thickness in the finally obtained laminate was 60 μm , and was then heat-treated at 120°C for 1 minute to form an adhesive coating layer on the silicon wafer serving as the semiconductor substrate. As a substrate on the carrier side, a 301 mm glass wafer (EAGLE-XG, manufactured by Corning Incorporated, thickness: 700 μm) was used.

Then, using a bonding apparatus, the glass wafer and the silicon wafer were bonded with the adhesive coating layer interposed therebetween, and the resulting structure was then subjected to post-heat treatment at 200°C for 10 minutes to prepare a laminate. In addition, bonding was performed at a temperature of 23°C and under a reduced pressure of 1,500 Pa. Note that laminates were manufactured in as many numbers as necessary.

Thereafter, peeling was performed using a peeling apparatus to confirm releasability. At the time of peeling, a scraper replacement blade (manufactured by ESCO Co., Ltd., blade thickness: 0.2 mm) was mounted on the tip of a Newton meter, and the replacement blade was inserted, parallel to the substrate, into the adhesive layer bonding the device substrate and the carrier substrate to initiate peeling. In addition, after the replacement blade was inserted, it was confirmed whether peeling could be easily performed by lifting the glass substrate on the carrier side. A case in which peeling was easily possible was rated as "o", and a case in which peeling was impossible was rated as "x". The results are shown in Table 3.

[0293]

[Table 3]

	Adhesive composition	Release agent component	Releasability
Example 1	1	SF-8411	o
Example 2	2	X-22-343	o

Example 3	3	KF-1001	○
Example 4	4	EMS-622	○
Comparative Example 1	5	TSF-4730	×

In the adhesive composition 5 in which the release agent component (B)-1 having a low epoxy value was used, peeling was impossible. The other adhesive compositions exhibited good releasability.

Reference Signs List

[0294]

- 1 Semiconductor substrate
- 2 Adhesive layer
- 2a Adhesive coating layer
- 3 Release agent layer
- 4 Support substrate
- 21 Semiconductor chip substrate
- 22 Adhesive layer
- 22' Adhesive coating layer
- 23 Release agent layer
- 24 Support substrate
- 25 Sealing resin
- 26 Electronic device layer
- 28 Wiring layer

CLAIMS

[claim 1] An adhesive composition comprising
two or more types of release agent components,
wherein one of the two or more types of release agent
components is an epoxy group-containing polyorganosiloxane
having an epoxy value of more than 0.02 mol/kg.

[claim 2] The adhesive composition according to claim 1,
wherein the epoxy group-containing polyorganosiloxane has
an epoxy value of 3.0 mol/kg or less.

[claim 3] The adhesive composition according to claim 1,
wherein one of the two or more types of release agent
components is a polyorganosiloxane other than the epoxy
group-containing polyorganosiloxane.

[claim 4] The adhesive composition according to claim 3,
wherein a mass ratio (EPOS:POS) of the epoxy group-
containing polyorganosiloxane (EPOS) to the
polyorganosiloxane (POS) is 0.2:1 to 1:0.2.

[claim 5] The adhesive composition according to claim 1,
wherein the adhesive composition contains an adhesive
component.

[claim 6] The adhesive composition according to claim 5,
wherein the adhesive component is a component that is cured
by a hydrosilylation reaction.

[claim 7] The adhesive composition according to claim 6,
wherein the component that is cured by a

hydrosilylation reaction contains:

a component (A-1) containing an alkenyl group having 2 to 40 carbon atoms, the alkenyl group being bonded to a silicon atom;

a component (A-2) containing a Si-H group; and

a platinum group metal-based catalyst (A-3).

[claim 8] The adhesive composition according to claim 7, wherein the component (A-1) contains a polyorganosiloxane (a1) containing an alkenyl group having 2 to 40 carbon atoms, the alkenyl group being bonded to a silicon atom.

[claim 9] The adhesive composition according to claim 7, wherein the component (A-2) contains a polyorganosiloxane containing a Si-H group.

[claim 10] A laminate comprising:

a semiconductor substrate or an electronic device layer;

a support substrate; and

an adhesive layer provided between the semiconductor substrate or the electronic device layer and the support substrate,

wherein the adhesive layer is an adhesive layer formed from the adhesive composition according to any one of claims 1 to 9.

[claim 11] A method for producing a processed semiconductor substrate or a processed electronic device

layer, the method comprising:

a step 5A of processing the semiconductor substrate of the laminate according to claim 10, or a step 5B of processing the electronic device layer of the laminate according to claim 10; and

a step 6A of separating the semiconductor substrate processed in the step 5A from the support substrate, or a step 6B of separating the electronic device layer processed in the step 5B from the support substrate.