DESCRIPTION

Title of Invention:

COMPOSITION FOR FORMING FOREIGN SUBSTANCE-REMOVING COATING FILM AND SEMICONDUCTOR SUBSTRATE

Technical Field

[0001]

The present invention relates to a composition for forming a foreign substance-removing coating film, a foreign substance-removing coating film, a semiconductor substrate, and a method for manufacturing a processed semiconductor substrate, which can prevent a foreign substance from remaining on a substrate by a simple method.

Background Art

[0002]

In semiconductor device manufacturing, particularly in a so-called post-process, studies have been made on a process of bonding a semiconductor substrate (for example, a wafer) to a support substrate, then subjecting the resultant substrate to back-grinding (grinding), a wiring formation step, and the like, and then peeling off the support substrate to obtain a desired semiconductor substrate.

[0003]

In such a process, a foreign substance may be

generated, and removal thereof is required. Therefore, for example, Patent Literatures 1 and 2 each disclose a composition for forming a substrate processing film and a method for processing a substrate, which can efficiently remove minute particles from a substrate surface and easily remove a formed substrate processing film from the substrate surface in a process of forming the substrate processing film on the surface of the semiconductor substrate and removing a foreign substance from the substrate surface.

Citation List

Patent Literature

[0004]

Patent Literature 1: WO 2017/056746 A

Patent Literature 2: WO 2020/008965 A

Summary of Invention

Technical Problem

[0005]

Meanwhile, when a semiconductor substrate is bonded to a support base material, the semiconductor substrate is bonded to the support base material using an adhesive layer (for example, a liquid composition containing a polymer, a back-grinding tape, or a dicing tape) having resistance to

subsequent steps (for example, a heating step and a chemical liquid treatment step). Alternatively, a support base material having a pressure-sensitive adhesive layer is used. Thereafter, a step of peeling off the semiconductor substrate is performed. At this time, the adhesive layer or the pressure-sensitive adhesive layer of the support base material may remain as a foreign substance (residue) on the substrate. This phenomenon particularly significantly occurs when an adhesive layer is formed directly on a surface of a semiconductor substrate on which wiring or the like is previously formed or when a support base material having a pressure-sensitive adhesive layer is directly bonded thereto. The foreign substance cannot be completely removed in some cases even if cleaning or the like is performed with a known organic solvent, a liquid chemical, or the like.

Therefore, it is required to prevent a peeling residue generated from an adhesive layer, a pressure-sensitive adhesive layer, or the like from remaining on a semiconductor substrate by a simple method.

On the other hand, when a film (foreign substance-removing coating film) is used for this purpose, it is required that the film can be easily removed from the semiconductor substrate after the step of peeling off the semiconductor substrate is performed (ease of removal). In

addition, when a chemical liquid is used in order to remove the film, it is required that the chemical liquid does not damage the semiconductor substrate.

[0006]

Therefore, an object of the present invention is to provide a composition for forming a foreign substance-removing coating film, the composition being capable of providing a foreign substance-removing coating film that can be removed by water, a foreign substance-removing coating film using the composition, a semiconductor substrate using the composition, and a method for manufacturing a processed semiconductor substrate using the composition.

Solution to Problem

[0007]

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

That is, the present invention includes the following.

[0008]

[1] A composition for forming a foreign substance-removing coating film, the composition containing a water-soluble compound and a solvent and being capable of forming

a coating film that can be removed by water.

[2] The composition for forming a foreign substance-removing coating film according to [1], wherein the water-soluble compound is at least one selected from the group consisting of cellulose and a derivative thereof, cyclodextrin and a derivative thereof, polyacrylic acid, a polymer having a structural unit derived from hydroxyalkyl (meth)acrylate, tannic acid, and a polymer having a lactam structure.

[3] The composition for forming a foreign substance-removing coating film according to [1] or [2], wherein the content of the water-soluble compound is 98% by mass or more with respect to film constituent components.

[4] A foreign substance-removing coating film formed from the composition for forming a foreign substance-removing coating film according to any one of [1] to [3].

[5] A semiconductor substrate having the foreign substance-removing coating film according to [4].

[6] A method for manufacturing a processed semiconductor substrate, including:

a first step of manufacturing a laminate by bonding the semiconductor substrate according to [5] to a support base material with the foreign substance-removing coating film interposed therebetween;

a second step of processing the laminate;

a third step of peeling off the support base material from the laminate; and

a fourth step of cleaning the semiconductor substrate or the support base material with a removing liquid to remove the foreign substance-removing coating film.

[7] The method for manufacturing a processed semiconductor substrate according to [6], wherein in the fourth step, a foreign substance is removed together with the foreign substance-removing coating film.

[8] The method for manufacturing a processed semiconductor substrate according to [6] or [7], wherein the first step is a step of manufacturing a laminate by bonding the semiconductor substrate to the support base material with the foreign substance-removing coating film and an adhesive layer interposed therebetween.

[9] The method for manufacturing a semiconductor substrate according to [8], wherein in the fourth step, a foreign substance as a peeling residue of the adhesive layer is removed together with the foreign substance-removing coating film.

[10] The method for manufacturing a processed semiconductor substrate according to any one of [6] to [9], wherein the processing includes connecting the semiconductor substrate to a second semiconductor substrate.

Advantageous Effects of Invention

[0009]

According to the present invention, it is possible to provide a composition for forming a foreign substance-removing coating film, the composition being capable of providing a foreign substance-removing coating film that can be removed by water, a foreign substance-removing coating film using the composition, a semiconductor substrate using the composition, and a method for manufacturing a processed semiconductor substrate using the composition.

Brief Description of Drawings

[0010]

[Fig. 1A] Fig. 1A is a schematic cross-sectional view for explaining an example of a method for manufacturing a processed semiconductor substrate (part 1).

[Fig. 1B] Fig. 1B is a schematic cross-sectional view for explaining the example of the method for manufacturing a processed semiconductor substrate (part 2).

[Fig. 1C] Fig. 1C is a schematic cross-sectional view for explaining the example of the method for manufacturing a processed semiconductor substrate (part 3).

[Fig. 1D] Fig. 1D is a schematic cross-sectional view

for explaining the example of the method for manufacturing a processed semiconductor substrate (part 4).

[Fig. 1E] Fig. 1E is a schematic cross-sectional view for explaining the example of the method for manufacturing a processed semiconductor substrate (part 5).

[Fig. 1F] Fig. 1F is a schematic cross-sectional view for explaining the example of a method for manufacturing a processed semiconductor substrate (part 6).

[Fig. 1G] Fig. 1G is a schematic cross-sectional view for explaining the example of the method for manufacturing a processed semiconductor substrate (part 7).

[Fig. 2A] Fig. 2A is a schematic cross-sectional view for explaining another example of the method for manufacturing a processed semiconductor substrate (part 1).

[Fig. 2B] Fig. 2B is a schematic cross-sectional view for explaining the other example of the method for manufacturing a processed semiconductor substrate (part 2).

[Fig. 2C] Fig. 2C is a schematic cross-sectional view for explaining the other example of the method for manufacturing a processed semiconductor substrate (part 3).

[Fig. 2D] Fig. 2D is a schematic cross-sectional view for explaining the other example of the method for manufacturing a processed semiconductor substrate (part 4).

[Fig. 2E] Fig. 2E is a schematic cross-sectional view for explaining the other example of the method for

manufacturing a processed semiconductor substrate (part 5).

[Fig. 2F] Fig. 2F is a schematic cross-sectional view for explaining the other example of the method for manufacturing a processed semiconductor substrate (part 6).

[Fig. 2G] Fig. 2G is a schematic cross-sectional view for explaining the other example of the method for manufacturing a processed semiconductor substrate (part 7).

[Fig. 2H] Fig. 2H is a schematic cross-sectional view for explaining the other example of the method for manufacturing a processed semiconductor substrate (part 8).

[Fig. 2I] Fig. 2I is a schematic cross-sectional view for explaining the other example of the method for manufacturing a processed semiconductor substrate (part 9).

[Fig. 2J] Fig. 2J is a schematic cross-sectional view for explaining the other example of the method for manufacturing a processed semiconductor substrate (part 10).

[Fig. 2K] Fig. 2K is a schematic cross-sectional view for explaining the other example of the method for manufacturing a processed semiconductor substrate (part 11).

Description of Embodiments

[0011]

(Composition for forming a foreign substance-removing

coating film)

The composition for forming a foreign substance-removing coating film of the present invention contains a water-soluble compound and a solvent.

The composition for forming a foreign substance-removing coating film can form a coating film that can be removed by water.

Since the coating film can be removed by water, the coating film can be easily removed from a semiconductor substrate. When water is used as a removing liquid, damage to the semiconductor substrate is less likely to be caused as compared with a case where an alkali solution or the like is used as the removing liquid.

[0012]

<Water-soluble compound>

The water-soluble compound is a compound that is soluble in an amount of 1 g or more in 100 g of water at 25°C.

The water-soluble compound is preferably a compound that is soluble in an amount of 5 g or more in 100 g of water at 25°C, and more preferably a compound that is soluble in an amount of 10 g or more in 100 g of water at 25°C.

[0013]

The water-soluble compound may be a low molecular

weight compound or a high molecular weight compound.

[0014]

The water-soluble compound may have or need not have, for example, a polar group or a polar bond.

Examples of the polar group include an amino group, a hydroxy group, and a carboxy group.

Examples of the polar bond include a urea bond, a urethane bond, an amide bond, and an ester bond.

[0015]

The water-soluble compound may have or need not have a cyclic structure.

Examples of the cyclic structure include a lactone ring, a lactam ring, cyclic glucose, and an aromatic ring. Examples of the aromatic ring include a benzene ring.

[0016]

The water-soluble compound is preferably at least one selected from the group consisting of cellulose and a derivative thereof, cyclodextrin and a derivative thereof, polyacrylic acid, a polymer having a structural unit derived from hydroxyalkyl (meth)acrylate, tannic acid, and a polymer having a γ-lactam structure from a viewpoint of suitably obtaining the effect of the present invention.

[0017]

<<Cellulose and a derivative thereof>>

Cellulose is a polysaccharide in which D-glucose is

bonded by a β-1,4 glucoside bond.

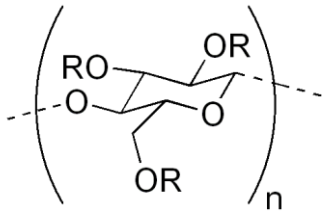
Examples of cellulose and a derivative thereof include cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, and carboxymethyl cellulose.

Among them, hydroxypropyl cellulose is preferable from a viewpoint of more suitably obtaining the effect of the present invention.

[0018]

A structural example of hydroxypropyl cellulose is illustrated below.

[Chem. 1]



R = H or $CH_2CH(OH)CH_3$

[0019]

<<Cyclodextrin and a derivative thereof>>

Cyclodextrin is a cyclic oligosaccharide in which D-glucose is bonded by an α-1,4 glucoside bond to form a cyclic structure, and examples thereof include a cyclodextrin containing 6 to 12 glucose units.

Specific examples of cyclodextrin include α-cyclodextrin in which six D-glucose units are cyclized, β-

cyclodextrin in which seven D-glucose units are cyclized, γ-cyclodextrin in which eight D-glucose units are cyclized, derivatives of these cyclodextrins, and a polymer partially having a cyclodextrin structure.

[0020]

The derivative of cyclodextrin is a compound in which some or all of the hydroxy groups at 2, 3, and 6 positions of glucose in the cyclodextrin are replaced with other functional groups, and examples thereof include an alkyl derivative, a hydroxyalkyl derivative, an alkoxy derivative, a sulfoalkyl ether derivative, and a sugar bond derivative.

Specific examples of the derivative of cyclodextrin include hydroxymethyl cyclodextrin, hydroxyethyl cyclodextrin, hydroxypropyl cyclodextrin, hydroxybutyl cyclodextrin, dimethylcyclodextrin, trimethylcyclodextrin, diethyl cyclodextrin, triethyl cyclodextrin, carboxymethyl cyclodextrin, glucosyl cyclodextrin, maltosyl cyclodextrin, dimaltosyl cyclodextrin, monochlorotriazinyl cyclodextrin, and cyclodextrin epichlorohydrin polymer.

[0021]

More specific examples of the derivative of cyclodextrin include a sugar bond derivative, an alkylated cyclodextrin, a hydroxyalkylated cyclodextrin, a carboxyalkylated cyclodextrin, a sulfoalkyl ether

derivative, and an alkoxylated cyclodextrin.

Examples of the sugar bond derivative include glucosyl-α-cyclodextrin, glucosyl-β-cyclodextrin, and glucosyl-γ-cyclodextrin.

Examples of the alkylated cyclodextrin include 2,6-di-O-methyl-α-cyclodextrin, 2,3,6-tri-O-methyl-α-cyclodextrin, 2,6-di-O-methyl-β-cyclodextrin, 2,3,6-tri-O-methyl-β-cyclodextrin, 2,6-di-O-methyl-γ-cyclodextrin, and 2,3,6-tri-O-methyl-γ-cyclodextrin.

Examples of the hydroxyalkylated cyclodextrin include 2-hydroxyethyl-α-cyclodextrin, 2-hydroxypropyl-α-cyclodextrin, 3-hydroxypropyl-α-cyclodextrin, 2,3-dihydroxypropyl-α-cyclodextrin, 2-hydroxyethyl-β-cyclodextrin, 2-hydroxypropyl-β-cyclodextrin, 2,3-dihydroxypropyl-β-cyclodextrin, 2-hydroxyethyl-γ-cyclodextrin, 2-hydroxypropyl-γ-cyclodextrin, 3-hydroxypropyl-γ-cyclodextrin, and 2,3-dihydroxypropyl-γ-cyclodextrin.

Examples of the carboxyalkylated cyclodextrin include O-carboxymethyl-α-cyclodextrin, O-carboxymethyl-β-cyclodextrin, and O-carboxymethyl-γ-cyclodextrin.

Examples of the sulfoalkyl ether derivative include sulfobutyl ether-α-cyclodextrin, sulfobutyl ether-β-cyclodextrin, and sulfobutyl ether-γ-cyclodextrin.

Examples of the alkoxylated cyclodextrin include

methoxycyclodextrin and ethoxycyclodextrin.

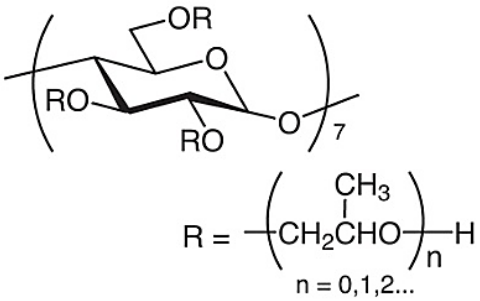
[0022]

Among them, a hydroxyalkylated cyclodextrin is preferable, and 2-hydroxypropyl-β-cyclodextrin is more preferable from a viewpoint of more suitably obtaining the effect of the present invention.

[0023]

A structural example of 2-hydroxypropyl-β-cyclodextrin is illustrated below.

[Chem. 2]



[0024]

<Polymer having structural unit derived from hydroxyalkyl (meth)acrylate>

Examples of the polymer having a structural unit derived from a hydroxyalkyl (meth)acrylate include a homopolymer of a hydroxyalkyl (meth)acrylate and a copolymer of a hydroxyalkyl (meth)acrylate and another monomer.

[0025]

The number of carbon atoms of a hydroxyalkyl group in the hydroxyalkyl (meth)acrylate is, for example, 1 to 6.

Examples of the hydroxyalkyl (meth)acrylate include 2-hydroxyethyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, and 6-hydroxyhexyl (meth)acrylate.

Note that the (meth)acrylate refers to acrylate and/or methacrylate.

[0026]

The other monomer used for copolymerization is not particularly limited, and examples thereof include (meth)acrylic acid, a (meth)acrylate compound, a (meth)acrylamide compound, a vinyl compound, a styrene compound, and acrylonitrile.

[0027]

Specific examples of the (meth)acrylate compound include methyl (meth)acrylate, ethyl (meth)acrylate, normal hexyl (meth)acrylate, i-propyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, anthrylmethyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, 2-methyl-2-adamantyl (meth)acrylate, and glycidyl (meth)acrylate.

[0028]

Specific examples of the (meth)acrylamide compound include (meth)acrylamide, N-methyl (meth)acrylamide, N-ethyl (meth)acrylamide, N-benzyl (meth)acrylamide, N-phenyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, and N-anthryl (meth)acrylamide.

[0029]

Specific examples of the vinyl compound include vinyl alcohol, 2-hydroxyethyl vinyl ether, methyl vinyl ether, ethyl vinyl ether, benzyl vinyl ether, vinyl acetate, vinyltrimethoxysilane, 2-chloroethyl vinyl ether, 2-methoxyethyl vinyl ether, vinylnaphthalene, and vinylanthracene.

[0030]

Specific examples of the styrene compound include styrene, hydroxystyrene, chlorostyrene, bromostyrene, methoxystyrene, cyanostyrene, and acetylstyrene.

[0031]

A constituent ratio of the other monomer in a case of a copolymer is not particularly limited as long as the polymer is water-soluble.

[0032]

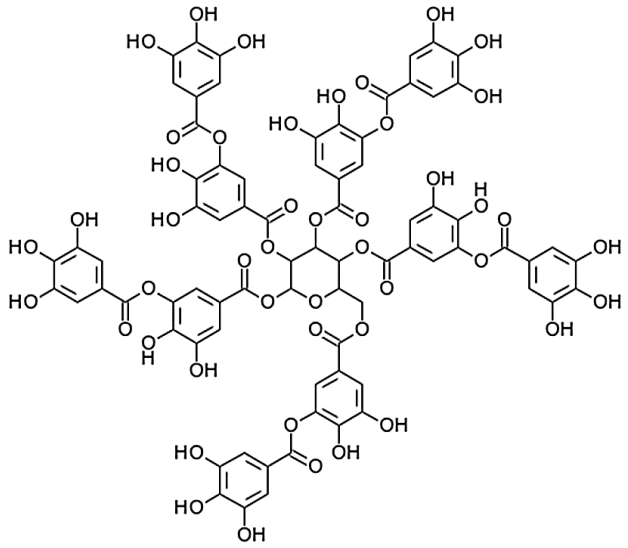
Among them, a homopolymer of 2-hydroxyethyl acrylate is preferable from a viewpoint of more suitably obtaining the effect of the present invention.

[0033]

<<Tannic acid>>

Tannic acid is represented by the following structure.

[Chem. 3]



[0034]

<<Polymer having lactam structure>>

Examples of the polymer having a lactam structure include a polymer having γ-lactam which is a 5-membered lactam in a side chain and a polymer having δ-lactam which is a 6-membered lactam in a side chain.

Examples of the lactam structure include a pyrrolidone ring and an alkylated pyrrolidone ring in which at least some hydrogen atoms of the pyrrolidone ring are replaced with alkyl groups. Examples of the alkyl group include an alkyl group having 1 to 6 carbon atoms.

[0035]

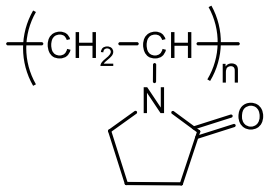
Examples of the polymer having a lactam structure include polyvinylpyrrolidone, an alkylated

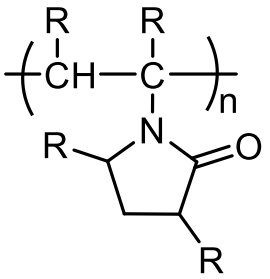
polyvinylpyrrolidone, and a vinylpyrrolidone-vinyl acetate copolymer.

[0036]

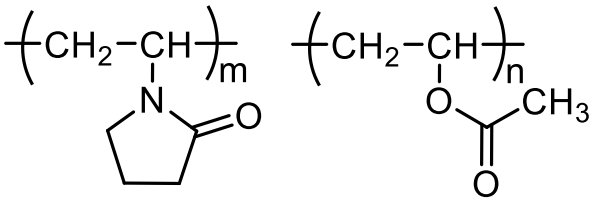
Structural examples of the polyvinylpyrrolidone, the alkylated polyvinylpyrrolidone, and the vinylpyrrolidone-vinyl acetate copolymer are illustrated below.

[Chem. 4]





R: H or alkyl group



[0037]

The polymer having a lactam structure may be a commercially available product. Examples of a commercially available product of polyvinylpyrrolidone include K-30 and K-90 (Nippon Shokubai Co., Ltd.). Examples of a commercially available product of the alkylated

polyvinylpyrrolidone include Ganex P-904 LC (Ashland Inc.). Examples of a commercially available product of the vinylpyrrolidone-vinyl acetate copolymer include PVP/VA S-630 (Ashland Inc.).

[0038]

A weight average molecular weight of the water-soluble compound is not particularly limited, and is preferably 700 to 5,000,000, and more preferably 900 to 100,000. Note that the weight average molecular weight is a value obtained by gel permeation chromatography (GPC) using polystyrene as a standard sample.

[0039]

The content of the water-soluble compound in the composition for forming a foreign substance-removing coating film is not particularly limited, and is preferably 80% by mass or more, more preferably 90% by mass or more, still more preferably 95% by mass or more, and particularly preferably 98% by mass, with respect to film constituent components.

The film constituent components refer to components other than the solvent in the composition for forming a foreign substance-removing coating film.

[0040]

<<Removing liquid>>

The removing liquid is not particularly limited as long

as it can remove a coating film formed from the composition for forming a foreign substance-removing coating film.

The coating film is formed on, for example, a semiconductor substrate. In this case, the removal refers to removal from the semiconductor substrate.

Here, examples of the mode of removal include dissolution removal and peeling removal. Examples of the peeling removal include peeling from an adherend by swelling.

[0041]

The removing liquid may contain water or an organic solvent.

Examples of the removing liquid include water, an organic solvent, an alkaline removing liquid, and an acidic removing liquid.

[0042]

The water is not particularly limited as long as it is water usually used in semiconductor manufacturing, and examples thereof include pure water, ultrapure water, and deionized water.

[0043]

The removing liquid may be a removing liquid containing an organic solvent in an amount of 50% by mass or more.

[0044]

Examples of the organic solvent include ethylene glycol

monomethyl ether, ethylene glycol monoethyl ether, methyl cellosolve acetate, ethyl cellosolve acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, propylene glycol, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, propylene glycol propyl ether acetate, toluene, xylene, methyl ethyl ketone, cyclopentanone, cyclohexanone, ethyl 2-hydroxypropionate, ethyl 2-hydroxy-2-methylpropionate, ethyl ethoxyacetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutanoate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, ethyl 3-ethoxypropionate, methyl 3-ethoxypropionate, methyl pyruvate, ethyl pyruvate, ethyl acetate, butyl acetate, ethyl lactate, butyl lactate, N,N-dimethylformamide, N,N-dimethylacetamide, and N-methylpyrrolidone.

[0045]

The alkaline removing liquid contains an alkali. Examples of the alkali include ammonia, an inorganic alkaline compound, quaternary ammonium hydroxide, an amine, and hydrazine.

The alkaline removing liquid may be a developer or a cleaning liquid used in a semiconductor manufacturing process and exhibiting alkalinity. Examples of the developer include NMD-3 (2.38% tetramethylammonium hydroxide aqueous solution, manufactured by TOKYO OHKA KOGYO CO., LTD.).

Examples of the inorganic alkaline compound include potassium hydroxide, sodium hydroxide, lithium hydroxide, diammonium hydrogen phosphate, dipotassium hydrogen phosphate, disodium hydrogen phosphate, lithium silicate, sodium silicate, potassium silicate, lithium carbonate, sodium carbonate, potassium carbonate, lithium borate, sodium borate, and potassium borate.

Examples of the quaternary ammonium hydroxide include tetramethylammonium hydroxide, tetraethylammonium hydroxide, trimethylhydroxyethylammonium hydroxide, and choline.

Examples of the amine include ethanolamine, methylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, n-propylamine, di-n-propylamine, isopropylamine, diisopropylamine, methyldiethylamine, dimethylethanolamine, triethanolamine, and ethylenediamine.

Examples of the hydrazine include hydrazine monohydrate.

The alkaline removing liquid may be SC-1 (ammonia-hydrogen peroxide solution).

[0046]

The acidic removing liquid contains an acid. Examples of the acid include an inorganic acid and an organic acid. Examples of the inorganic acid include sulfuric acid,

nitric acid, hydrochloric acid, phosphoric acid, and hydrofluoric acid.

The acidic removing liquid is, for example, an aqueous solution containing dilute hydrofluoric acid.

The acidic removing liquid may be, for example, an aqueous solution containing sulfuric acid and hydrogen peroxide, or an aqueous solution containing acetic acid or a chelating agent. Examples of the chelating agent include an organic acid, a salt of an organic acid, an amino acid, and a derivative of an amino acid.

[0047]

<Solvent>

Examples of the solvent contained in the composition for forming a foreign substance-removing coating film include ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, methyl cellosolve acetate, ethyl cellosolve acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, propylene glycol, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, propylene glycol propyl ether acetate, toluene, xylene, methyl ethyl ketone, cyclopentanone, cyclohexanone, ethyl 2-hydroxypropionate, ethyl 2-hydroxy-2-methylpropionate, ethyl ethoxyacetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutanoate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate,

ethyl 3-ethoxypropionate, methyl 3-ethoxypropionate, methyl pyruvate, ethyl pyruvate, ethyl acetate, butyl acetate, ethyl lactate, butyl lactate, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, and the like.

These solvents can be used singly or in combination of two or more types thereof.

Furthermore, a high-boiling-point solvent such as propylene glycol monobutyl ether or propylene glycol monobutyl ether acetate can be mixed and used.

[0048]

The composition for forming a foreign substance-removing coating film can be easily prepared, for example, by uniformly mixing the components, and is dissolved in an appropriate solvent and used in a solution state.

Preferably, the composition for forming a foreign substance-removing coating film thus prepared is filtered using a filter having a pore size of about 0.2 μm or the like and then used. The composition for forming a foreign substance-removing coating film thus prepared is also excellent in long-term storage stability at room temperature.

[0049]

A ratio of a solid content in the composition for forming a foreign substance-removing coating film is not particularly limited as long as the components are

uniformly dissolved. The ratio is, for example, 0.5 to 50% by mass, and is, for example, 1 to 30% by mass. Here, the solid content means a component left after removal of the solvent component from all the components of the composition for forming a foreign substance-removing coating film.

[0050]

In the present invention, the foreign substance means a substance other than a target, the foreign substance being attached onto the substrate. In semiconductor device manufacturing, the foreign substance is an unnecessary substance. Examples of the foreign substance include particles attached onto a wafer, metal impurities, etching residues, and peeling residues of an adhesive layer.

[0051]

The foreign substance-removing coating film is particularly preferably used, in a step of bonding wafers using an adhesive and then peeling off the adhesive, by forming the coating film of the present invention before applying the adhesive, then performing a step of bonding and peeling the wafers, and then peeling off a foreign substance (residues of the adhesive layer).

[0052]

The foreign substance-removing coating film can also be used to remove a foreign substance that is already present

on a semiconductor substrate.

[0053]

The expression that the foreign substance-removing coating film is soluble in a removing liquid means that when the coating film is immersed in the removing liquid, cleaned with the removing liquid, or the like, the coating film is dissolved in the removing liquid, and the coating film does not exist on an adherend such as a substrate. The term “dissolution” in the present invention means, for example, that at least 90% of the thickness of the film originally formed on a substrate is removed (that is, the thickness of the residual film is 10% or less of the original film thickness), or at least 95% of the thickness of the original film is removed (that is, the thickness of the residual film is 5% or less of the original film thickness), or at least 99% of the thickness of the original film is removed (that is, the thickness of the residual film is 1% or less of the original film thickness), and most preferably 100% of the thickness of the original film is removed (that is, the thickness of the residual film is 0% of the original film thickness (no residual film remains)).

[0054]

The composition may contain at least one of a crosslinking agent and an additive.

[0055]

<Crosslinking agent>

The crosslinking agent is not particularly limited.

The crosslinking agent has a structure different from that of the water-soluble compound.

[0056]

The crosslinking agent is preferably an aminoplast crosslinking agent or a phenoplast crosslinking agent.

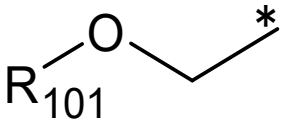
The aminoplast crosslinking agent is an addition condensate of a compound having an amino group, such as melamine or guanamine, and formaldehyde.

The phenoplast crosslinking agent is an addition condensate of a compound having a phenolic hydroxy group and formaldehyde.

[0057]

Examples of the crosslinking agent include a compound having two or more of the following structures.

[Chem. 5]



(In the structure, R_{101} represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, or an alkoxyalkyl group having 2 to 6 carbon atoms. * represents a bonding site.)

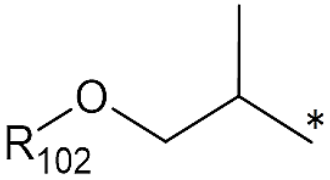
The bonding site is bonded to, for example, a nitrogen

atom or a carbon atom constituting an aromatic hydrocarbon ring.

[0058]

R_{101} is preferably a hydrogen atom, a methyl group, an ethyl group, or a group represented by the following structure.

[Chem. 6]



(In the structure, R_{102} represents a hydrogen atom, a methyl group, or an ethyl group. * represents a bonding site.)

[0059]

The crosslinking agent is preferably a melamine compound, a guanamine compound, a glycoluril compound, a urea compound, or a compound having a phenolic hydroxy group. These compounds can be used singly or in combination of two or more types thereof.

[0060]

Examples of the melamine compound include hexamethylolmelamine, hexamethoxymethylmelamine, a compound in which 1 to 6 methylol groups of hexamethylolmelamine are methoxymethylated or a mixture thereof, hexamethoxyethylmelamine, hexaacyloxymethylmelamine, and a

compound in which 1 to 6 methylol groups of hexamethylolmelamine are acyloxymethylated or a mixture thereof.

[0061]

Examples of the guanamine compound include tetramethylolguanamine, tetramethoxymethylguanamine, a compound in which 1 to 4 methylol groups of tetramethylolguanamine are methoxymethylated or a mixture thereof, tetramethoxyethylguanamine, tetraacyloxyguanamine, and a compound in which 1 to 4 methylol groups of tetramethylolguanamine are acyloxymethylated or a mixture thereof.

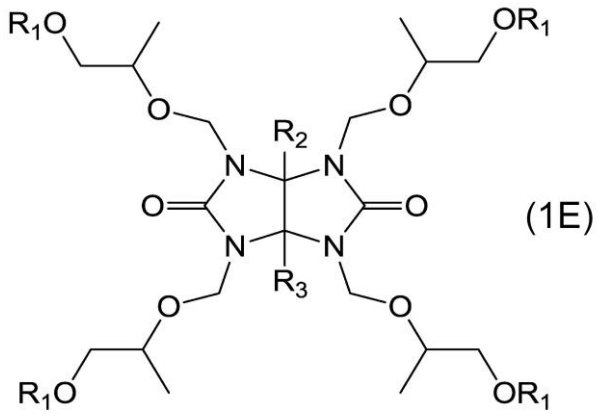
[0062]

Examples of the glycoluril compound include tetramethylolglycoluril, tetramethoxyglycoluril, tetramethoxymethylglycoluril, a compound in which 1 to 4 methylol groups of tetramethylolglycoluril are methoxymethylated or a mixture thereof, and a compound in which 1 to 4 methylol groups of tetramethylolglycoluril are acyloxymethylated or a mixture thereof.

[0063]

The glycoluril compound may be, for example, a glycoluril derivative represented by formula (1E) below.

[Chem. 7]

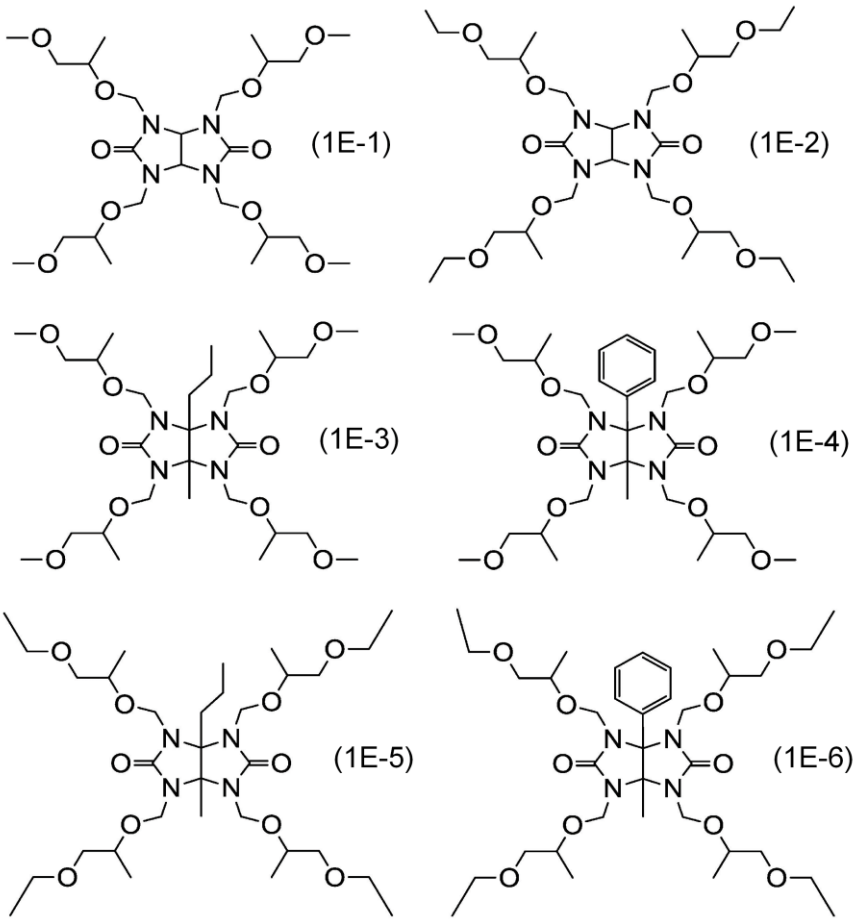


(In the formula (1E), four R_1s each independently represent a methyl group or an ethyl group, and R_2 and R_3 each independently represent a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, or a phenyl group.)

[0064]

Examples of the glycoluril derivative represented by the formula (1E) include compounds represented by the following formulas (1E-1) to (1E-6).

[Chem. 8]

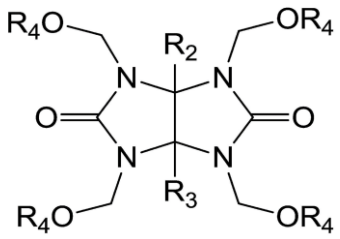


[0065]

The glycoluril derivative represented by the formula (1E) is obtained, for example, by allowing a glycoluril derivative represented by the following formula (2E) to react with at least one compound represented by the following formula (3d).

[0066]

[Chem. 9]

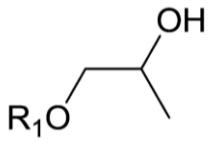


(2E)

(In the formula (2E), R_2 and R_3 each independently represent a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, or a phenyl group, and R_4s each independently represent an alkyl group having 1 to 4 carbon atoms.)

[0067]

[Chem. 10]



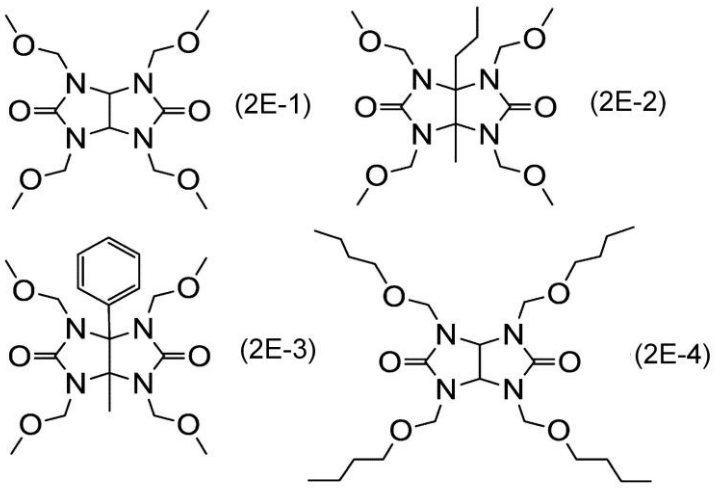
(3d)

(In the formula (3d), R_1 represents a methyl group or an ethyl group.)

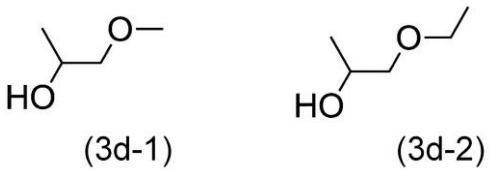
[0068]

Examples of the glycoluril derivative represented by the formula (2E) include compounds represented by the following formulas (2E-1) to (2E-4). Furthermore, examples of the compound represented by the formula (3d) include compounds represented by the following formulas (3d-1) and (3d-2).

[Chem. 11]



[Chem. 12]



(3d-1) (3d-2)

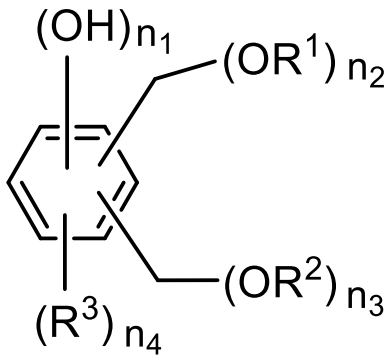
[0069]

Examples of the urea compound include tetramethylolurea, tetramethoxymethylurea, a compound in which 1 to 4 methylol groups of tetramethylolurea are methoxymethylated or a mixture thereof, and tetramethoxyethylurea.

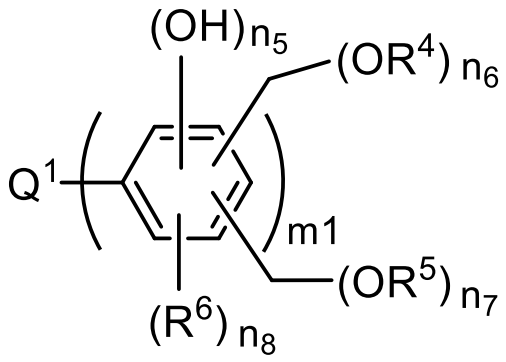
[0070]

Examples of the compound having a phenolic hydroxy group include a compound represented by the following formula (G-1) or (G-2).

[Chem. 13]



(G-1)



(G-2)

(In the formulas (G-1) and (G-2), Q^1 represents a single bond or an m1-valent organic group.

R^1 and R^4 each represent an alkyl group having 2 to 10 carbon atoms or an alkyl group having 2 to 10 carbon atoms and having an alkoxy group having 1 to 10 carbon atoms.

R^2 and R^5 each represent a hydrogen atom or a methyl group.

R^3 and R^6 each represent an alkyl group having 1 to 10 carbon atoms or an aryl group having 6 to 40 carbon atoms.

n_1 represents an integer satisfying $1 \leq n_1 \leq 3$, n_2 represents an integer satisfying $2 \leq n_2 \leq 5$, n_3 represents an integer satisfying $0 \leq n_3 \leq 3$, n_4 represents an integer satisfying $0 \leq n_4 \leq 3$, and $n_1 + n_2 + n_3 + n_4$ represents an integer satisfying $3 \leq (n_1 + n_2 + n_3 + n_4) \leq 6$.

n_5 represents an integer satisfying $1 \leq n_5 \leq 3$, n_6 represents an integer satisfying $1 \leq n_6 \leq 4$, n_7 represents an integer satisfying $0 \leq n_7 \leq 3$, n_8 represents an integer satisfying $0 \leq n_8 \leq 3$, and $n_5 + n_6 + n_7 + n_8$ represents an

integer satisfying $2 \leq (n_5 + n_6 + n_7 + n_8) \leq 5$.

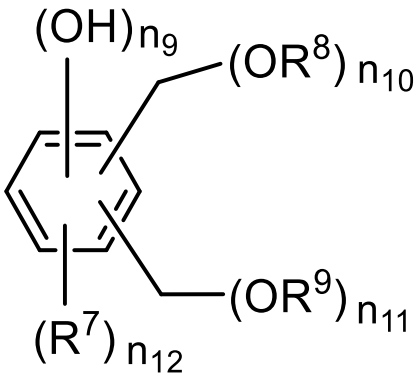
m1 represents an integer of 2 to 10.)

[0071]

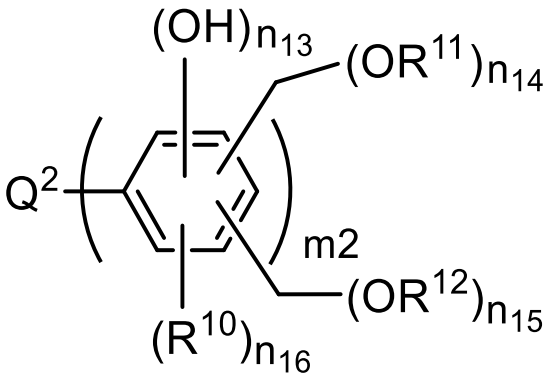
Examples of the compound having a phenolic hydroxy group include a compound represented by the following formula (G-3) or (G-4).

The compound represented by the formula (G-1) or (G-2) may be obtained by a reaction of a compound represented by the following formula (G-3) or (G-4) with a hydroxy group-containing ether compound or an alcohol having 2 to 10 carbon atoms.

[Chem. 14]



(G-3)



(G-4)

(In the formulas (G-3) and (G-4), Q^2 represents a single bond or an m2-valent organic group.

R^8, R^9, R^{11}, and R^{12} each represent a hydrogen atom or a methyl group.

R^7 and R^{10} each represent an alkyl group having 1 to 10 carbon atoms or an aryl group having 6 to 40 carbon atoms.

n_9 represents an integer satisfying $1 \leq n_9 \leq 3$, n_{10} represents an integer satisfying $2 \leq n_{10} \leq 5$, n_{11} represents an integer satisfying $0 \leq n_{11} \leq 3$, n_{12} represents an integer satisfying $0 \leq n_{12} \leq 3$, and $n_9 + n_{10} + n_{11} + n_{12}$ represents an integer satisfying $3 \leq (n_9 + n_{10} + n_{11} + n_{12}) \leq 6$.

n_{13} represents an integer satisfying $1 \leq n_{13} \leq 3$, n_{14} represents an integer satisfying $1 \leq n_{14} \leq 4$, n_{15} represents an integer satisfying $0 \leq n_{15} \leq 3$, n_{16} represents an integer satisfying $0 \leq n_{16} \leq 3$, and $n_{13} + n_{14} + n_{15} + n_{16}$ represents an integer satisfying $2 \leq (n_{13} + n_{14} + n_{15} + n_{16}) \leq 5$.

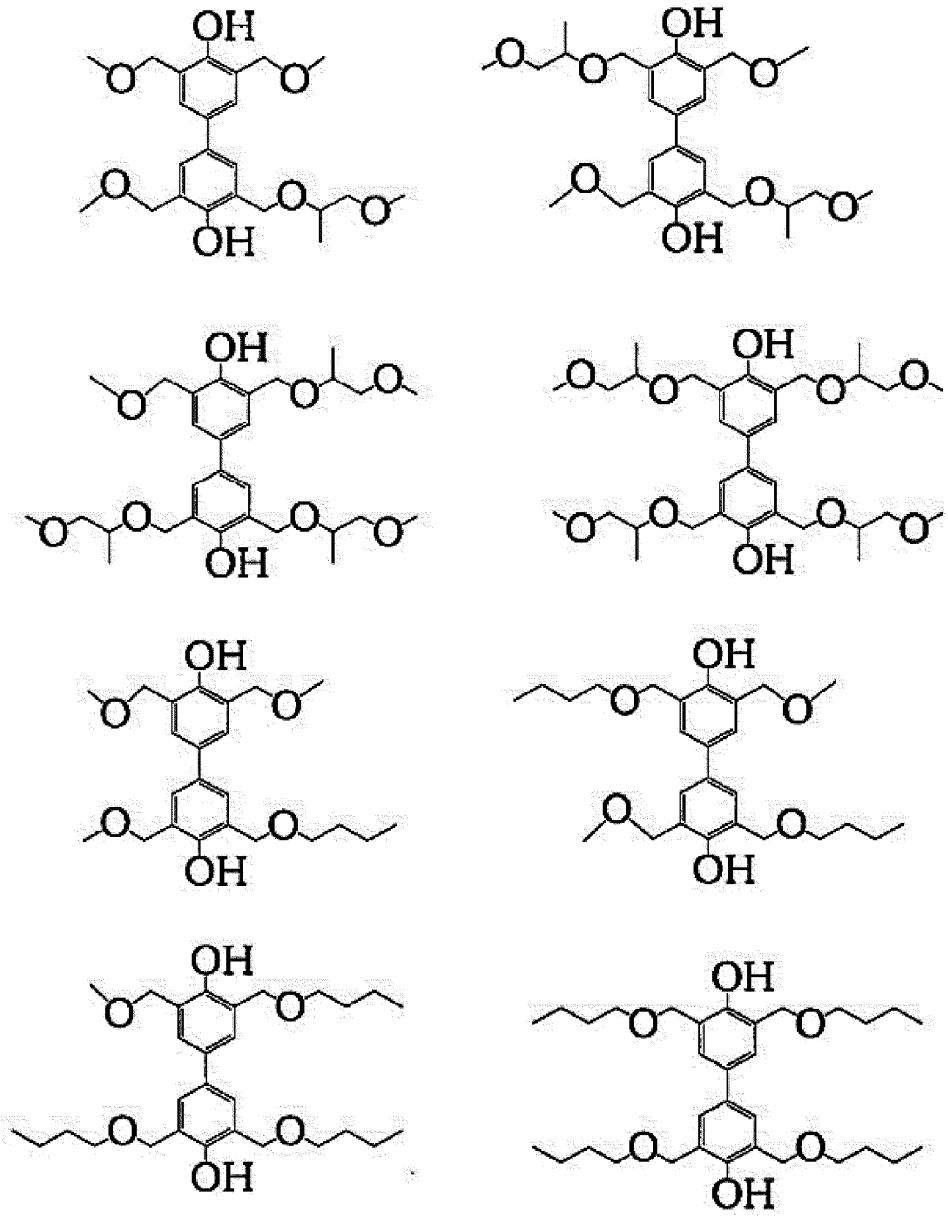
m2 represents an integer of 2 to 10.)

Examples of the m2-valent organic group in Q^2 include an m2-valent organic group having 1 to 4 carbon atoms.

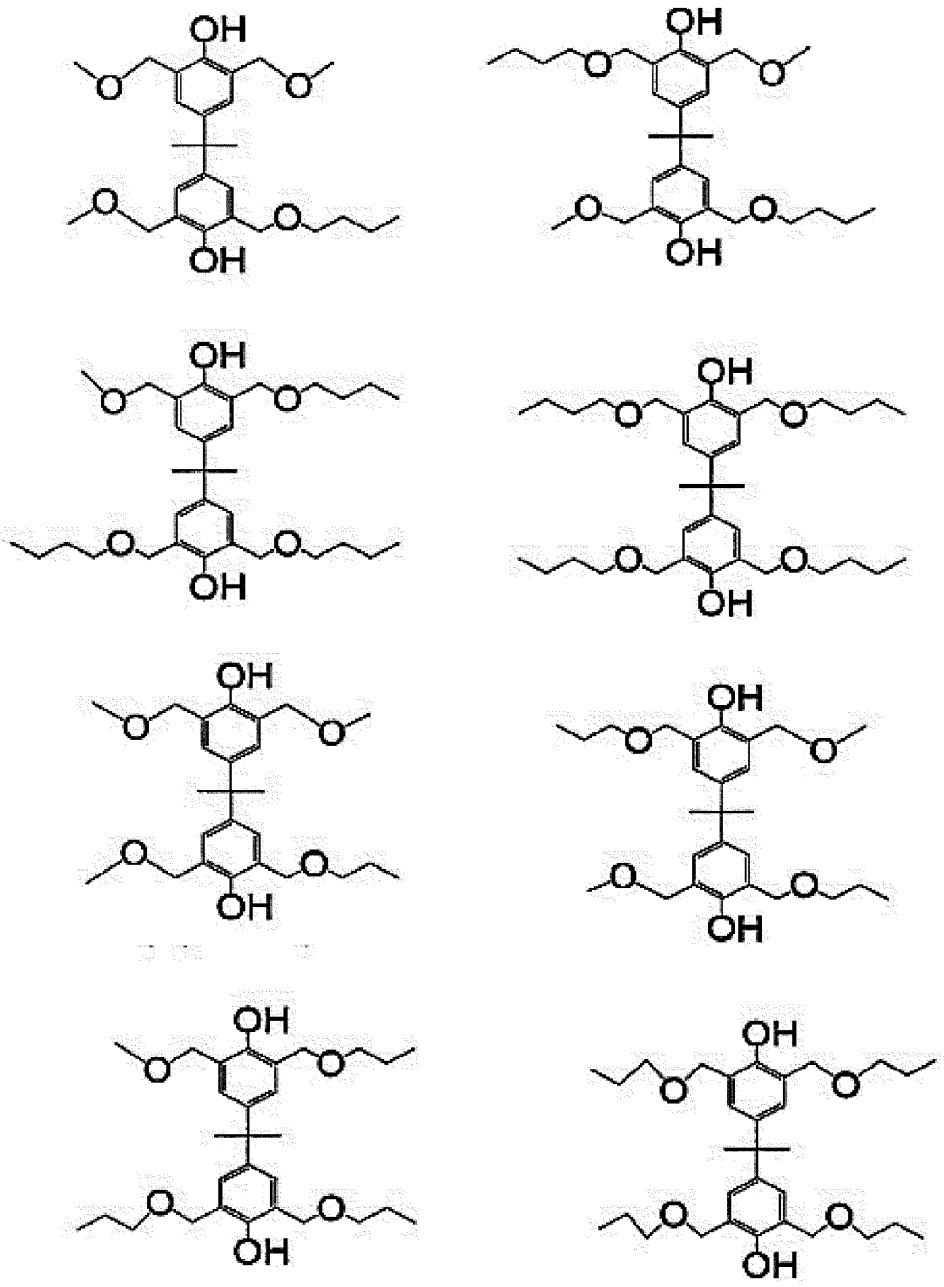
[0072]

Examples of the compound represented by the formula (G-1) or (G-2) include the following compounds.

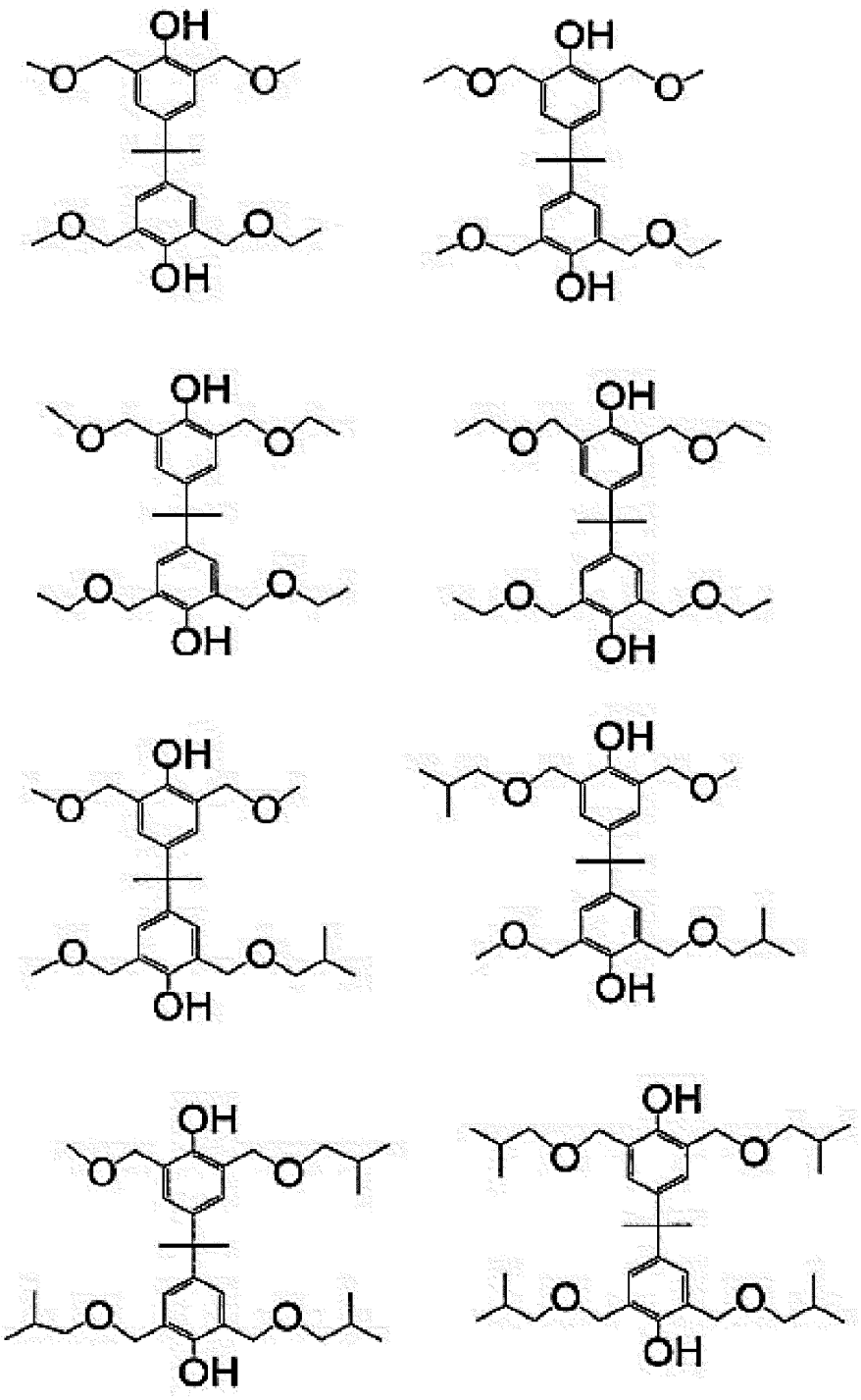
[Chem. 15]



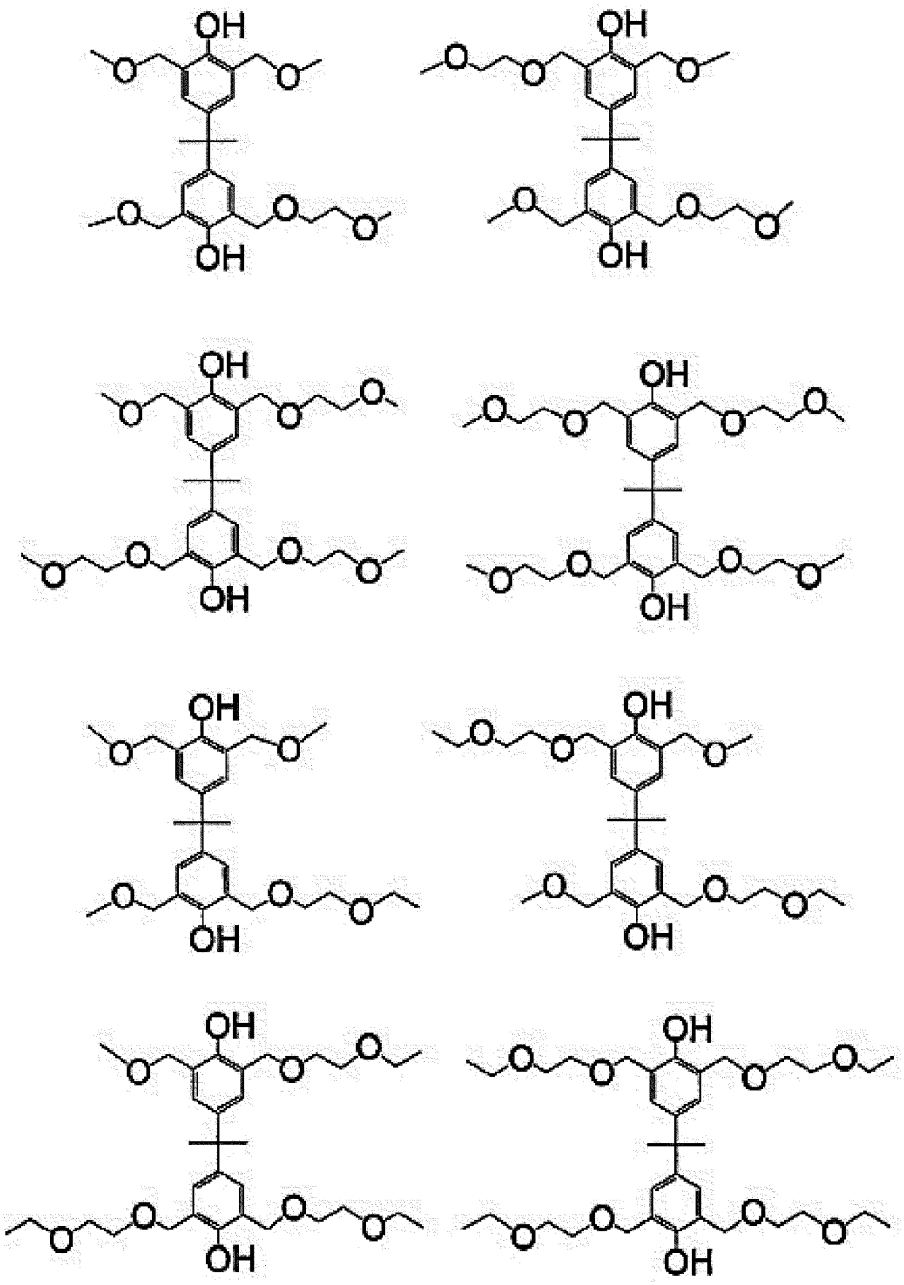
[Chem. 16]



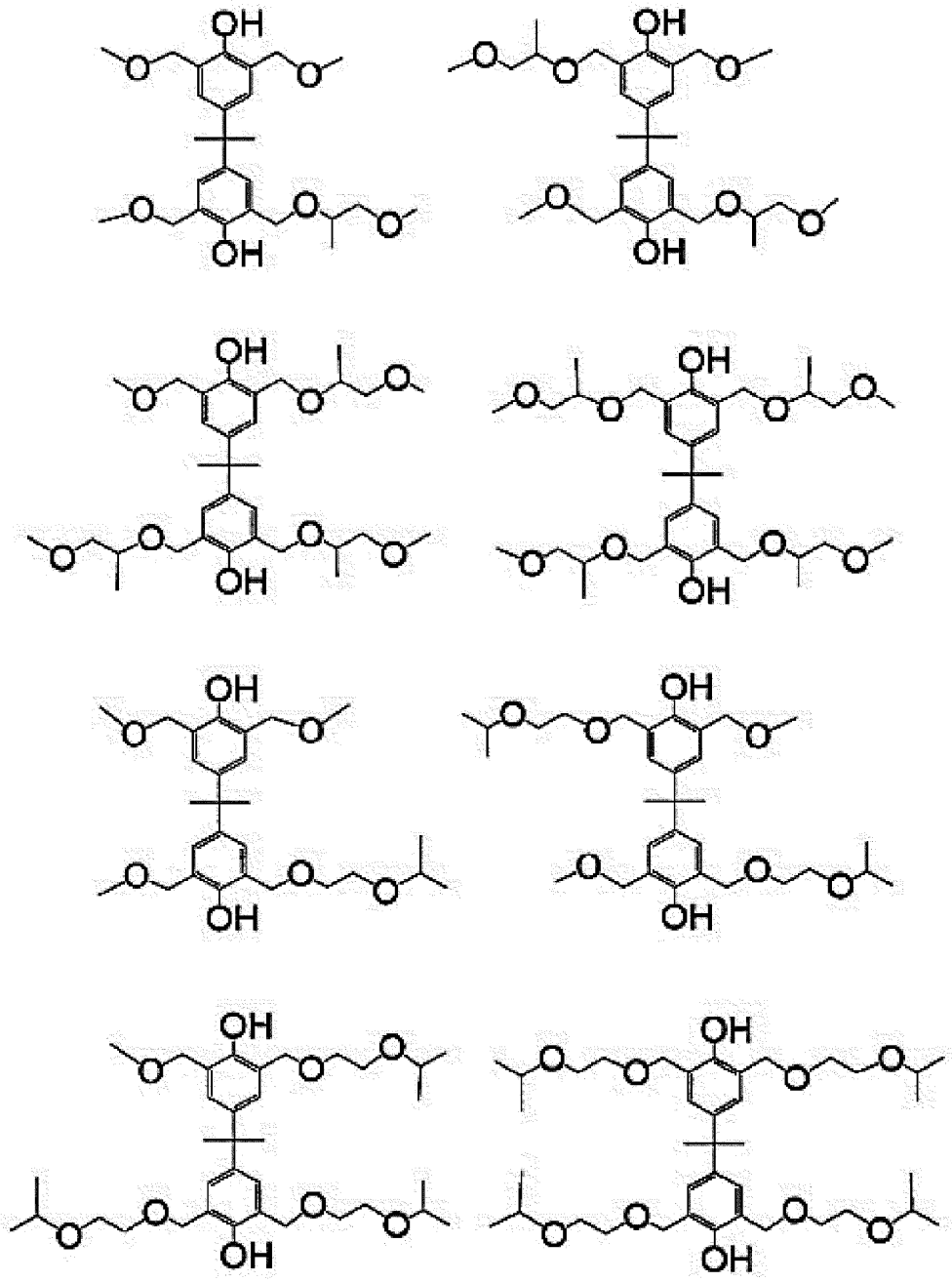
[Chem. 17]



[Chem. 18]



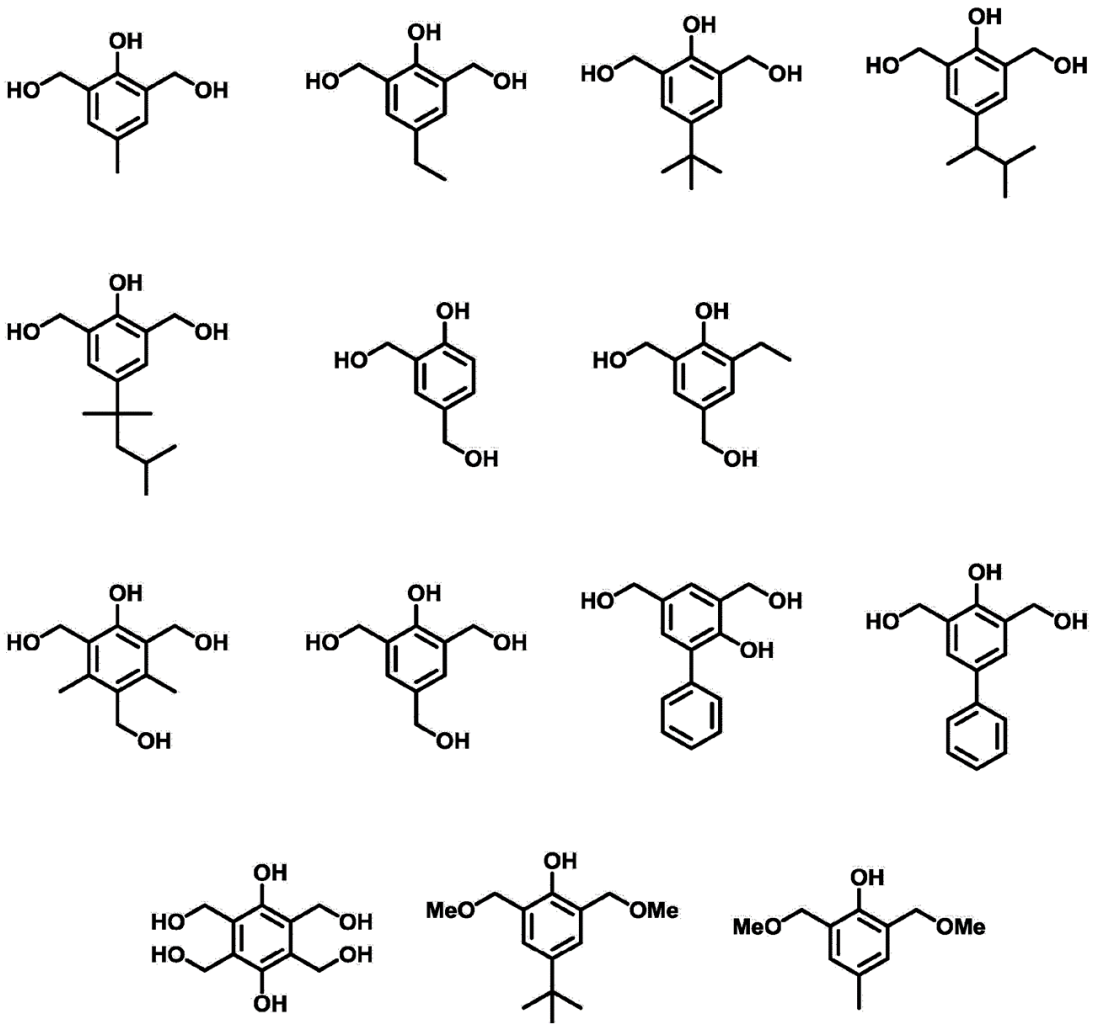
[Chem. 19]



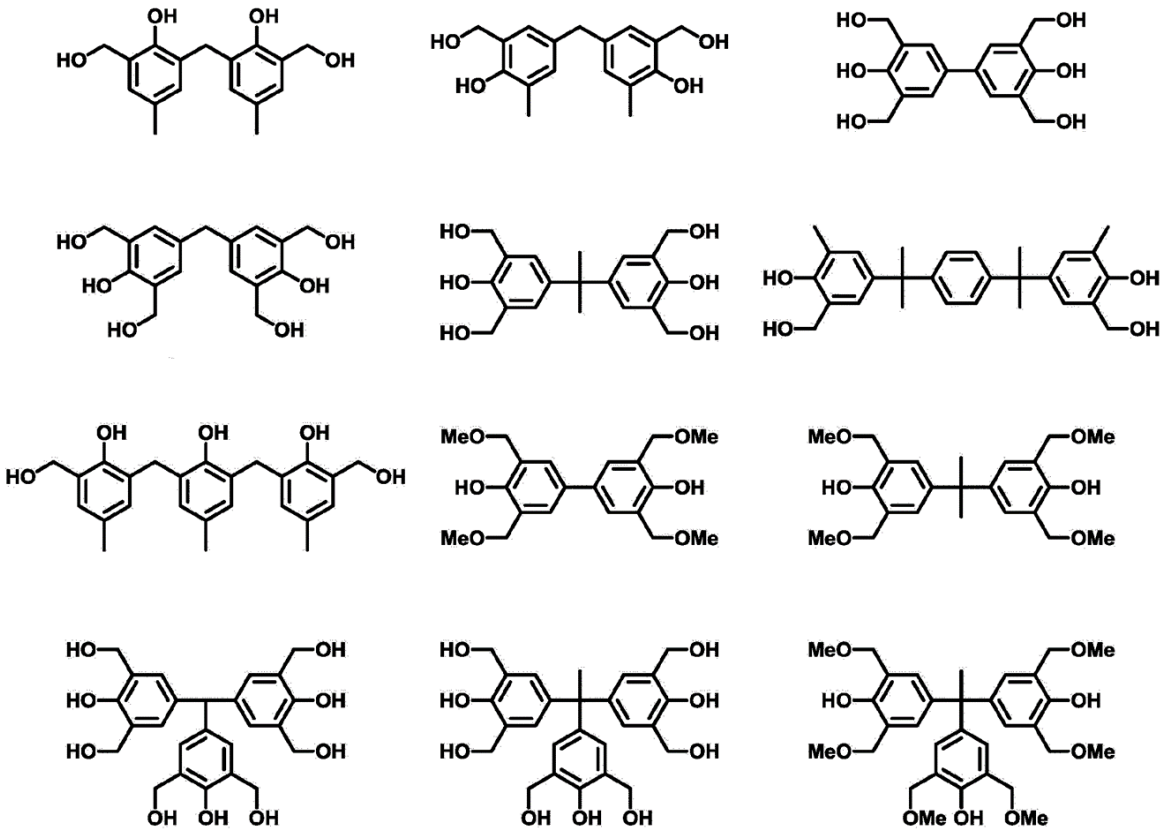
[0073]

Examples of the compound represented by the formula (G-3) or (G-4) include the following compounds.

[Chem. 20]


OH
HO
OH
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OH
OH
HO
OH
OH
HO
OH
OH
HO
OH
OH
MeO
OMe
OH
MeO
OMe

[Chem. 21]



The compounds are available as products of Asahi Yukizai Corporation and Honshu Chemical Industry Co., Ltd. Examples of the product include TMOM-BP (trade name) manufactured by Asahi Yukizai Corporation.

[0074]

Among these compounds, the glycoluril compound is preferable. Specifically, tetramethylol glycoluril, tetramethoxy glycoluril, tetramethoxymethyl glycoluril, a compound in which 1 to 4 methylol groups of tetramethylol glycoluril are methoxymethylated or a mixture thereof, and a compound in which 1 to 4 methylol groups of tetramethylol glycoluril are acyloxymethylated or a mixture thereof are

preferable, and tetramethoxymethyl glycoluril is more preferable.

[0075]

The molecular weight of the crosslinking agent is not particularly limited, and is preferably 1000 or less.

[0076]

The content of the crosslinking agent is, for example, 5 to 70 parts by mass, or 5 to 60 parts by mass, and preferably 5 to 45 parts by mass, with respect to 100 parts by mass of the water-soluble compound. The content of the crosslinking agent is preferably 5 parts by mass or more with respect to 100 parts by mass of the water-soluble compound from a viewpoint of the degree of curing of the coating film and prevention of intermixing with the adhesive layer, and is preferably 70 parts by mass or less with respect to 100 parts by mass of the water-soluble compound from a viewpoint of solubility in the removing liquid.

[0077]

<Additive>

The composition for forming a foreign substance-removing coating film can contain, as additives, a curing catalyst, a light-absorbing compound, a surfactant, an adhesion aid, a rheology modifier, and silica particles. These are components different from the water-soluble

compound in the present invention.

[0078]

As the curing catalyst, both a thermal acid generator and a photoacid generator can be used, but it is preferable to use a thermal acid generator.

Examples of the thermal acid generator include sulfonic acid compounds and carboxylic acid compounds such as p-toluenesulfonic acid, trifluoromethanesulfonic acid, pyridinium-p-toluenesulfonate (pyridinium-p-toluenesulfonic acid), pyridinium phenolsulfonate, pyridinium p-hydroxybenzenesulfonate (p-phenolsulfonic acid pyridinium salt), pyridinium-trifluoromethanesulfonate, salicylic acid, camphorsulfonic acid, 5-sulfosalicylic acid, 4-chlorobenzenesulfonic acid, 4-hydroxybenzenesulfonic acid, benzenedisulfonic acid, 1-naphthalenesulfonic acid, citric acid, benzoic acid, hydroxybenzoic acid, N-methylmorpholine-p-toluenesulfonate, N-methylmorpholine-p-hydroxybenzenesulfonate, and N-methylmorpholine-5-sulfosalicylate.

[0079]

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

[0080]

Examples of the onium salt compounds include iodonium

salt compounds such as diphenyliodonium hexafluorophosphate, diphenyliodonium trifluoromethanesulfonate, diphenyliodonium nonafluoronormalbutanesulfonate, diphenyliodonium perfluoronormaloctanesulfonate, diphenyliodonium camphorsulfonate, bis(4-tert-butylphenyl)iodonium camphorsulfonate, and bis(4-tert-butylphenyl)iodonium trifluoromethanesulfonate, and sulfonium salt compounds such as triphenylsulfonium hexafluoroantimonate, triphenylsulfonium nonafluoronormalbutanesulfonate, triphenylsulfonium camphorsulfonate, and triphenylsulfonium trifluoromethanesulfonate.

[0081]

Examples of the sulfonimide compounds include N-(trifluoromethanesulfonyloxy) succinimide, N-(nonafluoronormalbutanesulfonyloxy) succinimide, N-(camphorsulfonyloxy) succinimide, and N-(trifluoromethanesulfonyloxy) naphthalimide.

[0082]

Examples of the disulfonyldiazomethane compounds include bis(trifluoromethylsulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane, bis(phenylsulfonyl)diazomethane, bis(p-toluenesulfonyl)diazomethane, bis(2,4-dimethylbenzenesulfonyl)diazomethane, and methylsulfonyl-p-

toluenesulfonyl diazomethane.

[0083]

Only one type of curing catalyst can be used, or two or more types thereof can be used in combination.

[0084]

When a curing catalyst is used, a content ratio of the curing catalyst is, for example, 0.1% by mass to 50% by mass, and preferably 1% by mass to 30% by mass, with respect to the crosslinking agent.

[0085]

The light-absorbing compound is not particularly limited as long as it is a compound having absorption at an exposure wavelength to be used. A compound having an aromatic ring structure such as an anthracene ring, a naphthalene ring, a benzene ring, a quinoline ring, or a triazine ring is preferably used. A compound having a phenolic hydroxy group, a carboxy group, or a sulfonic acid group is preferably used from a viewpoint of not inhibiting solubility of the foreign substance-removing coating film in a removing liquid.

[0086]

Examples of the light-absorbing compound exhibiting large absorption for light having a wavelength of 248 nm include 1-naphthalenecarboxylic acid, 2-naphthalenecarboxylic acid, 1-naphthol, 2-naphthol, 1-

aminonaphthalene, 1-hydroxy-2-naphthalenecarboxylic acid, 3-hydroxy-2-naphthalenecarboxylic acid, 3,7-dihydroxy-2-naphthalenecarboxylic acid, 6-bromo-2-hydroxynaphthalene, 1,2-naphthalenedicarboxylic acid, 1,3-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 1,6-naphthalenedicarboxylic acid, 1,7-naphthalenedicarboxylic acid, 1,8-naphthalenedicarboxylic acid, 2,3-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 1,2-dihydroxynaphthalene, 1,3-dihydroxynaphthalene, 1,4-dihydroxynaphthalene, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 6-hydroxy-1-naphthalenecarboxylic acid, 1-hydroxy-2-naphthalenecarboxylic acid, 3-hydroxy-2-naphthalenecarboxylic acid, 6-hydroxy-2-naphthalenecarboxylic acid, 1-bromo-2-hydroxy-3-naphthalenecarboxylic acid, 1-bromo-4-hydroxy-3-naphthalenecarboxylic acid, 1,6-dibromo-2-hydroxy-3-naphthalenecarboxylic acid, 3-hydroxy-7-methoxy-2-naphthalenecarboxylic acid, 1-amino-2-naphthol, 1,5-dimercaptonaphthalene, 1,4,5,8-naphthalenetetracarboxylic acid, 3,5-dihydroxy-2-naphthalenecarboxylic acid, 1,4-dihydroxy-2-naphthalenecarboxylic acid, 2-ethoxy-1-

naphthalenecarboxylic acid, 2,6-dichloro-1-naphthol, methyl 2-hydroxy-3-naphthalenecarboxylate, methyl 6-hydroxy-2-naphthalenecarboxylate, methyl 3-hydroxy-7-methoxy-2-naphthalenecarboxylate, methyl 3,7-dihydroxy-2-naphthalenecarboxylate, 2,4-dibromo-1-naphthol, 1-bromo-2-naphthol, 2-naphthalenethiol, 4-methoxy-1-naphthol, 6-acetoxy-2-naphthalenecarboxylic acid, 1,6-dibromo-1-naphthol, 2,6-dibromo-1,5-dihydroxynaphthalene, 1-acetyl-2-naphthol, 9-anthracenecarboxylic acid, 1,4,9,10-tetrahydroxyanthracene, and 1,8,9-trihydroxyanthracene.

[0087]

Examples of the light-absorbing compound exhibiting large absorption for light having a wavelength of 193 nm include benzoic acid, 4-methylbenzoic acid, o-phthalic acid, m-phthalic acid, p-phthalic acid, 2-methoxybenzoic acid, isophthalic acid, terephthalic acid, 2-hydroxybenzoic acid, 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, 2-acetoxybenzoic acid, 2-aminobenzoic acid, 3-aminobenzoic acid, 4-aminobenzoic acid, trimesic acid, 1,4-benzenedicarboxylic acid, 2,3-dimethoxybenzoic acid, 2,4-dimethoxybenzoic acid, 2,5-dimethoxybenzoic acid, 2,4-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 4-acetyl benzoic acid, pyromellitic acid, trimesic anhydride, 2-s[bis-(4-hydroxyphenyl)-methyl]benzoic acid, 3,4,5-

trihydroxybenzoic acid, 2-benzophenone carboxylic acid, m-phenylbenzoic acid, 3-(4'-hydroxyphenoxy)benzoic acid, 3-phenoxybenzoic acid, phenol, 1,4-dihydroxybenzene, 1,3-dihydroxybenzene, 1,2-dihydroxybenzene, 2-methylphenol, 3-methylphenol, 4-methyphenol, 1,3,5-trihydroxybenzene, 2,2-bis-4-hydroxyphenylpropane, 2-hydroxybiphenyl, 2-aminophenol, 3-aminophenol, 4-aminophenol, and 4-benzyloxyphenol.

In order to suppress sublimation at the time of baking for forming the foreign substance-removing coating film, these light-absorbing compounds can be allowed to react with a polymer or a compound having one or more reactive groups before use.

[0088]

For example, in a case of a light-absorbing compound having a carboxyl group or a phenolic hydroxy group, there can be used a compound obtained by allowing the light-absorbing compound to react with a multifunctional epoxy compound such as tris(2,3-epoxypropyl) isocyanurate, 1,4-butanediol diglycidyl ether, 1,2-epoxy-4-(epoxyethyl)cyclohexane, glycerol triglycidyl ether, diethylene glycol diglycidyl ether, 2,6-diglycidyl phenyl glycidyl ether, 1,1,3-tris(p-(2,3-epoxypropoxy)phenyl)propane, 1,2-cyclohexanedicarboxylic acid diglycidyl ester, 4,4'-methylenebis(N,N-diglycidyl

aniline), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, trimethylolethane triglycidyl ether, bisphenol-A-diglycidyl ether, or pentaerythritol polyglycidyl ether, or with a polymer containing a structure having an epoxy group, such as glycidyl methacrylate.

[0089]

The above light-absorbing compounds can be used singly or in combination of two or more types thereof. When a light-absorbing compound is used, the content of the light-absorbing compound is, for example, 1 to 300 parts by mass or 1 to 200 parts by mass, and is, for example, 1 to 100 parts by mass or 5 to 100 parts by mass, with respect to 100 parts by mass of the water-soluble compound. When the content of the light-absorbing compound is 300 parts by mass or less with respect to 100 parts by mass of the water-soluble compound, solubility of the foreign substance-removing coating film in a removing liquid is excellent, and intermixing of the foreign substance-removing coating film with the adhesive layer is less likely to be caused.

[0090]

The composition for forming a foreign substance-removing coating film can contain a surfactant. Examples of the surfactant include nonionic surfactants including

polyoxyethylene alkyl ethers such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene cetyl ether, and polyoxyethylene oleyl ether, polyoxyethylene alkyl aryl ethers such as polyoxyethylene octylphenol ether and polyoxyethylene nonylphenol ether, polyoxyethylene polyoxypropylene block copolymers, sorbitan fatty acid esters such as 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-based surfactants such as EFTOP EF301, EF303, and EF352 (trade name, manufactured by Tochem Products Co., Ltd.), MEGAFAC F171 and F173 (trade name, manufactured by DIC Corporation), Fluorad FC430 and FC431 (trade name, manufactured by Sumitomo 3M Limited), Asahi Guard AG710, Surflon S-382, SC101, SC102, SC103, SC104, SC105, and SC106 (trade name, manufactured by AGC Corporation), and an organosiloxane polymer KP341 (trade name, manufactured by Shin-Etsu Chemical Co., Ltd.). The blending amount of these surfactants is usually 0.2% by mass or less, and preferably 0.1% by mass or less, with respect to all

components of the composition for forming a foreign substance-removing coating film. These surfactants may be added singly, or two or more types thereof can be added in combination.

[0091]

The composition for forming a foreign substance-removing coating film can contain silica particles. Examples of the silica particles include a silicone powder having a predetermined mean particle size and a silica sol containing silica having a predetermined mean particle size.

[0092]

Specific examples of the silicone powder include, but are not limited to, Silicone Powder KMP series KMP-600, KMP-601, KMP-602, KMP-605, and X-52-7030 (manufactured by Shin-Etsu Chemical Co., Ltd.).

[0093]

Specific examples of the colloidal silica (silica sol) include, but are not limited to, MA-ST-S (silica sol dispersed in methanol), MT-ST (silica sol dispersed in methanol), MA-ST-UP (silica sol dispersed in methanol), trade name MA-ST-M (silica sol dispersed in methanol), MA-ST-L (silica sol dispersed in methanol), IPA-ST-S (silica sol dispersed in isopropanol), IPA-ST (silica sol dispersed in isopropanol), IPA-ST-UP (silica sol dispersed in

isopropanol), IPA-ST-L (silica sol dispersed in isopropanol), IPA-ST-ZL (silica sol dispersed in isopropanol), NPC-ST-30 (silica sol dispersed in n-propyl cellosolve), PGM-ST (silica sol dispersed in 1-methoxy-2-propanol), DMAC-ST (silica sol dispersed in dimethylacetamide), XBA-ST (silica sol dispersed in xylene-n-butanol solvent mixture), trade name EAC-ST (silica sol dispersed in ethyl acetate), PMA-ST (silica sol dispersed in propylene glycol monomethyl ether acetate), MEK-ST (silica sol dispersed in methyl ethyl ketone), MEK-ST-UP (silica sol dispersed in methyl ethyl ketone), MEK-ST-L (silica sol dispersed in methyl ethyl ketone), and MIBK-ST (silica sol dispersed in methyl isobutyl ketone) (all manufactured by Nissan Chemical Corporation).

[0094]

(Foreign substance-removing coating film)

The foreign substance-removing coating film of the present invention is formed from the composition for forming a foreign substance-removing coating film of the present invention.

[0095]

The foreign substance-removing coating film of the present invention can be formed, for example, in the following manner.

The composition for forming a foreign substance-

removing coating film of the present invention is applied onto a semiconductor substrate by an appropriate application method such as methods using a spinner, a coater, and immersion, and then baked to form a foreign substance-removing coating film. Baking conditions are appropriately selected from a baking temperature of 80°C to 300°C, and a baking time of 0.3 to 60 minutes.

[0096]

The film thickness of the foreign substance-removing coating film is usually 5 nm to 1 μm, preferably 10 nm to 500 nm, and most preferably 15 nm to 300 nm.

[0097]

A dissolution rate of the foreign substance-removing coating film to be formed in a removing liquid as a rate of decrease in film thickness is, for example, 0.1 nm to 50 nm per second, preferably 0.2 nm to 40 nm per second, and more preferably 0.3 to 20 nm. When the dissolution rate is lower than this range, time required to remove the foreign substance-removing coating film becomes long, leading to deterioration of productivity.

[0098]

In the foreign substance-removing coating film formed from the composition for forming a foreign substance-removing coating film of the present invention, the dissolution rate of the foreign substance-removing coating

film in a removing liquid can be controlled by changing baking conditions at the time of the formation of the film. In a case of a constant baking time, as the baking temperature is increased, a foreign substance-removing coating film having a lower dissolution rate in a removing liquid can be formed.

[0099]

The foreign substance-removing coating film may be exposed to light after the film is formed. A surface of a wafer may be fully exposed to light, or may be exposed through a mask having a predetermined pattern. The light exposure can be performed using a KrF excimer laser (wavelength: 248 nm), an ArF excimer laser (wavelength: 193 nm), an F2 excimer laser (wavelength: 157 nm), or the like. After the light exposure, post exposure bake (PEB) can be performed as necessary.

[0100]

(Semiconductor Substrate)

The semiconductor substrate of the present invention has the foreign substance-removing coating film of the present invention thereon.

[0101]

A 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, and a compound semiconductor.

The shape of the semiconductor substrate is not particularly limited, and is, for example, a disk shape. Note that 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 only needs to be appropriately determined depending on a 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 only needs to be appropriately determined depending on a purpose of use of the semiconductor substrate and the like, and is not particularly limited, and is, for example, 100 to 1,000 mm.

[0102]

The semiconductor substrate may have a bump. The bump is a protruding terminal.

When the semiconductor substrate has a bump, the semiconductor substrate has the bump on a support base material 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 conditions of a bump height of about 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 alloy plating mainly containing Sn, 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.

[0103]

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

[0104]

(Method for manufacturing processed semiconductor substrate)

The method for manufacturing a processed semiconductor substrate of the present invention includes a first step, a second step, a third step, and a fourth step.

The first step is a step of manufacturing a laminate by bonding the semiconductor substrate of the present invention (semiconductor substrate having the foreign substance-removing coating film of the present invention) to a support base material with the foreign substance-removing coating film interposed therebetween.

The second step is a step of processing the laminate.

The third step is a step of peeling off the support base material from the laminate.

The fourth step is a step of cleaning the semiconductor substrate or the support base material with a removing liquid to remove the foreign substance-removing coating film.

In the first embodiment, the foreign substance-removing

coating film of the present invention having heat resistance is used as the foreign substance-removing coating film.

[0105]

<First step>

The first step is a step of manufacturing a laminate by bonding the semiconductor substrate of the present invention (semiconductor substrate having the foreign substance-removing coating film of the present invention) to a support base material with the foreign substance-removing coating film interposed therebetween.

[0106]

The support base material is not particularly limited as long as it is a member capable of supporting the semiconductor substrate when the laminate (for example, the semiconductor substrate) is processed, and examples thereof include a flexible support base material and a glass support base material.

[0107]

The shape of the support base material is not particularly limited, and examples thereof include a disk shape.

The thickness of the disk-shaped support base material only needs to 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 base material only needs to 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.

[0108]

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

[0109]

The first step is preferably a step of manufacturing a laminate by bonding the semiconductor substrate to the support base material with the foreign substance-removing coating film and an adhesive layer interposed therebetween.

[0110]

The adhesive layer is not particularly limited as long as the support base material can be peeled off from the laminate in the third step.

The adhesive layer can be formed with a known adhesive by a known method. As the adhesive, for example, an application type of wafer temporarily bonding adhesive described in, for example, WO 2015/190438 A, a temporarily bonding material of Thin Materials AG (Nissan Chemical

Corporation), a semiconductor wafer temporarily bonding material manufactured by Toray Industries, Inc., WaferBOND (registered trademark) CR-200 and HT-10.10 (manufactured by Brewer Science, Inc.) may be used, or a tape-shaped adhesive (for example, a back-grinding tape (for example, 3MTM temporarily fixing pressure-sensitive adhesive tape ATT-4025 (manufactured by 3M Japan Limited), E-series, P-series, S-series (trade names, manufactured by LINTEC Corporation), ICROS Tape (registered trademark) (manufactured by Mitsui Chemicals Tohcello, Inc.)), or a dicing tape (for example, Solvent Resistance Dicing Tape (trade name, manufactured by Nitto Denko Corporation), a temperature-sensitive adhesive sheet: Intelimer (registered trademark) tape (manufactured by Nitta Corporation), or Intelimer (registered trademark) tape (manufactured by Anchor Techno. Ltd.))) may be used.

A wafer adhesive applied in a specific wafer handling system (for example, Zero Newton (registered trademark) (manufactured by TOKYO OHKA KOGYO CO., LTD.)) may be used.

As the adhesive layer, one referred to as a pressure-sensitive adhesive layer, a pressure-sensitive adhesive tape, or a temporarily fixing material may be used. Examples of such an adhesive layer include a pressure-sensitive adhesive layer described in WO 2021/225163 A, an adhesive layer described in WO 2022/065376 A, and a light-

curable type adhesive layer described in WO 2022/065388 A.

[0111]

For example, the back-grinding tape includes a base material film, a pressure-sensitive adhesive layer, and a release film. As the base material film, a soft thermoplastic film such as an ethylene-vinyl acetate copolymer (EVA) has been used; however, for the purpose of improving the supporting properties of a wafer, the use of a rigid stretched film, such as polyethylene terephthalate (PET), is being attempted. Thereafter, further improvements have been made, and a design of lamination of two types of films having different moduli, for example, a design of lamination of PET and an ethylene copolymer and a design of lamination of polypropylene (PP) and an ethylene copolymer have been reported.

[0112]

The pressure-sensitive adhesive is generally acrylic. As the acrylic pressure-sensitive adhesive, a design is known in which a curing agent is allowed to react with an acrylic copolymer mainly containing a monomer having a low glass transition temperature, such as butyl acrylate, to cause crosslinking. Since the back-grinding tape is used by being bonded to a wafer circuit surface, and thus, there is a concern about contamination derived from the pressure-sensitive adhesive after the tape is peeled off.

Therefore, a design using an emulsion type pressure-sensitive adhesive is also reported assuming that the pressure-sensitive adhesive is removed by being cleaned with water even if the pressure sensitive adhesive remains, but it is difficult to completely remove the pressure-sensitive adhesive. Therefore, by forming the foreign substance-removing coating film of the present application on the circuit surface and then forming the adhesive layer, a foreign substance (residue of the adhesive layer) at the time of the subsequent peeling step can be completely removed by cleaning with a removing liquid, and a wiring portion such as a circuit is not damaged.

[0113]

The thickness of the adhesive layer is not particularly limited, and is, for example, 5 μm to 500 μm, preferably 10 μm to 300 μm, more preferably 20 μm to 200 μm, and particularly preferably 30 μm to 150 μm.

[0114]

Before performing the first step, the adhesive layer may be formed on the foreign substance-removing coating film, may be formed on the support base material, or may be formed on the semiconductor substrate.

[0115]

When the adhesive layer is not used, the support base material preferably has a pressure-sensitive adhesive

layer. The support base material includes, for example, a flexible support and a pressure-sensitive adhesive layer. Examples of the flexible support include a polyimide film. The pressure-sensitive adhesive layer is not particularly limited, and examples thereof include a layer formed from the pressure-sensitive adhesive described above.

[0116]

Bonding is performed, for example, under heating and pressurization.

A heating temperature is not particularly limited as long as it is room temperature (25°C) or higher, and is usually 50°C or higher, and from a viewpoint of avoiding excessive heating, the heating temperature is usually 220°C or lower, and in some modes, 170°C or lower.

A load is not particularly limited as long as the substrate and the layer can be bonded to each other and the substrate and the layer are not damaged, and is, for example, 0.5 to 50 kN.

A pressure during bonding is, for example, 0.1 to 20 N/mm^2. Note that the pressure refers to a force (load) per unit area (mm^2) of a substrate in contact with a jig to which a load is applied.

The degree of pressure reduction is not particularly limited as long as the substrate and the layer can be bonded to each other and the substrate and the layer are

not damaged, and is, for example, 10 to 10,000 Pa.

[0117]

When the adhesive layer is used, the layer structure of the laminate manufactured in the first step may be a semiconductor substrate/foreign substance-removing coating film/adhesive layer/support base material, for the purpose of removing a foreign substance as a peeling residue of the adhesive layer together with the foreign substance-removing coating film in the fourth step and achieving a state in which no foreign substance exists on the semiconductor substrate.

In addition, when the adhesive layer is used, the layer structure of the laminate manufactured in the first step may be a semiconductor substrate/adhesive layer/foreign substance-removing coating film/support base material, for the purpose of removing a foreign substance as a peeling residue of the adhesive layer together with the foreign substance-removing coating film in the fourth step and achieving a state in which no foreign substance exists on the support base material. In this case, it is easy to reuse the support base material.

In addition, the layer structure of the laminate manufactured in the first step may be a semiconductor substrate/foreign substance-removing coating film/adhesive layer/foreign substance-removing coating film/support base

material, for the purpose of, for example, achieving a state in which no foreign substance exists on the semiconductor substrate and the support base material.

[0118]

The laminate manufactured in the first step may have a laser release layer between the semiconductor substrate and the support base material. When the laminate has a laser release layer, in the third step, the support base material may be peeled off from the laminate, for example, by irradiation of the laser release layer with a laser. The laser is applied to the laser release layer, for example, from a side of the support base material having laser light transmissivity.

When the laminate has the laser release layer, the layer structure of the laminate manufactured in the first step may be, for example, a semiconductor substrate/foreign substance-removing coating film/laser release layer/adhesive layer/support base material, for the purpose of removing a foreign substance as a peeling residue of the laser release layer and adhesive layer, together with the foreign substance-removing coating film in the fourth step and achieving a state in which no foreign substance exists on the semiconductor substrate.

When the laminate has the laser release layer, the layer structure of the laminate manufactured in the first

step may be, for example, a semiconductor substrate/adhesive layer/laser release layer/foreign substance-removing coating film/support base material, for the purpose of removing a foreign substance as a peeling residue of the laser release layer and the adhesive layer, together with the foreign substance-removing coating film in the fourth step and achieving a state in which no foreign substance exists on the support base material. In this case, it is easy to reuse the support base material.

When a peeling residue of the laser release layer remains on the adhesive layer after peeling off the support base material from the laminate by irradiation of the laser release layer with a laser, a foreign substance derived from the laser release layer may be reattached to the semiconductor substrate or the support base material, or a time required to clean the adhesive layer may be increased. For the purpose of preventing these problems and removing the residue of the laser release layer on the adhesive layer, the layer structure of the laminate manufactured in the first step may be a semiconductor substrate/adhesive layer/foreign substance-removing coating film/laser release layer/support base material, or a semiconductor substrate/laser release layer/foreign substance-removing coating film/adhesive layer/support base material.

[0119]

<Second step>

The second step is a step of processing the laminate.

The processing in the second step is not particularly limited, and examples thereof include a process of polishing a semiconductor substrate, a process of forming a through electrode of a semiconductor substrate, and a process of connecting a semiconductor substrate to a second semiconductor substrate. The processing in the second step may include one of these processes, or may include two or more of the processes.

[0120]

<<Polishing process>>

The process of polishing a semiconductor substrate is not particularly limited as long as it is a process of polishing a surface of the semiconductor substrate opposite to a surface on the side of the foreign substance-removing coating film to thin the semiconductor substrate, and examples thereof include physical polishing using a polishing agent or a grindstone.

The polishing process can be performed using a general polishing device used for polishing a semiconductor substrate (for example, a silicon wafer).

The polishing process results in a reduction in the thickness of the semiconductor substrate, and a semiconductor substrate thinned to a desired thickness is

formed. The thickness of the thinned semiconductor substrate is not particularly limited, and may be, for example, 30 to 300 μm or 30 to 100 μm.

[0121]

<<Through electrode forming process>>

For example, a through electrode for achieving conduction between thinned semiconductor substrates when a plurality of thinned semiconductor substrates is stacked may be formed on the polished semiconductor substrate.

Therefore, a through electrode forming process of forming a through electrode on the polished semiconductor substrate may be included after the polishing process and before the peeling step.

A method for forming the through electrode on the semiconductor substrate is not particularly limited, and examples thereof include forming a through hole and filling the formed through hole with a conductive material.

The through hole is formed by, for example, photolithography.

The filling of the conductive material into the through hole is performed by, for example, a plating technique.

Note that, in the second step, the through electrode forming process may be performed without performing the polishing process.

[0122]

<<Connection process>>

The connection process is, for example, a process of connecting the semiconductor substrate to a second semiconductor substrate.

The second semiconductor substrate is not particularly limited, and examples thereof include the semiconductor substrates exemplified in the description of the semiconductor substrate described above.

The connection process is performed, for example, under heating. In addition, the connection process is performed, for example, under pressurization.

A heating temperature is not particularly limited, and is, for example, 100°C to 350°C.

[0123]

In the connection process, for example, wiring of the semiconductor substrate is electrically connected to wiring of the second semiconductor substrate. Such connection is performed, for example, by connecting ends of the wiring.

The material, shape, and structure of the wiring in the semiconductor substrate are not particularly limited.

The material, shape, and structure of the wiring in the second semiconductor substrate are not particularly limited.

[0124]

<Third step>

The third step is a step of peeling off the support base material from the laminate. The third step can be said to be a step of separating the semiconductor substrate from the support base material.

Examples of a peeling method include, but are not limited to, solvent peeling, peeling by light irradiation (laser light or non-laser light), mechanical peeling with equipment having a sharp portion (what is called a debonder), and manual peeling between the semiconductor substrate and the support base material.

In particular, when the laminate includes an adhesive layer, and the adhesive layer is an adhesive layer formed using an organic resin that absorbs light and causes deterioration necessary for improving peeling ability, the adhesive layer can be peeled off by, for example, laser irradiation from the support base material side.

The irradiation with laser light is performed using, for example, ultraviolet light having a wavelength of 190 nm to 400 nm or 190 nm to 600 nm (for example, 308 nm, 355 nm, or 532 nm).

The peeling can be performed by setting a processing energy density of pulse laser to about 50 to 500 mJ/cm^2.

When the laminate includes an adhesive layer, peeling usually occurs inside the adhesive layer or at an interface between the adhesive layer and an adjacent substrate or

layer (for example, a foreign substance-removing coating film). The expression that peeling occurs inside the adhesive layer means that the adhesive layer is cleaved.

[0125]

<Fourth step>

The fourth step is a step of cleaning the semiconductor substrate or the support base material with a removing liquid to remove the foreign substance-removing coating film.

For example, the foreign substance-removing coating film remains on the semiconductor substrate peeled off from the support base material. Thus, the foreign substance-removing coating film is removed with a removing liquid.

In the fourth step, for example, a foreign substance is removed together with the foreign substance-removing coating film.

In the fourth step, for example, a foreign substance as a peeling residue of the adhesive layer is removed together with the foreign substance-removing coating film.

[0126]

Examples of the removing liquid include the removing liquids exemplified in the description of the composition for forming a foreign substance-removing coating film of the present invention. Among these, water is preferable.

A cleaning method is not particularly limited, and

examples thereof include a method for immersing, in a removing liquid, the semiconductor substrate on which the foreign substance-removing coating film remains, and a method for spraying a removing liquid onto the semiconductor substrate on which the foreign substance-removing coating film remains.

Conditions for cleaning are not particularly limited. For example, the temperature of the cleaning liquid is 5°C to 50°C. A cleaning time is appropriately selected from 2 to 500 seconds or 3 to 400 seconds.

[0127]

For example, preferably, the foreign substance-removing coating film can be easily peeled off at room temperature (for example, 25°C) using a widely used 2.38% by mass tetramethylammonium hydroxide aqueous solution.

[0128]

An example of the method for manufacturing a processed semiconductor substrate will be described with reference to the drawings.

First, a semiconductor substrate 11 is prepared (Fig. 1A).

Next, a foreign substance-removing coating film 12 is formed on the semiconductor substrate 11 (Fig. 1B).

Next, the semiconductor substrate 11 including the foreign substance-removing coating film 12 illustrated in

Fig. 1B and a support base material 14 including a flexible support 14A and a pressure-sensitive adhesive layer 14B are bonded to each other such that the foreign substance-removing coating film 12 and the pressure-sensitive adhesive layer 14B face each other (Fig. 1C).

Next, a surface of the semiconductor substrate 11 opposite to the surface on the side of the foreign substance-removing coating film 12 is polished to thin the semiconductor substrate 11 (Fig. 1D).

Next, the support base material 14 is separated from the semiconductor substrate 11 (Figs. 1E and 1F).

A peeling residue 14C of the pressure-sensitive adhesive layer 14B remains on the foreign substance-removing coating film 12 after separation (Fig. 1F). Thus, the foreign substance-removing coating film 12 is removed with a removing liquid (Fig. 1G). This makes it possible to prevent the peeling residue 14C as a foreign substance from remaining on the semiconductor substrate 11.

[0129]

Another example of the method for manufacturing a processed semiconductor substrate will be described with reference to the drawings.

First, a semiconductor substrate 1 having wiring 1A is prepared (Fig. 2A).

Next, a foreign substance-removing coating film 2 is

formed on the semiconductor substrate 1 (Fig. 2B).

Meanwhile, a glass substrate 4 having an adhesive layer 3 formed on a surface thereof is prepared (Fig. 2C).

Then, the semiconductor substrate 1 including the foreign substance-removing coating film 2 illustrated in Fig. 2B and the glass substrate 4 including the adhesive layer 3 illustrated in Fig. 2C are bonded to each other such that the foreign substance-removing coating film 2 and the adhesive layer 3 face each other (Figs. 2D and 2E).

Next, a surface of the semiconductor substrate 1 opposite to the side of the surface on the foreign substance-removing coating film 2 is polished to thin the semiconductor substrate 1 (Fig. 2F). Then, the wiring 1A is exposed.

Next, the laminate illustrated in Fig. 2F and a second semiconductor substrate 5 having wiring 5A are bonded to each other such that a surface of the semiconductor substrate 1 opposite to the surface on the side of the foreign substance-removing coating film 2 faces a surface of the second semiconductor substrate 5 on which the wiring 5A is exposed (Figs. 2G and 2H).

Next, the adhesive layer 3 and the glass substrate 4 are separated from the semiconductor substrate 1 (Fig. 2I). The separation can be easily performed, for example, by irradiating the adhesive layer 3 with a laser to lower an

adhesive force of the adhesive layer 3.

A peeling residue 3A of the adhesive layer 3 remains on the foreign substance-removing coating film 2 after separation (Figs. 2I and 2J). Thus, the foreign substance-removing coating film 2 is removed with a removing liquid (Fig. 2K). This makes it possible to prevent peeling residue 3A as a foreign substance from remaining on the semiconductor substrate 1.

[0130]

The method for manufacturing a processed semiconductor substrate of the present invention can be suitably used for hybrid bonding to connect semiconductor substrates to each other.

[0131]

<Another embodiment>

An embodiment of the present invention may be a method for removing a foreign substance that is already present on a substrate for manufacturing a semiconductor. For example, as described in WO 2017/056746 A and WO 2020/008965 A, a composition for forming a substrate processing film and a method for processing a substrate are disclosed, which can efficiently remove minute particles from a substrate surface and easily remove a formed substrate processing film from the substrate surface, in a process of forming a substrate processing film on a surface

of a semiconductor substrate and removing a foreign substance from this substrate surface. The composition for forming a foreign substance-removing coating film of the present invention can also be used in a similar method/application to those described above.

[0132]

The above example will be specifically described below. In this application example, the composition for forming a foreign substance-removing coating film of the present invention is used as a composition for forming a coating film on a semiconductor substrate. First, a step of forming a coating film is performed. That is, the composition for forming a foreign substance-removing coating film is applied onto a semiconductor substrate to form a coating film. The semiconductor substrate may be what is called a solid substrate (flat) in an unprocessed state or a state in which various films are formed, or may be one in which the shape of wiring or the like is processed for manufacturing a semiconductor device. Examples of a coating method include rotational coating (spin coating), casting coating, and roll coating. Next, the coating film is heated (baked) and/or depressurized to efficiently remove a part or all of the solvent contained in the coating film, whereby solidification and/or curing of a solid content contained in the coating film can be

promoted. The term “solidification” as used herein means becoming solid, and the term “curing” means an increase in molecular weight (for example, crosslinking or polymerization) due to linkage of molecules. In this manner, the coating film is formed. At this time, particles attached to a circuit of the semiconductor substrate are incorporated into the coating film and efficiently separated from the circuit or the like. Next, a step of removing the coating film is performed. That is, the coating film is entirely removed from the semiconductor substrate by supplying a removing liquid that dissolves the coating film onto the coating film. As a result, the particles are removed from the semiconductor substrate together with the coating film.

Examples

[0133]

Next, the contents of the present invention will be specifically described with reference to Examples, but the present invention is not limited thereto.

[0134]

<Example 1>

To 1.30 g of hydroxypropyl cellulose (HPC-SSL, Nippon Soda Co., Ltd.), 98.70 g of propylene glycol monomethyl ether was added, and then the resulting mixture was

filtered using a PTFE syringe filter having a pore size of 0.20 μm to prepare a composition for forming a foreign substance-removing coating film.

[0135]

<Example 2>

To 2.00 g of hydroxypropyl-β-cyclodextrin (Tokyo Chemical Industry Co., Ltd.), 98.00 g of propylene glycol monomethyl ether was added, and then the resulting mixture was filtered using a PTFE syringe filter having a pore size of 0.20 μm to prepare a composition for forming a foreign substance-removing coating film.

[0136]

<Example 3>

To 0.90 g of polyacrylic acid (Sigma-Aldrich Co. LLC), 99.10 g of propylene glycol monomethyl ether was added, and then the resulting mixture was filtered using a PTFE syringe filter having a pore size of 0.20 μm to prepare a composition for forming a foreign substance-removing coating film.

[0137]

<Example 4>

To 1.50 g of tannic acid (FUJIFILM Wako Pure Chemical Corporation), 98.50 g of propylene glycol monomethyl ether was added, and then the resulting mixture was filtered using a PTFE syringe filter having a pore size of 0.20 μm

to prepare a composition for forming a foreign substance-removing coating film.

[0138]

<Example 5>

To 1.00 g of polyvinylpyrrolidone K-30 (Nippon Shokubai Co., Ltd.), 99.99 g of propylene glycol monomethyl ether was added, and then the resulting mixture was filtered using a PTFE syringe filter having a pore size of 0.20 μm to prepare a composition for forming a foreign substance-removing coating film.

[0139]

<Example 6>

To 0.70 g of polyvinylpyrrolidone K-90 (Nippon Shokubai Co., Ltd.), 99.30 g of propylene glycol monomethyl ether was added, and then the resulting mixture was filtered using a PTFE syringe filter having a pore size of 0.20 μm to prepare a composition for forming a foreign substance-removing coating film.

[0140]

<Example 7>

To 1.00 g of Ganex P-904 LC (Ashland Inc.), 99.99 g of propylene glycol monomethyl ether was added, and then the resulting mixture was filtered using a PTFE syringe filter having a pore size of 0.20 μm to prepare a composition for forming a foreign substance-removing coating film.

[0141]

<Example 8>

To 1.05 g of PVP/VA S-630 (Ashland Inc.), 98.95 g of propylene glycol monomethyl ether was added, and then the resulting mixture was filtered using a PTFE syringe filter having a pore size of 0.20 μm to prepare a composition for forming a foreign substance-removing coating film.

[0142]

<Example 9>

To 0.90 g of poly(2-hydroxyethyl acrylate) synthesized according to Synthesis Example 1 of WO 2004/074938, 99.10 g of propylene glycol monomethyl ether was added, and then the resulting mixture was filtered using a PTFE syringe filter having a pore size of 0.20 μm to prepare a composition for forming a foreign substance-removing coating film.

[0143]

[Water dissolution test]

Each of the compositions for forming a foreign substance-removing coating film prepared in Examples 1 to 9 was applied (spin-coated) onto a silicon wafer with a spin coater. The applied silicon wafer was heated on a hot plate at 140°C for one minute to form a coating film having a thickness of 40 nm. Next, in order to confirm water solubility of the coating film, the silicon wafer after

formation of the coating film was immersed in ultrapure water for 30 seconds. The film thicknesses of the coating film before and after immersion in water were measured with a light interference film thickness meter (product name: Lambda Ace VM-3210, manufactured by SCREEN Holdings Co., Ltd.).

The water solubility was evaluated by calculating a film thickness reduction ratio (%) of the coating film removed by water immersion according to the following calculation formula.

Film thickness reduction ratio (%) = ((A - B) ÷ A) × 100

A: Film thickness before water immersion

B: Film thickness after water immersion

The results are presented in Table 1. Note that if the film thickness reduction ratio is about 99% or more, it can be said that the film has sufficient water solubility.

[0144]

[Table 1]

	Film thickness reduction ratio
Example 1	> 99%
Example 2	> 99%
Example 3	> 99%
Example 4	> 99%
Example 5	> 99%
Example 6	> 99%

Example 7	> 99%
Example 8	> 99%
Example 9	> 99%

[0145]

From the above results, it was confirmed that the compositions for forming a foreign substance-removing coating film of Examples 1 to 9 were soluble in water.

CLAIMS

[claim 1] A composition for forming a foreign substance-removing coating film, the composition comprising a water-soluble compound and a solvent and being capable of forming a coating film that can be removed by water.

[claim 2] The composition for forming a foreign substance-removing coating film according to claim 1, wherein the water-soluble compound is at least one selected from the group consisting of cellulose and a derivative thereof, cyclodextrin and a derivative thereof, polyacrylic acid, a polymer having a structural unit derived from hydroxyalkyl (meth)acrylate, tannic acid, and a polymer having a lactam structure.

[claim 3] The composition for forming a foreign substance-removing coating film according to claim 1, wherein a content of the water-soluble compound is 98% by mass or more with respect to film constituent components.

[claim 4] A foreign substance-removing coating film formed from the composition for forming a foreign substance-removing coating film according to any one of claims 1 to 3.

[claim 5] A semiconductor substrate comprising the foreign substance-removing coating film according to claim 4.

[claim 6] A method for manufacturing a processed

semiconductor substrate, comprising:

a first step of manufacturing a laminate by bonding the semiconductor substrate according to claim 5 to a support base material with the foreign substance-removing coating film interposed therebetween;

a second step of processing the laminate;

a third step of peeling off the support base material from the laminate; and

a fourth step of cleaning the semiconductor substrate or the support base material with a removing liquid to remove the foreign substance-removing coating film.

[claim 7] The method for manufacturing a processed semiconductor substrate according to claim 6, wherein in the fourth step, a foreign substance is removed together with the foreign substance-removing coating film.

[claim 8] The method for manufacturing a processed semiconductor substrate according to claim 6, wherein the first step is a step of manufacturing a laminate by bonding the semiconductor substrate to the support base material with the foreign substance-removing coating film and an adhesive layer interposed therebetween.

[claim 9] The method for manufacturing a semiconductor substrate according to claim 8, wherein in the fourth step, a foreign substance as a peeling residue of the adhesive layer is removed together with the foreign substance-

removing coating film.

[claim 10] The method for manufacturing a processed semiconductor substrate according to claim 6, wherein the processing includes connecting the semiconductor substrate to a second semiconductor substrate.