

DESCRIPTION

Title of Invention

PHOTOSENSITIVE ADHESIVE COMPOSITION AND SEMICONDUCTOR DEVICE

5

Technical Field

[0001]

The present invention relates to a photosensitive adhesive composition and a semiconductor device.

10

Background Art

[0002]

Thus far, the integration degree of semiconductor devices has been increasing every year according to a prediction called a so-called Moore's law. However, in recent years, the miniaturization of structures which are formed in semiconductor elements has almost reached the physical limit, and the pace of boosting the integration of semiconductor devices has slowed down. Therefore, there has been a proposal of a method for increasing the apparent integration degree of semiconductor devices by laminating a plurality of semiconductor elements instead of increasing the density of a single semiconductor element.

15

20

[0003]

25

A plurality of semiconductor elements are laminated by,

for example, adhering semiconductor elements (silicon pieces) together through a film-like adhesive (for example, refer to PTL 1).

[0004]

5 In addition, in recent years, for example, in response to the distribution of mobile devices, there has been a demand for the size reduction or thickness reduction of semiconductor devices as well as an increase in the integration of semiconductor devices. Therefore, in semiconductor devices
10 having a structure in which a plurality of semiconductor elements are laminated together as described above, there are attempts to reduce the thicknesses of the respective semiconductor elements.

[0005]

15 A thin semiconductor element can be formed by reducing the thickness of a wafer, which will become the semiconductor element, by means of etching. In addition, the etching is carried out in a state in which a film-like adhesive is adhered to the wafer in order to prevent the damage of the wafer.

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Citation List

Patent Literature

[0006]

[PTL 1] Japanese Unexamined Patent Application

25 Publication No. 2004-051970

Summary of Invention

Technical Problem

[0007]

5 However, the present inventors found a problem in that,
if the etching time becomes long when etching is carried out
as described above, air bubbles (voids) are generated in the
interface between the wafer and the film-like adhesive. When
the above-described problem is caused, if the wafer is divided
10 into small pieces, and then semiconductor elements are adhered
together through the film-like adhesive, the adhesiveness
(adhesion properties) between the semiconductor elements
degrades due to the air bubbles. As a result, there are cases
in which the reliability of semiconductor devices degrades.

15 [0008]

An object of the present invention is to provide a
photosensitive adhesive composition capable of enhancing
adhesiveness (adhesion properties) between semiconductor
elements and a highly reliable semiconductor device including
20 a laminated semiconductor element obtained by adhering
semiconductor elements together through a cured substance of
the above-described photosensitive adhesive composition.

Solution to Problem

25 [0009]

The above-described objects are achieved by the present inventions (1) to (18) below.

(1) A photosensitive adhesive composition including:

(A) an alkali-soluble resin;

5 (B) a photo-acid-generating agent;

(C) an epoxy compound; and

(D) a phenolic compound having a melting point of 50°C to 150°C.

[0010]

10 (2) The photosensitive adhesive composition according to (1), further including: a phenolic compound (X) having a melting point higher than that of the phenolic compound (D).

[0011]

(3) The photosensitive adhesive composition according to 15 (2), in which the melting point of the phenolic compound (X) is 151°C to 250°C.

[0012]

(4) The photosensitive adhesive composition according to 20 (2) or (3), in which the phenolic compound (X) includes a phenolic compound having a plurality of phenolic skeletons.

[0013]

(5) The photosensitive adhesive composition according to 25 (4), in which the phenolic compound having the plurality of the phenolic skeletons has a substituent which has a cyclic structure and is bonded to at least one of the phenolic skeletons.

[0014]

(6) The photosensitive adhesive composition according to any one of (1) to (5), in which the phenolic compound (D) includes at least one of a phenolic compound having a substituent
5 including an aliphatic hydrocarbon group and a phenolic compound having a plurality of phenolic skeletons.

[0015]

(7) The photosensitive adhesive composition according to (6), in which a hydroxyl group equivalent of the phenolic
10 compound having the substituent including the aliphatic hydrocarbon group is 150 to 250 g/eq.

[0016]

(8) The photosensitive adhesive composition according to (6) or (7), in which the plurality of the phenolic skeletons
15 of the phenolic compound (D) form a linked polycyclic structure.

[0017]

(9) The photosensitive adhesive composition according to any one of (6) to (8), in which a hydroxyl group equivalent of the phenolic compound having the plurality of the phenolic
20 skeletons is 50 to 150 g/eq.

[0018]

(10) The photosensitive adhesive composition according to any one of (1) to (9), in which the alkali-soluble resin (A) includes a cyclic olefin-based resin.

25 [0019]

(11) The photosensitive adhesive composition according to (10), in which the cyclic olefin-based resin includes a norbornene-based resin.

[0020]

5 (12) The photosensitive adhesive composition according to any one of (1) to (11), in which the alkali-soluble resin (A) has an acidic group.

[0021]

10 (13) The photosensitive adhesive composition according to any one of (1) to (12), in which the alkali-soluble resin (A) has a linear substituent having 2 to 30 carbon atoms.

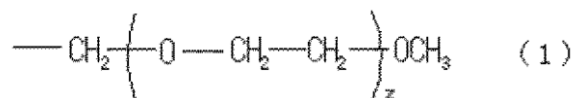
[0022]

15 (14) The photosensitive adhesive composition according to (13), in which the linear substituent has an alkyl ether structure.

[0023]

(15) The photosensitive adhesive composition according to (13) or (14), in which the linear substituent is a group represented by Formula (1) below.

20 [0024]



(In the Formula (1), z represents an integer of 1 or more and 10 or less)

[0025]

(16) The photosensitive adhesive composition according to any one of (13) to (15), in which the alkali-soluble resin (A) includes 20 to 60 mol% of a repeating unit having the linear substituent.

5 [0026]

(17) The photosensitive adhesive composition according to any one of (1) to (16), in which the epoxy compound (C) has two or more glycidyl groups.

[0027]

10 (18) A semiconductor device including a laminated semiconductor element, in which the laminated semiconductor element has a plurality of semiconductor elements and a cured substance of the photosensitive adhesive composition according to any one of (1) to (17) which is provided between the
15 semiconductor elements and joins the semiconductor elements.

Advantageous Effects of Invention

[0028]

When used as an adhesive layer that adheres semiconductor
20 elements together, a cured substance of the photosensitive adhesive composition of the present invention is capable of reducing the generation of air bubbles (voids) in the interfaces between the semiconductor element and the adhesive layer and, even when air bubbles are generated in the interfaces, is capable
25 of removing the generated air bubbles. Therefore, it is

possible to enhance the adhesiveness (adhesion properties)
between semiconductor elements.

[0029]

In addition, according to the present invention, a highly
5 reliable semiconductor device including a laminated
semiconductor element in which the adhesiveness between
semiconductor elements is high can be obtained.

Brief Description of Drawings

10 [0030]

FIG. 1 is a cross-sectional view illustrating an example
of a semiconductor device of the present invention.

FIG. 2 is a view for describing a method for manufacturing
the semiconductor device illustrated in FIG. 1.

15 FIG. 3 is a view for describing a method for manufacturing
the semiconductor device illustrated in FIG. 1.

FIG. 4 is a view for describing a method for manufacturing
the semiconductor device illustrated in FIG. 1.

FIG. 5 is a view for describing a method for manufacturing
20 the semiconductor device illustrated in FIG. 1.

Description of Embodiments

[0031]

Hereinafter, a photosensitive adhesive composition and a
25 semiconductor device of the present invention will be described

in detail on the basis of preferred embodiments illustrated in the accompanying drawings.

[0032]

<Semiconductor device>

5 First, an example of the semiconductor device of the present invention will be described.

[0033]

FIG. 1 is a cross-sectional view illustrating an example of the semiconductor device of the present invention.

10 A semiconductor device 10 illustrated in FIG. 1 is an example having a ball grid array (BGA)-type semiconductor package. The semiconductor device 10 has a plurality of semiconductor chips 20 (semiconductor elements) laminated together, adhesive layers 601 adhering the semiconductor chips
15 20 together, a package substrate 30 supporting the semiconductor chips 20, an adhesive layer 101 adhering the semiconductor chip 20 and the package substrate 30, a mold portion 50 sealing the semiconductor chips 20, and solder balls 80 provided below the package substrate 30. Hereinafter, the constitutions of the
20 respective portions will be sequentially described.

[0034]

The semiconductor chip 20 may be any type of element, and examples thereof include memory elements such as NAND (Not AND) flash memories and dynamic random access memories (DRAM),
25 integrated circuit elements such as integrated circuits (IC)

and large scale integration (LSI), and the like.

[0035]

The constituent material of the semiconductor chip 20 is not particularly limited, and examples thereof include
5 single-crystal materials such as silicon, silicon carbide, and compound semiconductors, polycrystalline materials, amorphous materials, and the like.

[0036]

A plurality of the semiconductor chips 20 are laminated
10 together in a slightly misaligned manner in the in-plane direction and constitute a chip laminate 200 (laminated semiconductor element). In addition, the semiconductor chips 20 are adhered together through the adhesive layer 601. The adhesive layer 601 is also provided on the top surface of the
15 chip laminate 200. In addition, the adhesive layer 601 is constituted of a cured substance of the photosensitive adhesive composition of the present invention (a cured photosensitive adhesive composition). Meanwhile, the photosensitive adhesive composition will be described below in detail.

20 [0037]

The package substrate 30 illustrated in FIG. 1 is a build-up substrate including a core substrate 31, an insulating layer 32, a solder resist layer 33, wires 34, and conductive vias 35.

25 [0038]

The core substrate 31 is a substrate supporting the package substrate 30 and is constituted of, for example, a composite material obtained by filling a glass cloth with a resin material.

[0039]

5 In addition, the insulating layer 32 is an interlayer insulating layer insulating the wires 34 from each other or the wires 34 and the conductive vias 35 and is constituted of, for example, a resin material. In addition, the solder resist layer 33 is a surface protective layer protecting wires formed on the
10 outer surface of the package substrate 30 and is constituted of, for example, a resin material.

[0040]

In addition, the wires 34 and the conductive vias 35 are respectively transmission paths of electric signals and are
15 constituted of, for example, a metallic material such as Au, Ag, Cu, Al, Ni, or an alloy thereof.

[0041]

The solder balls 80 are electrically connected with the wires 34 and function as electrodes for connecting the wires
20 34 to other electric circuits by being fused to external electric circuits.

[0042]

The chip laminate 200 formed by laminating a plurality of the semiconductor chips 20 is mounted on the top surface of the
25 package substrate 30. The chip laminate 200 and the package

substrate 30 are adhered together using the adhesive layer 101.

[0043]

In addition, some of the wires 34 in the package substrate 30 are exposed on the top surface of the package substrate 30 and constitute exposed portions. These exposed portions and electrode portions of the respective semiconductor chips 20 are connected to each other using bonding wires 70.

[0044]

The mold portion 50 illustrated in FIG. 1 is constituted so as to cover the side surfaces and the top surface of the chip laminate 200 and cover the entire top surface of the package substrate 30. Therefore, it is possible to protect the chip laminate 200 from the external environment. The above-described mold portion 50 is constituted of, for example, a variety of resin materials such as epoxy-based resins and phenolic resins.

[0045]

<Method for manufacturing semiconductor device>

Next, the method for manufacturing the semiconductor device 10 will be described.

[0046]

FIGS. 2 to 5 are respectively views for describing the method for manufacturing the semiconductor device illustrated in FIG. 1. Meanwhile, in the following description, for the convenience of description, the upper side of FIGS. 2 to 5 will

be referred to as "up" and the lower side will be referred to as "down".

[0047]

The method for manufacturing the semiconductor device 10 has an application step of applying a liquid including a photosensitive adhesive composition onto a wafer (semiconductor substrate) so as to obtain a coated film, an exposure step of exposing the obtained coated film, a development step of patterning the coated film by means of development, a treatment step of carrying out an etching treatment and an ashing treatment on the wafer provided with the coated film, a back grinding step of grinding the back surface of the wafer, a dicing step of dividing the wafer into a plurality of semiconductor chips by means of dicing, and a mounting step of picking up the semiconductor chip, mounting the semiconductor chip on a package substrate, then, picking up another semiconductor chip, and pressing the semiconductor chip onto the previously-mounted semiconductor chip (member to be joined). Hereinafter, the respective steps will be sequentially described.

20 [0048]

[1] Application step

First, a wafer 201 (refer to FIG. 2(a)) for cutting out the semiconductor chips 20 is prepared, and a liquid including a photosensitive adhesive composition is applied thereon (on one surface side). Therefore, a coated film 601a is formed on

25

the wafer 201 as illustrated in FIG. 2(b). Meanwhile, on the wafer 201, semiconductor circuits, electrode pads, and the like are formed in advance in accordance with the respective semiconductor chips 20. That is, the wafer 201 is subjected to a so-called preceding step of the semiconductor-manufacturing step. Therefore, when the wafer 201 is cut and divided into small pieces in steps described below, a plurality of semiconductor chips 20 can be cut out from the wafer 201.

[0049]

The application method is not particularly limited, and examples thereof include a spin coating method, a spray coating method, an ink jet method, a roll coating method, a printing method, and the like.

[0050]

If necessary, the applied liquid including a photosensitive adhesive composition (liquid-form coating) may be dried by means of heating. In this case, the heating temperature is preferably 70°C to 160°C and more preferably 80°C to 150°C. In addition, the heating time is appropriately set depending on the heating temperature and is preferably 5 seconds to 30 minutes and more preferably 10 seconds to 15 minutes.

[0051]

The liquid including a photosensitive adhesive composition is prepared by appropriately adding a solvent or the like capable of dissolving the photosensitive adhesive

composition of the present invention to the photosensitive adhesive composition of the present invention. In addition, the solvent being used is preferably a solvent that can be volatilized and removed when being heated in steps described below. Specific examples of such solvent include toluene, xylene, benzene, dimethylformamide, tetrahydrofuran, ethyl cellosolve, ethyl acetate, N-methyl-2-pyrrolidone, γ -butyrolactone, N,N-dimethylacetoamide, dimethylsulfoxide, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, methyl lactate, ethyl lactate, butyl lactate, methyl ethyl ketone, cyclohexanone, tetrahydrofuran, methyl-1,3-butylene glycol acetate, 1,3-butylene glycol-3-monomethyl ether, methyl pyruvate, ethyl pyruvate, methyl-3-methoxypropionate, and the like. One of these solvents or a combination of two or more solvents can be used. Among these, solvents including any of propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, γ -butyrolactone, and cyclohexanone are particularly preferred since the solvents have a high solubility and are easily volatilized and removed.

[0052]

[2] Exposure step

Next, a mask 4 is provided so as to come into contact with

the coated film 601a formed on the wafer 201, and an exposure treatment is carried out on desired regions (exposure regions) in the coated film 601a (refer to FIG. 2(c)). Therefore, a light reaction is caused in the coated film 601a in the exposure regions, and the coated film is latently patterned (a latent image is formed).

[0053]

As light that is used in the exposure treatment, electromagnetic waves of a variety of wavelengths, particle beams, and the like are used, and examples thereof include ultraviolet rays such as i rays, visible light rays, laser light, X rays, electron beams, and the like. Among these, ultraviolet rays or visible light rays having a wavelength of approximately 200 to 700 μm are preferably used. In addition, the exposure treatment can be carried out in, for example, an air atmosphere, an inert gas atmosphere, or a reduced-pressure atmosphere.

[0054]

In this exposure step, a mask provided away from the coated film 601a may also be used instead of the mask 4 provided in contact with the coated film 601a. Meanwhile, in a case in which a highly directive X ray or electron beam is used in the exposure treatment, the mask may not be used.

[0055]

The exposure amount in the exposure treatment is appropriately set depending on the thickness of the coated film

601a, the sensitivity of the photosensitive adhesive composition, and the like and, as an example, is preferably approximately 30 to 3,000 mJ/cm².

[0056]

5 [3] Development step

Next, a development treatment is carried out on the coated film 601a on which the exposure treatment has been carried out. Therefore, the exposed portions (the exposure region in the coated film 601a) are removed, and desired patterning is carried
10 out as illustrated in FIG. 2(d). The above-described development treatment enables to expose, for example, electrode pads for connecting the bonding wires 70 to the semiconductor chips 20. In addition, it is possible to remove the coated film 601a on dicing lines which serves as cutting margins in the dicing
15 step described below.

[0057]

In the development treatment, a developer is brought into contact with the coated film 601a on which the exposure treatment has been carried out. Therefore, the coated film 601a in the
20 exposed portions is removed by being dissolved in the developer. Therefore, opening portions 601b are formed in the coated film 601a. Examples of the developer include carbonates of alkali metal, hydroxides of alkali metal, alkaline developers such as tetraammonium hydroxide, organic developers such as dimethyl
25 formamide and N-methyl-2-pyrrolidone, and the like. Among

these, alkaline developers are particularly preferably used as the developer. Meanwhile, alkaline developers cause small loads on the environment and do not easily generate residues.

[0058]

5 In addition, examples of the method for supplying the developer include spraying, paddling, immersion, ultrasonic waves, and the like.

[0059]

 Meanwhile, in the present embodiment, the coated film 601a
10 has so-called positive photosensitivity, but the coated film 601a may have so-called negative photosensitivity.

[0060]

[4] Treatment step

 Next, an etching treatment is carried out on the wafer 201
15 provided with the coated film 601a. At this time, the coated film 601a including the opening portions 601b functions as an etching mask. Therefore, the etching treatment is selectively carried out on the surface (top surface) of the wafer 201 in regions corresponding to the opening portions 601b. As a result,
20 in a case in which a passivation film is formed on the surface of the wafer 201, it is possible to remove the passivation film and expose the electrode pads for connecting the bonding wires 70.

[0061]

25 Examples of the etching treatment include a plasma etching

treatment (dry etching treatment) by means of the supply of plasma to the wafer 201 as illustrated in FIG. 3(f), a variety of wet etching treatments, and the like. The plasma etching treatment can be carried out under generally-known conditions and, for example, can be carried out under conditions in which a fluorine compound gas (CF_4 or CHF_3), a mixture gas of a fluorine compound gas (CF_4 or CHF_3) and an oxygen gas (O_2), or a mixture gas of a fluorine compound gas (CF_4 or CHF_3) and an argon gas (Ar) is used as the treatment gas, the output is 200 to 2,000 W, the time is 0.2 to 15 minutes, and the gas flow rate is 50 to 1,000 sccm.

[0062]

After that, if necessary, an ashing treatment is carried out on the wafer 201 provided with the coated film 601a. Therefore, it is possible to remove treatment residues and the like generated due to the etching treatment and clean the coated film 601a surface or the electrode pad surfaces. As a result, it is possible to increase the adhesive force of the adhesive layer 601 described below or increase the joining force of the bonding wires 70 to the electrode pads.

[0063]

Examples of the ashing treatment include a plasma treatment, a wet treatment in which a chemical is used, and the like. The plasma treatment can be carried out under conditions in which an oxygen gas (O_2), a mixture gas of an oxygen gas (O_2)

and an argon gas (Ar), or the like is used as the treatment gas, the output is 200 to 2,000 W, the time is 0.2 to 15 minutes, and the gas flow rate is 50 to 1,000 sccm.

[0064]

5 [5] Back grinding step

Next, a back grind film 90 is attached onto the coated film 601a as illustrated in FIG. 3(g). The back grind film 90 supports the wafer 201 during a back grinding treatment and suppresses the generation of disadvantages such as defects or cracks in
10 the wafer 201.

[0065]

Next, the back surface (the other surface side) of the wafer 201 is ground (back grinding treatment). Therefore, the broken line portion in FIG. 3(h) is removed, whereby the
15 thickness of the wafer 201 can be thinned. Although varying depending on the original thickness of the wafer 201, the thickness of the wafer 201 can be thinned to approximately 20 to 100 μm by means of the back grinding treatment.

In the back grinding treatment, for example, a device
20 called a back grinding wheel is used.

[0066]

Meanwhile, the adhesive layer 601 developing a sufficient adhesive force to the semiconductor chips 20 can be cut out by cutting the coated film 601a obtained from the photosensitive
25 adhesive composition of the present invention. Additionally,

the coated film 601a obtained from the photosensitive adhesive composition of the present invention also develops a sufficient adhesive force to the back grind film 90. Therefore, when the back grind film 90 is attached onto the coated film 601a, the back grind film 90 is capable of reliably supporting the coated film 601a and the wafer 201. Therefore, the position of the wafer 201 is not deviated from the back grind film 90 during the back grinding treatment, and thus it is possible to carry out a high-accuracy back grinding treatment on the wafer 201.

Therefore, unevenness in the thickness of the wafer 201 can be suppressed. As a result, it is possible to obtain the semiconductor chips 20 which are not easily inclined when laminated.

[0067]

In addition, in the case of the present embodiment, the coated film 601a is formed on the wafer 201 which is to be subjected to the back grinding step, and the back grinding treatment is carried out in that state. As described above, the coated film 601a has mechanical characteristics enabling the reliable adhesion between the semiconductor chips 20.

Therefore, the coated film 601a also has a function of mechanically supporting the wafer 201 by being interposed between the wafer 201 and the back grind film 90. In addition, the coated film 601a is formed on the wafer 201 in a liquid-phase state and then slightly cured and thus has favourable adhesion

properties to the wafer 201. Therefore, when the back grinding treatment is carried out on the wafer 201 provided with the coated film 601a, the treatment becomes more uniform.

[0068]

5 As the back grind film 90, a UV peelable back grind film can be used. The use of the above-described back grind film 90 enables a significant decrease in the adhesive force between the back grind film 90 and the coated film 601a merely by carrying out a UV irradiation treatment on the coated film 601a through
10 the back grind film 90 when it is necessary to peel the back grind film 90 off from the coated film 601a after the back grinding treatment. As a result, it is possible to smoothly peel the back grind film 90 from the coated film 601a without causing a huge burden on the coated film 601a.

15 [0069]

[6] Dicing step

Next, a dicing treatment is carried out on the wafer 201. Therefore, the wafer 201 is divided into a plurality of the semiconductor chips 20 (divided by cutting).

20 [0070]

The dicing treatment is carried out in a state in which the wafer 201 is attached to a dicing die attach film or a dicing film. This dicing die attach film or the dicing film is used to fix the wafer 201 during the dicing treatment.

25 [0071]

FIG. 3(i1) and FIG. 3(i2) are respectively views illustrating examples in which a dicing film 100a is attached to the back surface side of the wafer 201 which is ground in the back grinding step. Meanwhile, FIG. 3(i1) illustrates the wafer 201 for cutting out the semiconductor chip 20 which is used as the lowest layer (a layer closest to the package substrate 30) of the chip laminate 200 and the like. On the other hand, FIG. 3(i2) illustrates the wafer 201 for cutting out the semiconductor chip 20 which is used as a layer other than the lowest layer of the chip laminate 200 and the like.

[0072]

In FIG. 3(i1), a dicing die attach film 100 which is a laminate of the dicing film 100a and a die attach film 100b is attached to the back surface of the wafer 201. On the other hand, in FIG. 3(i2), the dicing film 100a is attached to the back surface of the wafer 201.

[0073]

Next, as illustrated in FIG. 4(j1) and FIG. 4(j2), the back grind film 90 is peeled off from the coated film 601a.

[0074]

Next, a dicing treatment is carried out on the wafer 201 provided with the coated film 601a. The dicing treatment is carried out so that a dicing blade 110 reaches the dicing film 100a as illustrated in FIGS. 4(k1) and 4(k2). As a result, the coated film 601a, the wafer 201, and the die attach film 100b

are respectively divided into small pieces, and, as illustrated in FIG. 4(k1), individual pieces 21 formed of the adhesive layer 601, the semiconductor chip 20 (first semiconductor element), and the adhesive layer 101 laminated together are cut out. Similarly, the coated film 601a and the wafer 201 are respectively divided into small pieces, and, as illustrated in FIG. 4(k2), individual pieces 22 formed of the adhesive layer 601 and the semiconductor chip 20 (second semiconductor element) laminated together are cut out.

10 [0075]

Meanwhile, in the present embodiment, the dicing treatment is carried out on one wafer 201 (a joined body of a plurality of the semiconductor chips 20), thereby cutting out a plurality of semiconductor chips 20. However, the present invention is not limited thereto, and a plurality of the semiconductor chips 20 that have been divided into small pieces in advance may be used. In this case, the dicing step may not be carried out. In addition, in a case in which the wafer 201 or the semiconductor chip 20 is thin from the beginning, the back grinding step may not be carried out.

[0076]

In addition, the step sequence of the back grinding step and the dicing step is not limited to the above-described sequence, and the sequence may be reversed. That is, it is possible to carry out the dicing treatment on the wafer 201 and

then carry out the back grinding treatment.

[0077]

[7] Mounting step

FIG. 4(L1) and FIG. 4(L2) are respectively views
5 illustrating examples in which the cut-out individual piece 21
and individual piece 22 are picked up using a collet 121 of a
bonding device 120.

[0078]

First, the individual piece 21 is picked up using the
10 collet 121 of the bonding device 120 and is pressed (mounted)
onto the package substrate 30 as illustrated in FIG. 5(a). At
this time, the back surface of the semiconductor chip 20 and
the package substrate 30 are adhered to each other through the
adhesive layer 101. Meanwhile, this adhesive layer 101 is
15 formed by dividing the die attach film 100b into small pieces.
However, the adhesive layer 101 may be formed of, for example,
a non-cured substance or semi-cured substance of the
photosensitive adhesive composition of the present invention
(the photosensitive adhesive composition that is not completely
20 cured). In this case, the package substrate 30 also corresponds
to a non-joining member that is joined to the semiconductor
element 20. That is, the photosensitive adhesive composition
of the present invention can be used not only for joining between
the semiconductor element 20 and the semiconductor element
25 (member to be joined) 20 but also for joining between the

semiconductor element 20 and the package substrate (member to be joined) 30. Meanwhile, the member to be joined is not limited thereto.

[0079]

5 Subsequently, the individual piece 22 is pressed onto the previously-mounted individual piece 21. Therefore, two semiconductor chips 20 can be laminated together through the adhesive layer 601 as illustrated in FIG. 5(b). After that, this step is repeated, whereby the chip laminate 200 formed by
10 laminating a number of the semiconductor chips 20 as illustrated in FIG. 5(c) is obtained. At this time, if the semiconductor chips 20 are laminated together in a non-aligned manner, it is possible to ensure regions in which the bonding wire 70 is connected to the semiconductor chip 20 (regions corresponding
15 to the opening portions 601b in the coated film 601a). That is, the electrode portions of the semiconductor chips 20 can be exposed by laminating the semiconductor chips 20 in a non-aligned manner.

[0080]

20 In addition, the semiconductor chips 20 are mounted while the adhesive layer 601 is heated. Therefore, the adhesive layer 601 develops a sufficient adhesive force, and the semiconductor chips 20 can be strongly adhered together. In this case, the heating temperature is preferably approximately 30°C to 150°C.
25 In addition, during mounting, the pressing load is preferably

approximately 0.1 N to 100 N, and the pressing time is preferably approximately 0.1 to 10 seconds.

[0081]

After that, the electrode portions of the respective
5 semiconductor chips 20 and the exposed portions of the wires
34 in the package substrate 30 are connected to each other using
the bonding wires 70 as illustrated in FIG. 5(d).

[0082]

In addition, the mold portion 50 is molded so as to cover
10 the chip laminate 200 and the package substrate 30, thereby
obtaining the semiconductor device 10 illustrated in FIG. 1.

[0083]

The mold portion 50 can be molded by, for example, using
a transfer molder and injecting a sealing material into a molding
15 die. In this case, in the molding die, it is preferable to set
the temperature to approximately 130°C to 250°C, set the
injection pressure to approximately 3 to 10 MPa, and set the
holding time after injection to approximately 10 seconds to 10
minutes.

20 [0084]

When the compact is heated as necessary after being
released from the die, the mold portion 50 and the adhesive layer
601 can be finally cured (completely cured). In this case, the
heating temperature is preferably approximately 130°C to 250°C,
25 and the heating time is preferably approximately 10 minutes to

10 hours.

[0085]

Meanwhile, the method for manufacturing the semiconductor device of the present invention may have a heating step between
5 the development step [3] and the treatment step [4]. In this heating step, the coated film 601a on which the development treatment has been carried out is heated (refer to FIG. 2(e)). Therefore, a predetermined curing reaction (thermal curing reaction) is caused in the photosensitive adhesive composition
10 constituting the coated film 601a. As a result, the photosensitive adhesive composition is slightly cured (semi-cured), whereby the adhesiveness of the coated film 601a enhances.

[0086]

15 The heating temperature of the coated film 601a is not particularly limited, but is preferably 80°C to 170°C and more preferably 120°C to 160°C. In addition, the heating time is appropriately set depending on the heating temperature and is preferably 35 to 120 minutes and more preferably 40 to 100 minutes.
20 Therefore, the mechanical characteristics such as elastic modulus of the coated film 601a are optimized, and the coated film 601a is imparted with sufficient resistance to the etching treatment or the ashing treatment.

[0087]

25 In addition, the coated film 601a is formed of the

photosensitive adhesive composition of the present invention,
and the adhesive layer 601 formed of the above-described coated
film 601a exhibits a relatively high solubility in organic
solvents. Therefore, for example, even in a case in which it
5 becomes necessary to remove the coated film 601a after the coated
film 601a is formed on the wafer 201, it is possible to
efficiently dissolve and remove the coated film 601a while
suppressing the generation of residues (residual substances).
Therefore, the wafer 201 is not wasted and can be subjected to
10 another adhesion process (can be reworked). As a result, the
step yield of the semiconductor device 10 can be improved.

[0088]

Meanwhile, the method for manufacturing the semiconductor
device may have a step of irradiating the entire surface of the
15 coated film with light (light irradiation step) in addition to
the heating step or in place of the heating step.

[0089]

<Photosensitive adhesive composition>

Next, the photosensitive adhesive composition
20 constituting the adhesive layer 601 (the photosensitive
adhesive composition of the present invention) will be
described.

[0090]

<<Composition>>

25 The photosensitive adhesive composition includes (A) an

alkali-soluble resin, (B) a photo-acid-generating agent, (C) an epoxy compound, and (D) a phenolic compound.

[0091]

Hereinafter, the respective materials constituting the
5 photosensitive adhesive composition will be described in detail.

<(A) Alkali-soluble resin>

The alkali-soluble resin (A) is a material that serves as the base material of the adhesive layer 601. In addition, when
10 the photosensitive adhesive composition includes the alkali-soluble resin (A), it is possible to enhance the adhesive force (adhering force) of the adhesive layer 601 to the semiconductor chips 20. Therefore, it is possible to more strongly adhere the semiconductor chips 20 together using the
15 adhesive layer 601. Furthermore, when the photosensitive adhesive composition includes the alkali-soluble resin (A), it is possible to impart the coated film 601a with solubility in alkaline developers. Therefore, it is possible to use alkaline developers having a small environment load and reduce the
20 environment load in the development step.

[0092]

Specific examples of the alkali-soluble resin (A) include phenolic resins, acrylic resins, cyclic olefin-based resins, polyamide-based resins, polyimide-based resins, polyvinyl
25 phenolic resins, and the like, and it is possible to use one

of the above-described resins or a combination of two or more resins. Among these, the alkali-soluble resin (A) is particularly preferably a cyclic olefin-based resin. Examples of the cyclic olefin-based resin include norbornene-based
5 resins, benzocyclobutene-based resins, and the like. Among these, the cyclic olefin-based resin is preferably a norbornene-based resin. When the photosensitive adhesive composition including the cyclic olefin-based resin is used, it is possible to further enhance the adhesive force of the
10 adhesive layer 601 to the semiconductor chips 20. Particularly, when the photosensitive adhesive composition including the norbornene-based resin is used, it is possible to further enhance the adhering force of the adhesive layer 601 to the semiconductor chip 20. In addition, since the norbornene-based resins are
15 highly hydrophobic, the use of the photosensitive adhesive composition including the norbornene-based resin enables the formation of the adhesive layer 601 the dimensions of which are not easily changed due to water absorption.

[0093]

20 Hereinafter, a case in which the alkali-soluble resin (A) is the cyclic olefin-based resin will be described as a representative. The cyclic olefin-based resin preferably has an acidic group (a substituent exhibiting acidity). Specifically, the cyclic olefin-based resin preferably has at
25 least one repeating unit having an acidic group (first repeating

unit).

[0094]

The first repeating unit includes a structure derived from a cyclic olefin as a main skeleton (cyclic olefin monomer) and
5 a substituent which is bonded to the above-described structure and has an acidic group.

[0095]

Examples of the structure derived from a cyclic olefin include structures derived from a monocyclic body such as
10 cyclohexene or cyclooctene and structures derived from a polycyclic body such as norbornene, norbornadiene, dicyclopentadiene, dihydrodicyclopentadiene, tetracyclododecene, tricyclopentadiene, dihydrotricyclopentadiene, tetracyclopentadiene, or
15 dihydrotetracyclopentadiene. Among these, the structure derived from a cyclic olefin is particularly preferably a structure derived from norbornene. The structure derived from norbornene contributes to the improvement of the adhesive force of the adhesive layer 601 to the semiconductor chips 20. In
20 addition, the structure derived from norbornene also contributes to the improvement of the heat resistance of the photosensitive adhesive composition and the flexibility of the cured photosensitive adhesive composition.

[0096]

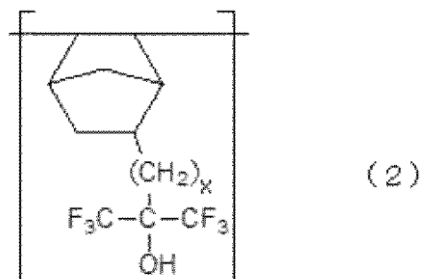
25 Examples of the substituent having an acidic group include

substituents having a carboxyl group, a phenolic hydroxyl group,
 $-\text{C}(\text{OH})-(\text{CF}_3)_2$, $-\text{N}(\text{H})-\text{S}(\text{O})_2-\text{CF}_3$, or the like, and, among these,
 substituents having any one of a carboxyl group and $-\text{C}(\text{OH})-(\text{CF}_3)_2$
 are particularly preferred. When the cyclic olefin-based resin
 5 includes the above-described substituent having an acidic group,
 it is possible to enhance the solubility of the photosensitive
 adhesive composition in alkaline developers. Therefore, in the
 manufacturing of semiconductor devices, it is possible to reduce
 the amount of the developed photosensitive adhesive composition
 10 left undissolved and further enhance patterning properties
 during development.

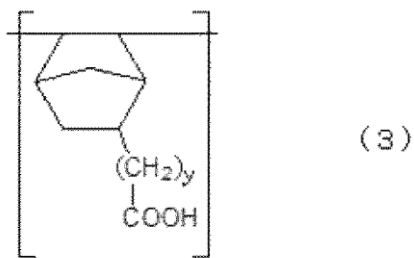
[0097]

Due to what has been described above, the first repeating
 unit is preferably, particularly, at least one of Formula (2)
 15 below and Formula (3) below. When the cyclic olefin-based resin
 includes the above-described first repeating unit, it is
 possible to further improve the adhesiveness of the adhesive
 layer 601 to the semiconductor chips 20 and the solubility of
 the photosensitive adhesive composition in alkaline developers.

20 [0098]



[0099]



[0100]

In Formula (2) and Formula (3), each of x and y is preferably an integer of 0 or more and 10 or less and more preferably an integer of 1 or more and 5 or less. In such a case, it is possible to obtain the adhesive layer 601 capable of strongly adhering the semiconductor chips 20 together.

[0101]

The cyclic olefin-based resin simply needs to have at least one type of first repeating unit, but preferably has two or more different types of first repeating units and more preferably has the first repeating units of both Formula (2) and Formula (3). In such a case, it is possible to further improve the adhesiveness of the adhesive layer 601 to the semiconductor chips 20 and the solubility of the photosensitive adhesive composition in alkaline developers.

[0102]

The optimal value of the content fraction of the first repeating unit in the cyclic olefin-based resin can be determined in consideration of the solubility of the photosensitive adhesive composition in alkaline developers, and the content fraction is, for example, preferably 10 to 80 mol% and more

preferably 20 to 70 mol%. When the content fraction of the first repeating unit is less than the lower limit value, there are cases in which it becomes difficult to sufficiently develop the solubility of the photosensitive adhesive composition in
5 alkaline developers. In addition, when the content fraction of the first repeating unit is more than the upper limit value, depending on the type of the first repeating unit, there is a concern that it may not be possible to sufficiently develop the characteristics of constitutions other than the first repeating
10 unit in the cyclic olefin-based resin.

[0103]

The content of the acidic group in the cyclic olefin-based resin is preferably 0.001 to 0.01 mol and more preferably 0.0015 to 0.006 mol per gram of the polymer. In such a case, it is
15 possible to particularly enhance the solubility of the photosensitive adhesive composition in alkaline developers.

[0104]

Furthermore, the cyclic olefin-based resin preferably also has the second repeating unit that is different from the
20 above-described first repeating unit.

[0105]

The second repeating unit includes a structure derived from a cyclic olefin as a main skeleton and a substituent which is bonded to the above-described structure and is different from
25 the substituent in the first repeating unit.

[0106]

As the main skeleton of the second repeating unit, it is possible to use the structures exemplified above as the first repeating unit. Among these, the main skeleton of the second repeating unit is particularly preferably a structure derived from norbornene from the viewpoint of the heat resistance of the photosensitive adhesive composition, the flexibility of the cured photosensitive adhesive composition, and the like. In addition, the main skeletons of the first and second repeating units may be different from each other, but are preferably identical to each other. Particularly, the main skeletons of the first and second repeating units are both preferably a structure derived from norbornene. Therefore, it is possible to further enhance the adhesive force of the adhesive layer 601 to the semiconductor chips 20 and appropriately decrease the elastic modulus of the adhesive layer 601. Therefore, it is possible to more strongly adhere the semiconductor chips 20 together using the adhesive layer 601 and relax stress concentration that is generated in the joining interface between the semiconductor chips 20 by appropriately enhancing the flexibility of the adhesive layer 601.

[0107]

The substituent in the second repeating unit preferably has 2 to 30 carbon atoms and more preferably has 4 to 15 carbon atoms. When the number of carbon atoms is in the above-described

range, the elastic modulus of the cured photosensitive adhesive composition decreases, and the flexibility of the adhesive layer 601 can be enhanced. Therefore, it is possible to further suppress cracks that are generated in the semiconductor chips 20 or the adhesive layer 601 which are caused by stress concentration in the joining interface between the semiconductor chips 20 or peeling between the semiconductor chip 20 and the adhesive layer 601. In addition, it is possible to suppress the occurrence of breakage or the like of the semiconductor chips 20 or the adhesive layers 601 which is caused by external impacts.

[0108]

In addition, the substituent in the second repeating unit may be a cyclic structure, a branched structure, or the like, but is preferably a linear structure. Therefore, it is possible to further decrease the elastic modulus of the cured photosensitive adhesive composition and further enhance the flexibility of the adhesive layer 601.

[0109]

Examples of linear substituents having 2 to 30 carbon atoms include alkyl groups, alkenyl groups, alkynyl groups, aryl groups, aralkyl groups, groups having an alkyl ether structure, and the like. Among these, the linear substituent having 2 to 30 carbon atoms is particularly preferably a group having an alkyl ether structure. Therefore, the cured photosensitive

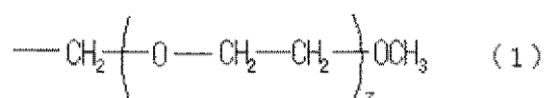
adhesive composition can be highly flexible.

[0110]

The group having an alkyl ether structure is preferably, particularly, a group represented by Formula (1) below.

5 Therefore, it is possible to further enhance the flexibility of the adhesive layer 601.

[0111]



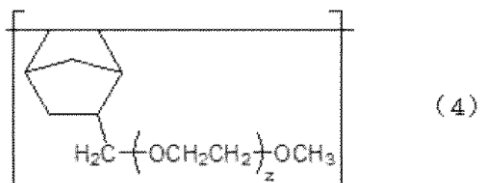
[0112]

10 In Formula (1), z is preferably an integer of 1 or more and 10 or less and more preferably an integer of 2 or more and 6 or less. In such a case, the adhesive layer 601 having more preferred flexibility can be obtained.

[0113]

15 Due to what has been described above, the second repeating unit is preferably, particularly, Formula (4) below. When the alkali-soluble resin (A) has the second repeating unit represented by Formula (4) in addition to the first repeating unit, it is possible to preferably satisfy the function of the
20 first repeating unit capable of sufficiently enhancing the solubility of the photosensitive adhesive composition in alkaline developers and the function of the second repeating unit providing an appropriate value as the elastic modulus of the cured photosensitive adhesive composition.

[0114]



[0115]

Particularly, in Formula (4), z is preferably an integer of 1 or more and 10 or less and more preferably an integer of 2 or more and 5 or less. In such a case, it is possible to provide a more appropriate value as the elastic modulus of the cured photosensitive adhesive composition.

[0116]

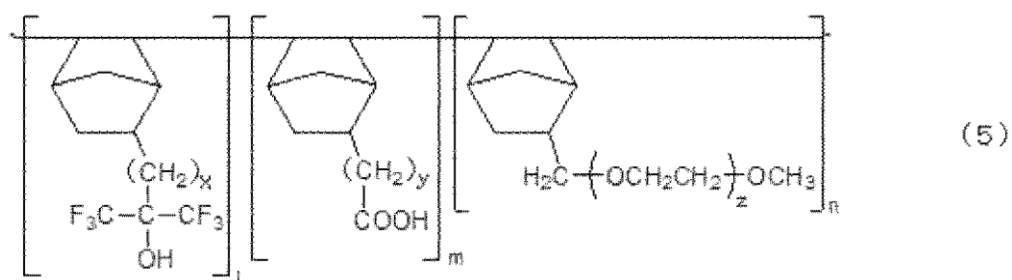
In addition, in a case in which the cyclic olefin-based resin includes the second repeating unit, the content fraction of the second repeating unit in the cyclic olefin-based resin is, for example, preferably 20 to 60 mol% and more preferably 25 to 50 mol%. When the content fraction of the second repeating unit is less than the lower limit value, there are cases in which, depending on the type of the second repeating unit, it is difficult to adjust the elastic modulus of the cured photosensitive adhesive composition to a desired value. In addition, when the content fraction of the second repeating unit is more than the upper limit value, depending on the type of the second repeating unit, there is a concern that it may not be possible to sufficiently develop the characteristics of constitutions other than the second repeating unit in the cyclic

olefin-based resin.

[0117]

Due to what has been described above, a cyclic olefin-based resin represented by Formula (5) below is preferably used. When the photosensitive adhesive composition includes the cyclic olefin-based resin represented by Formula (5), it is possible to impart a necessary mechanical strength and a more appropriate flexibility (stress relaxation properties) to the adhesive layer 601. Furthermore, the photosensitive adhesive composition is capable of exhibiting a particularly excellent solubility in alkaline developers. Additionally, it is possible to obtain the adhesive layer 601 that is particularly excellent in terms of the adhesive force to the semiconductor chips 20.

15 [0118]



[0119]

In Formula (5), l , m , and n are an integer of 1 or more and 100 or less. Meanwhile, as described above, x is preferably an integer of 0 or more and 10 or less, y is preferably an integer of 0 or more and 10 or less, and z is preferably an integer of 1 or more and 10 or less.

[0120]

In Formula (5), the polymerization degree of the second repeating unit to the polymerization degree of the first repeating unit (that is, $n/(1+m)$) is preferably 0.3 to 2.0 and
5 more preferably 0.4 to 1.5. In such a case, it is possible to obtain the adhesive layer 601 capable of particularly relaxing stress concentration that is generated in the joining interface between the semiconductor chips 20 and more strongly adhering the semiconductor chips 20 together.

10 [0121]

In addition, the weight-average molecular weight (M_w) of the cyclic olefin-based resin is preferably 5,000 to 500,000, more preferably 7,000 to 200,000, and still more preferably 8,000 to 100,000. In such a case, it is possible to obtain the adhesive
15 layer 601 that is particularly excellent in terms of the adhesive force to the semiconductor chips 20.

[0122]

Meanwhile, the weight-average molecular weight (M_w) of the cyclic olefin-based resin can be measured using a cyclic
20 olefin-based resin which is used as a reference and gel permeation chromatography (GPC) according to ASTM D 3536-91.

[0123]

In addition, the glass transition temperature of the cyclic olefin-based resin is preferably 100°C to 250°C. When
25 the cyclic olefin-based resin having the above-described glass

transition temperature is used, the heat resistance of the photosensitive adhesive composition becomes more favorable, and it is possible to further enhance the reliability of the semiconductor device 10 at high temperatures.

5 [0124]

The glass transition temperature of the cyclic olefin-based resin can be obtained using, for example, differential scanning calorimetry as a temperature at which an exothermic reaction is caused when the temperature is increased
10 from normal temperature at a temperature-increase rate of 5°C/minute.

Meanwhile, when synthesized so as to satisfy the same conditions as for the cyclic olefin-based resin, the alkali-soluble resins (A) other than the cyclic olefin-based
15 resin are also capable of producing the same effects as described above.

[0125]

<(B) Photo-acid-generating agent>

The photo-acid-generating agent (B) has a function as a
20 positive-type photo-acid-generating agent capable of generating acids in light reactions during exposure by energy ray irradiation and increasing the solubility of the photosensitive adhesive composition in alkaline developers in the exposed portions. Therefore, in the manufacturing of
25 semiconductor devices, it is possible to reduce the amount of

the developed photosensitive adhesive composition left undissolved in the exposed portions which are exposed portions in the photosensitive adhesive composition (coated film 601a). Therefore, it is possible to improve patterning properties during development. Meanwhile, when including the photo-acid-generating agent (B), the photosensitive adhesive composition may have a function as a negative-type photo-acid-generating agent capable of accelerating reactions in which the epoxy compound (C) described below crosslinks the alkali-soluble resin (A) by energy ray irradiation in the manufacturing of semiconductor devices.

[0126]

Specific examples of the photo-acid-generating agent (B) include onium salts, halogenated organic compounds, quinone diazide compounds, α,α -bis(sulfonyl)diazomethane-based compounds, α -carbonyl- α -sulfonyl-diazomethane-based compounds, sulfone compounds, organic acid ester compounds, organic acid amide compounds, organic acid imide compounds, and the like, and one of the above-described photo-acid-generating agents or a combination of two or more photo-acid-generating agents can be used. Among these, the photo-acid-generating agent (B) is particularly preferably a quinone diazide compound. Examples of the quinone diazide compound include compounds having a 1,2-benzoquinone diazide or 1,2-naphthoquinone diazide structure and the like. More specifically, the

photo-acid-generating agent (B) preferably includes an ester compound of 1,2-naphthoquinone-2-diazide-5-sulfonic acid or 1,2-naphthoquinone-2-diazide-4-sulfonic acid and a phenolic compound. These photo-acid-generating agents generate

5 carboxyl groups in light reactions during exposure by energy ray irradiation (particularly radiation irradiation) and are thus capable of further enhancing the solubility of the exposed portion in alkaline developers. Therefore, the photosensitive adhesive composition is capable of exhibiting a higher
10 solubility in alkaline developers even with a particularly small irradiation amount. As a result, it is possible to further improve patterning properties during development.

[0127]

The content of the photo-acid-generating agent (B) is not
15 particularly limited, but is preferably 1 to 50 parts by mass and more preferably 5 to 30 parts by mass with respect to 100 parts by mass of the alkali-soluble resin (A). When the content of the photo-acid-generating agent (B) is less than the lower limit value, depending on the type and the like of the
20 photo-acid-generating agent (B), there is a possibility that the exposure and development characteristics of the photosensitive adhesive composition degrade. In addition, when the content of the photo-acid-generating agent (B) is more than the upper limit value, the additional enhancement of the effects
25 is not expected, and, depending on the type of the

photo-acid-generating agent (B), there is a concern that it may not be possible to sufficiently develop the characteristics of materials other than the photo-acid-generating agent (B) in the photosensitive adhesive composition.

5 [0128]

<(C) Epoxy compound>

The epoxy compound (C) has a function of crosslinking the alkali-soluble resin (A) (particularly, the cyclic olefin-based resin).

10 [0129]

The epoxy compound (C) may be any one of an aromatic epoxy compound including an aromatic ring in the molecule or an aliphatic epoxy compound including no aromatic rings in the molecule. However, the epoxy compound (C) is more preferably an aliphatic epoxy compound. In such a case, it is possible to provide an appropriate value as the crosslinking density of the alkali-soluble resin (A) in the photosensitive adhesive composition and appropriately enhance the flexibility of the adhesive layer 601.

20 [0130]

In addition, the epoxy compound (C) is preferably a branched structure or a linear structure and more preferably a branched structure. When the photosensitive adhesive composition include the epoxy compound (C) forming a branched structure, it is possible to provide an appropriate value as

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the crosslinking density of the alkali-soluble resin (A) in the photosensitive adhesive composition and appropriately enhance the flexibility of the adhesive layer 601. Therefore, the adhesive layer 601 which has a necessary mechanical strength and superior stress relaxation properties that relax stress concentration that is generated in the joining interface between the semiconductor chips 20 can be obtained.

[0131]

In addition, the epoxy compound (C) preferably contains two or more glycidyl groups in the molecule and more preferably three or more and nine or less glycidyl groups in the molecule. In such a case, it is possible to provide an appropriate value as the crosslinking density of the alkali-soluble resin (A) in the photosensitive adhesive composition and obtain the adhesive layer 601 which has a necessary mechanical strength and superior stress relaxation properties.

[0132]

Examples of the above-described epoxy compound (C) include ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, trimethylolpropane triglycidyl ether, trimethylolethane triglycidyl ether, sorbitol polyglycidyl ether, pentaerythritol polyglycidyl ether, EXA-830CRP, EXA-830VLP, EXA-835LV, EXA-850CRP, EPICLON-830-S, EPICLON-840-S, EPICLON-850-S, EPICLON-850-CRP, EPICLON-850-LC,

HP-7200, HP-7200L, HP-7200H (manufactured by DIC Corporation),
YH-300, YH-301, YD-8125G, YDF-8170G, YD-825GS, YD-825GSH,
YD-870GS, ZX-1059, ZX-1542, PG-207GS, ZX-1658GS (manufactured
by Nippon Steel & Sumikin Chemical Co., Ltd.), YL980, YL983U,
5 YL6810, YL7410, YX7700, YX8000, YX8034, YED216D, jER152,
jER157S70, jER1032H60 (manufactured by Mitsubishi Chemical
Corporation), EP-3300S, EP-3950L, EP-4000L, EP-4010L, EP-4088L
(ADEKA Corporation), CELLOXIDE 2021P, CELLOXIDE 2081 (Daicel
Corporation), EPPN-201-L, EPPN-501H, EPPN-501HY, EPPN-502H,
10 XD-1000 (Nippon Kayaku Co., Ltd.), LX-01 (Daiso Chemical Co.,
Ltd.), PG-100, EG-200, EG-280, CG-400, CG-500 (Osaka Gas
Chemicals Co., Ltd.), EX-211L, EX-212L, EX-214L, EX-216L,
EX-321L, EX-850L, EX-946L (Nagase Chemtex Corporation), VG3101L
(Printec Corporation), SR-14BJ, SR-16H, SR-TMPL, SR-PG, SR-PTMG,
15 SR-8EGS (Sakamoto Yakuhin Kogyo Co., Ltd.), cyclohexene
oxide-type epoxy resins, and the like, and, one of the
above-described epoxy compounds or a combination of two or more
epoxy compounds can be used. Among these, the epoxy compound
(C) is particularly preferably trimethylolpropane triglycidyl
20 ether, 1,6-hexanediol diglycidyl ether, polypropylene glycol
diglycidyl ether, polyethylene glycol diglycidyl ether,
polytetramethylene glycol diglycidyl ether, or hydrogenated
bisphenol A diglycidyl ether. Therefore, it is possible to more
easily and reliably obtain the adhesive layer 601 which is
25 capable of accelerating the crosslinking reactions of the

alkali-soluble resin (A) in the photosensitive adhesive composition and has superior stress relaxation properties.

[0133]

The content of the epoxy compound (C) is not particularly limited, but is preferably 1 to 100 parts by mass and more preferably 5 to 50 parts by mass with respect to 100 parts by mass of the alkali-soluble resin (A). When the content of the epoxy compound (C) is less than the lower limit value, depending on the type and the like of the epoxy compound (C), there is a possibility that the stress relaxation properties of the adhesive layer 601 degrade. On the other hand, when the content of the epoxy compound (C) is more than the upper limit value, there are cases in which the viscosity of the photosensitive adhesive composition becomes excessively higher than necessary.

[0134]

<(D) Phenolic compound having melting point of 50°C to 150°C>

When the photosensitive adhesive composition includes the phenolic compound having a melting point of 50°C to 150°C (D) (hereinafter, in some cases, also referred to simply as "the phenolic compound (D)"), it is possible to suppress the generation of air bubbles between the adhesive layer 601 and the semiconductor chip 20 during, for example, the etching of the wafer 201 including the coated film 601a or the pressing of the semiconductor chips 20 together through the adhesive layer

601. In addition, even in a case in which air bubbles are generated between the adhesive layer 601 and the semiconductor chip 20, it is possible to remove the generated air bubbles. When it becomes difficult for air bubbles to remain in the interfaces between the adhesive layer 601 and the semiconductor chip 20 as described above, it is possible to enhance the adhesive force of the adhesive layer 601 to the semiconductor chip 20 and thus strongly adhere the semiconductor chips 20 together. Therefore, finally, it is possible to obtain the highly reliable chip laminate 200.

[0135]

Furthermore, when the photosensitive adhesive composition including the phenolic compound (D) is used, the adhesive layer 601 exhibiting a relatively high solubility in organic solvents can be obtained. Therefore, for example, even in a case in which it becomes necessary to remove the coated film 601a obtained by applying the photosensitive adhesive composition to the wafer 201, it is possible to efficiently dissolve and remove the coated film 601a while suppressing the generation of residues (residual substances). Therefore, the wafer 201 is not wasted and can be subjected to another adhesion process (can be reworked). As a result, the step yield of the semiconductor device 10 can be improved.

[0136]

In addition, the phenolic compound (D) has a melting point

of 50°C to 150°C, but the melting point is preferably 60°C to 130°C and more preferably 70°C to 120°C. In such a case, it is possible to more significantly develop the above-described effects of the photosensitive adhesive composition including the phenolic compound (D). The above-described phenolic compound (D) preferably includes at least one of a phenolic compound having a substituent including an aliphatic hydrocarbon group and a phenolic compound having a plurality of phenolic skeletons.

10 [0137]

In addition, the hydroxyl group equivalent of the phenolic compound (D) (particularly, the phenolic compound having a substituent including an aliphatic hydrocarbon group) is preferably 150 to 250 g/eq, more preferably 160 to 240 g/eq, and still more preferably 180 to 220 g/eq. When the hydroxyl group equivalent is in the above-described range, the photosensitive adhesive composition having a more favorable solubility in alkaline developers can be obtained. In contrast, when the hydroxyl group equivalent is less than the lower limit value, depending on the type, amount added, or the like of the phenolic compound (D), the water absorption percentage of the photosensitive adhesive composition increases, and there is a possibility that the reliability degrades. In addition, when the hydroxyl group equivalent is more than the upper limit value, the solubility of the photosensitive adhesive composition in

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alkaline developers significantly decreases, and there is a concern that the photosensitive adhesive composition may be left undissolved after development.

[0138]

5 Meanwhile, the hydroxyl group equivalent of the phenolic compound (D) can be measured using a method in which a solution into which the phenolic compound (D) is mixed is titrated against a reference alkali solution.

[0139]

10 In a case in which the phenolic compound (D) includes a phenolic compound having a substituent including an aliphatic hydrocarbon group (a substituent having an alkyl chain $(-\text{CH}_2-)_n$), it is possible to further enhance the solubility of the adhesive layer 601 in organic solvents. Therefore, even in a case in which
15 it becomes necessary to remove the coated film 601a, it is possible to more efficiently dissolve and remove the coated film 601a, and thus the rework properties can be enhanced.

[0140]

 In the alkyl chain $(-\text{CH}_2-)_n$, the value of n is preferably
20 1 to 6 and more preferably 2 to 4. In such a case, it is possible to further enhance the solubility of the adhesive layer 601 in organic solvents.

[0141]

 Examples of the above-described substituent including an
25 aliphatic hydrocarbon group include methylene groups, ethylene

groups, trimethylene groups, butyl groups, 2,2-dimethyl butyl groups, and the like.

[0142]

In addition, the phenolic compound (D) preferably has a structure derived from benzoic acid. Specifically, the phenolic compound preferably has a structure derived from benzoic acid, a monohydroxy benzoate such as 2-hydroxybenzoate or 3-hydroxybenzoate, a dihydroxy benzoate such as 2,4-hydroxybenzoate, or the like.

10 [0143]

Specific examples of the phenolic compound (D) include 4-(1,1-dimethylpropyl)phenol, 4-cyclohexylphenol, 4-(1,1,3,3-tetramethylbutyl) phenol, 4-(4-hydroxyphenyl)-2-butanone, 4'-hydroxybutyrophenone, 4'-hydroxyvalerophenone, 4'-hydroxyhexanophenone, 3-(4-hydroxyphenyl)propionic acid, methyl 3-hydroxybenzoate, ethyl 3-hydroxybenzoate, methyl 4-hydroxybenzoate, ethyl 4-hydroxybenzoate, propyl 4-hydroxybenzoate, isopropyl 4-hydroxybenzoate, butyl 4-hydroxybenzoate, isobutyl 4-hydroxybenzoate, hexyl 4-hydroxybenzoate, benzyl 4-hydroxybenzoate, 1,3-bis[2-(4-hydroxyphenyl)-2-propyl]benzene, BisP-DED (manufactured by Honshu Chemical Industry Co., Ltd.), and the like, and one of the phenolic compounds or a combination of two or more phenolic compounds can be used. Among these, the

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phenolic compound (D) is particularly preferably propyl
4-hydroxybenzoate, methyl 4-hydroxybenzoate, butyl
4-hydroxybenzoate, or hexyl 4-hydroxybenzoate. Therefore, it
is possible to obtain the adhesive layer 601 which has a
5 particularly strong adhesive force to the semiconductor chips
20 and a superior solubility in organic solvents.

[0144]

In addition, in a case in which the phenolic compound (D)
includes a phenolic compound having a plurality of phenolic
10 skeletons, the hydroxyl group equivalent is preferably 50 to
150 g/eq, more preferably 70 to 130 g/eq, and still more
preferably 90 to 110 g/eq. In addition, a plurality of the
phenolic skeletons may be any one of a linking-type polycyclic
structure in which phenolic skeletons are linked to each other
15 through a single bond and are not directly bonded to each other
or a condensation-type (fusion-type) polycyclic structure in
which phenolic skeletons do not have any single bond interposed
therebetween and are directly bonded to each other, but are
preferably the linking-type polycyclic structure. In such a
20 case, it is possible to obtain the adhesive layer 601 which has
a particularly strong adhesive force to the semiconductor chips
20 and a superior solubility in organic solvents.

[0145]

The content of the phenolic compound (D) is preferably 0.5
25 to 30 parts by mass and more preferably 1 to 20 parts by mass

with respect to 100 parts by mass of the alkali-soluble resin (A). When the content of the phenolic compound (D) is less than the lower limit value, depending on the type and the like of the phenolic compound (D), there is a possibility that the solubility of the photosensitive adhesive composition in organic solvents degrades. Even when the content of the phenolic compound (D) is more than the upper limit value, the additional enhancement of the effects is not expected. In addition, depending on the type of the phenolic compound (D), there is a concern that the characteristics of materials other than the phenolic compound (D) in the photosensitive adhesive composition may not be sufficiently developed.

[0146]

In addition, the photosensitive adhesive composition preferably includes two or more types of the above-described phenolic compounds (D). Specifically, the photosensitive adhesive composition preferably includes two or more types of the phenolic compounds (D) having mutually different melting points and more preferably includes two types of the phenolic compounds (D) having mutually different melting points. In such a case, it is possible to further enhance the adhesiveness, stress relaxation properties, and solubility in organic solvents of the photosensitive adhesive composition (the adhesive layer 601).

[0147]

Meanwhile, in a case in which the photosensitive adhesive composition includes two or more types of the phenolic compounds (D), the total content thereof is preferably in the above-described range.

5 [0148]

When the photosensitive adhesive composition includes the alkali-soluble resin (A), the photo-acid-generating agent (B), the epoxy compound (C), and the phenolic compound (D) described above, in the manufacturing of semiconductor devices, air bubbles do not easily remain in the interfaces between the adhesive layer 601 and the semiconductor chip 20 during, for example, the etching of the wafer 201 including the coated film 601a or the pressing of the semiconductor chips 20 together through the adhesive layer 601. Therefore, it is possible to strongly adhere the semiconductor chips 20 together using the adhesive layer 601 and thus obtain a highly reliable chip laminate 200. In addition, the adhesive layer 601 has stress relaxation properties as well as sufficient adhesiveness although being a singly-layer structure. Therefore, it is not necessary to provide two layer of a layer having excellent adhesiveness and a layer having excellent stress relaxation properties between the semiconductor chips 20, and thus it is possible to prevent the total thickness of the chip laminate 200 from becoming significantly thick. As a result, it is possible to obtain the highly reliable semiconductor device 10

having a low profile and excellent adhesiveness and stress relaxation properties. The above-described semiconductor device 10 is particularly useful for, for example, electronic devices which have an extremely small inner capacity and are
5 used in a mobile manner such as mobile devices. That is, the above-described semiconductor device 10 is useful since the semiconductor device 10 contributes to the size reduction, thickness reduction, and weight reduction of electronic devices and has functions that are not easily impaired even in a case
10 in which electronic devices are dropped or flung.

[0149]

In addition, a cured substance of the photosensitive adhesive composition includes the alkali-soluble resin (A), the photo-acid-generating agent (B), the epoxy compound (C), and
15 the phenolic compound (D) is excellent in terms of solubility in organic solvents and rework properties.

[0150]

In addition, the above-described photosensitive adhesive composition preferably includes (X) a phenolic compound having
20 a higher melting point than the phenolic compound (D). In such a case, it is possible to particularly improve the adhesiveness of the adhesive layer 601. Meanwhile, the melting point of the phenolic compound (X) is preferably 151°C to 250°C and more preferably 181°C to 230°C. In addition, the phenolic compound
25 (X) preferably includes a phenolic compound having a plurality

of phenolic skeletons. The above-described phenolic compound having a plurality of phenolic skeletons preferably has a substituent which is a substituent including a cyclic structure and is bonded to at least one of the above-described phenolic skeletons. In such a case, it is possible to more significantly exhibit the above-described effects.

[0151]

In addition, the content of the phenolic compound (X) is preferably 0.2 to 20 parts by mass and more preferably 0.5 to 10 parts by mass with respect to 100 parts by mass of the alkali-soluble resin (A). When the content of the phenolic compound (X) is in the above-described range, it is possible to more significantly exhibit the above-described effects.

[0152]

In addition, it is particularly preferable that the photosensitive adhesive composition includes two types of the phenolic compounds (D) and further includes the phenolic compound (X). In such a case, it is possible to obtain the adhesive layer 601 that is particularly excellent in terms of adhesiveness, stress relaxation properties, and solubility in organic solvents.

[0153]

In addition, the photosensitive adhesive composition may further include, if necessary, phenolic compounds other than the phenolic compound (D) and the phenolic compound (X), a

leveling agent, a flame retardant, a plasticizer, a curing accelerator, an antioxidant, an adhesion aid, or the like.

[0154]

Examples of the antioxidant include phenolic antioxidants, amine-based antioxidants, phosphorus-based antioxidants, and thioether-based antioxidants, and one of these antioxidants or a combination of two or more antioxidants can be used. However, among these, as the antioxidant, a combination of a phenolic antioxidant and an amine-based antioxidant is preferably used.

[0155]

The inclusion of the above-described antioxidant enables to suppress oxidation during the curing of the photosensitive adhesive composition and the oxidation of the photosensitive adhesive composition (the coated film 601a) in the subsequent processes and the like.

[0156]

Examples of the phenolic antioxidant include pentaerythrityl tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 3,9-bis{2-(3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-1,1-dimethylethyl} 2,4,8,10-tetraoxaspiro[5,5]undecane, octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 1,6-hexanediol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)b

enzene, 2,6-di-t-butyl-4-methylphenol,
 2,6-di-t-butyl-4-ethylphenol,
 2,6-diphenyl-4-octadecyloxyphenol,
 2,6-bis[(2-hydroxy-5-methyl phenyl)methyl]-4-methyl phenol,
 5 stearyl (3,5-di-t-butyl-4-hydroxyphenyl)propionate, distearyl
 (3,5-di-t-butyl-4-hydroxybenzyl)phosphonate, thiodiethylene
 glycol bis[(3,5-di-t-butyl-4-hydroxyphenyl)propionate],
 4,4'-thiobis(6-t-butyl-m-cresol),
 2-octylthio-4,6-di(3,5-di-t-butyl-4-hydroxyphenoxy)-s-triaz
 10 ine, 2,2'-methylenebis(4-methyl-6-t-butyl-6-butylphenol),
 2,2'-methylenebis(4-ethyl-6-t-butylphenol),
 bis[3,3-bis(4-hydroxy-3-t-butylphenyl)butyric acid]glycol
 ester, 4,4'-butylidenebis(6-t-butyl-m-cresol),
 2,2'-ethylidenebis(4,6-di-t-butylphenol),
 15 2,2'-ethylidenebis(4-s-butyl-6-t-butylphenol),
 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane,
 bis[2-t-butyl-4-methyl-6-(2-hydroxy-3-t-butyl-5-methylbenzy
 1)phenyl]terephthalate,
 1,3,5-tris(2,6-dimethyl-3-hydroxy-4-t-butylbenzyl)isocyanur
 20 ate,
 1,3,5-tris(3,5-di-t-butyl-4-hydroxybenzyl)-2,4,6-trimethylb
 enzene,
 1,3,5-tris[(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxyethy
 1]isocyanurate,
 25 tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propio

nate]methane,
 2-t-butyl-4-methyl-6-(2-acryloyloxy-3-t-butyl-5-methylbenzy
 1)phenol,
 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro
 5 [5,5]undecane-bis[β -(3-t-butyl-4-hydroxy-5-methylphenyl)pro
 pionate], triethylene glycol
 bis[β -(3-t-butyl-4-hydroxy-5-methylphenyl)propionate],
 1,1'-bis(4-hydroxyphenyl)cyclohexane,
 2,2'-methylenebis(4-methyl-6-t-butylphenol),
 10 2,2'-methylenebis(4-ethyl-6-t-butylphenol),
 2,2'-methylenebis(6-(1-methylcyclohexyl)-4-butylphenol),
 4,4'-butylidenebis(3-methyl-6-t-butylphenol),
 3,9-bis(2-(3-t-butyl-4-hydroxy-5-methylphenylpropionyloxy)
 1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane,
 15 4,4'-thiobis(3-methyl-6-t-butylphenol),
 4,4'-bis(3,5-di-t-butyl-4-hydroxybenzyl) sulfide,
 4,4'-thiobis(6-t-butyl-2-methylphenol),
 2,5-di-t-butylhydroquinone, 2,5-di-t-amylhydroquinone,
 2-t-butyl-6-(3-t-butyl-2-hydroxy-5-methylbenzyl)-4-methylph
 20 enyl acrylate, 2,4-dimethyl-6-(1-methylcyclohexyl, styrenated
 phenol, 2,4-bis((octylthio)methyl)-5-methylphenol, and the
 like. Among these, phenolic antioxidants such as
 2,6-bis[(2-hydroxy-5-methylphenyl)methyl]-4-methylphenol are
 preferred.

Examples of the amine-based antioxidants include

N,N'-di-sec-butyl-p-phenylenediamine,

4,4'-dimethoxydiphenylamine, 4-isopropoxydiphenylamine,

N-isopropyl-N'-phenyl-p-phenylenediamine,

5 N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine,

4,4'-di(α , α -dimethylbenzyl)diphenylamine, and the like.

Among these, the amine-based antioxidant is preferably a diphenylamine-based compound such as

4,4'-dimethoxydiphenylamine, 4-isopropoxydiphenylamine, or

10 4,4'-di(α , α -dimethylbenzyl)diphenylamine.

[0158]

Examples of the phosphorus-based antioxidants include

bis-(2,6-di-t-butyl-4-methylphenyl) pentapentaerythritol

diphosphite, tris(2,4-di-t-butylphenylphosphite),

15 tetrakis(2,4-di-t-butyl-5-methylphenyl)-4,4'-biphenylene

diphosponite, 3,5-di-t-butyl-4-hydroxybenzylphosphonate

diethyl ester, bis-(2,6-dicumylphenyl) pentaerythritol

diphosphite,

2,2-methylenenbis(4,6-di-t-butylphenyl)octylphosphite,

20 tris(mixed mono- and di-nonylphenylphosphite),

bis(2,4-di-t-butylphenyl) pentapentaerythritol-di-phosphite,

bis(2,6-di-t-butyl-4-methoxycarbonylethyl phenyl)

pentaerythritol diphosphite,

bis(2,6-di-t-butyl-4-octadecyloxycarbonylethyl phenyl)

25 pentaerythritol diphosphite, and the like. Among these, the

phosphorus-based antioxidant is preferably phosphite or phosphate.

[0159]

Examples of the thioether-based antioxidants include
5 dilauryl 3,3'-thiodipropionate,
bis(2-methyl-4-(3-n-dodecyl)thiopropionyloxy)-5-t-butylphenyl)sulfide, distearyl-3,3'-thiodipropionate, pentaerythritol tetrakis(3-lauryl)thiopropionate, and the like.

[0160]

10 In a case in which the photosensitive adhesive composition includes an antioxidant, the content of the antioxidant is preferably 0.1 to 50 parts by mass and more preferably 0.5 to 30 parts by mass with respect to 100 parts by mass of the alkali-soluble resin (A).

15 [0161]

In addition, examples of the adhesion aid include vinyltrimethoxysilane, vinyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldiethoxysilane,
20 3-glycidoxypropyltriethoxysilane, 5,6-epoxyhexyltriethoxysilane, p-stryltrimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropylmethyldiethoxysilane,
25 3-methacryloxypropyltriethoxysilane,

3-acryloxypropyltrimethoxysilane,
 bis[3-(triethoxysilyl)propyl]tetrasulfide,
 bis[3-(triethoxysilyl)propyl]disulfide,
 3-isocyanatepropyltriethoxysilane, phenyltrimethoxysilane,
 5 phenyltriethoxysilane, phenyltriethoxysilane,
 benzoyloxypropyltrimethoxysilane,
 benzoyloxypropyltriethoxysilane,
 1,6-bis(trimethoxysilyl)hexane, norbornenyl trimethoxysilane,
 norbornenyl triethoxysilane, 3-(triethoxysilyl)propylsuccinic
 10 acid anhydride, 6-azidesulfonylhexyltriethoxysilane,
 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane,
 tris(3-trimethoxysilylpropyl)isocyanurate,
 [2-(3-cyclohexenyl)ethyl]trimethoxysilane,
 15 [2-(3-cyclohexenyl)ethyl]triethoxysilane,
 (3-cyclopentadienylpropyl)triethoxysilane,
 pentyltrimethoxysilane, pentyltriethoxysilane,
 n-hexyltrimethoxysilane, n-hexyltriethoxysilane,
 n-octyltrimethoxysilane, n-octyltriethoxysilane,
 20 decyltrimethoxysilane, decyltriethoxysilane,
 dodecyltrimethoxysilane, dodecyltriethoxysilane,
 bis(trimethoxysilyl)methane, bis(trimethoxysilyl)ethane,
 bis(trimethoxysilyl)ethane, bis(trimethoxysilyl)hexane,
 bis(trimethoxysilyl)hexane, bis(trimethoxysilyl)octane,
 25 bis(trimethoxysilyl)octane, bis(trimethoxysilyl)benzene,

bis[(3-methyldimethoxysilyl)propyl]polypropylene oxide,
polymethacrylate trimethoxysilyl ester, polymethacrylate
triethoxysilyl ester, trifluoropropyltrimethoxysilane,
1,3-dimethyltetramethoxydisiloxane, and the like. However,
5 the adhesion aid is not limited thereto. These adhesion aids
may be used singly or two or more adhesion aids may be used in
a mixed form. When the photosensitive adhesive composition
includes the above-described adhesion aid, it is possible to
further enhance the adhesive force (adhering force) of the
10 adhesive layer 601 to the semiconductor chips 20.

[0162]

In a case in which the photosensitive adhesive composition
includes an adhesion aid, the content of the adhesion aid is
preferably 0.1 to 30 parts by mass and more preferably 0.2 to
15 20 parts by mass with respect to 100 parts by mass of the
alkali-soluble resin (A).

[0163]

<<Properties>>

Next, the properties of the photosensitive adhesive
20 composition (the properties of the adhesive layer 601) will be
described in detail.

[0164]

The elastic modulus of the cured photosensitive adhesive
composition, that is, the adhesive layer 601 at 25°C is preferably
25 2.0 to 3.5 GPa. In addition, the elastic modulus of the

photosensitive adhesive composition to be cured at 25°C is preferably 70% to 120% of the elastic modulus of the cured photosensitive adhesive composition at 25°C. In addition, the adhesive force of the photosensitive adhesive composition which has been subjected to the etching treatment and the ashing treatment and is yet to be cured to the semiconductor chips 20 at 25°C is preferably 20.0 to 200.0 N. In other words, when a film is formed on the semiconductor chip 20 having a planar size of 4 mm×4 mm using the photosensitive adhesive composition, the film is not cured (completely cured), and the etching treatment and the ashing treatment are carried out on the semiconductor chip 20 including the film in a non-cured or semi-cured state (the photosensitive adhesive composition to be cured), the adhesive force of the film to the semiconductor chips 20 at 25°C is preferably 20.0 to 200.0 N. When converted to a value per unit area in terms of the planar size of the semiconductor chip 20, this pressure-sensitive adhesive force reaches 1.25 to 12.5 MPa (N/mm²).

[0165]

When the above-described elastic modulus of the photosensitive adhesive composition to be cured at 25°C is in a predetermined range of the elastic modulus of the cured photosensitive adhesive composition at 25°C, the concern of, for example, the significant deformation or outflow from the wafer

201 of the photosensitive adhesive composition to be cured becomes small. Therefore, it is possible to increase the accuracy of alignment when the semiconductor chips 20 are laminated together. Furthermore, since the amount of the elastic modulus changed before and after curing is relatively small, it is also possible to reduce the amount of shrinkage caused by solarization. As a result, it is possible to reduce stress that is generated in the interfaces between the adhesive layer 601 and the semiconductor chip 20 due to curing shrinkage. From such a viewpoint, the above-described elastic modulus also contributes to the improvement of the reliability of the chip laminate 200.

[0166]

Meanwhile, the photosensitive adhesive composition which has been subjected to the etching treatment and the ashing treatment and is yet to be cured has a sufficient adhering force to the semiconductor chips 20 which is required for die bonding. Therefore, the adhesive layer 601 more strongly fix the semiconductor chips 20 together and contributes to the improvement of the reliability of the chip laminate 200.

[0167]

When the photosensitive adhesive composition satisfying the above-described conditions is used, it is possible to easily obtain the adhesive layer 601 which satisfies both sufficient adhesiveness and stress relaxation properties. In other words,

the adhesive layer 601 alone has both an element protection function (buffer coating function) of a buffer coating film and an adhesion function (die bonding function) of a die bonding film. Therefore, it becomes possible to form the chip laminate 200 without causing the degradation of the reliability of the chip laminate 200, and the chip laminate 200 can be thinned compared with chip laminators in the related art for which two layers are used. In addition, the thickness reduction of the chip laminate 200 enables to reduce the volume of the mold portion 50 or the length of the bonding wires 70 and thus also contributes to weight reduction and cost reduction.

[0168]

In addition, the elastic modulus of the cured photosensitive adhesive composition at 25°C is more preferably set to 2.2 to 3.2 GPa and still more preferably set to 2.4 to 3.0 GPa. Meanwhile, when the elastic modulus of the cured photosensitive adhesive composition is less than the lower limit value, depending on the composition of the photosensitive adhesive composition, there is a concern that the adhesive force of the adhesive layer 601 may slightly weaken. In addition, in a case in which filler is included in the mold portion 50, there is a concern that the filler may penetrate through the adhesive layer 601 and adversely affect the semiconductor chips 20. On the other hand, when the elastic modulus of the cured photosensitive adhesive composition is more than the upper limit

value, depending on the composition of the photosensitive adhesive composition, the flexibility of the adhesive layer 601 degrades, and thus the stress relaxation properties degrade. Therefore, it is not possible to relax, for example, residual stress generated due to the lamination of the semiconductor chips 5 20 or the local concentration of thermal stress caused by the thermal expansion difference between the semiconductor chip 20 and the adhesive layer 601, and there is a concern that cracks may be generated in the semiconductor chips 20.

10 [0169]

Meanwhile, the elastic modulus of the cured photosensitive adhesive composition can be obtained by means of, for example, a measurement using a nanoindentation tester ENT-1000 (manufactured by Elionix Inc.) and a Bercovici indenter 15 (triangular pyramid with a dihedral angle of 115°) at a measurement temperature of 25°C and a load of 2 mN for one second according to ISO 14577.

[0170]

In addition, the elastic modulus of the cured 20 photosensitive adhesive composition can be obtained from the elastic modulus of the coated film 601a after the mounting step.

[0171]

In addition, the elastic modulus of the photosensitive adhesive composition to be cured at 25°C is more preferably set 25 to 75% to 115% and still more preferably set to 80% to 110% of

the elastic modulus of the cured photosensitive adhesive composition at 25°C. Meanwhile, in a case in which the elastic modulus of the photosensitive adhesive composition to be cured is less than the lower limit value, the pressure-sensitive adhesiveness of the photosensitive adhesive composition increases, but the coating of the photosensitive adhesive composition is likely to deform. As a result, for example, when the semiconductor chips 20 are temporarily disposed through this coating, there is a concern that the positions thereof may be easily deviated from each other or the photosensitive adhesive composition may flow out from the wafer 201. On the other hand, in a case in which the elastic modulus of the photosensitive adhesive composition to be cured is more than the upper limit value, the pressure-sensitive adhesiveness degrades, and there is a concern that it may become difficult to temporarily dispose the semiconductor chips 20.

Meanwhile, the elastic modulus of the photosensitive adhesive composition to be cured can also be measured in the same manner as the elastic modulus of the cured photosensitive adhesive composition.

[0172]

In addition, the elastic modulus of the photosensitive adhesive composition to be cured can be obtained from the elastic modulus of the coated film 601a after the treatment step and before the mounting step.

[0173]

Meanwhile, the adhesive force of the photosensitive adhesive composition which has been subjected to the etching treatment and the ashing treatment and is yet to be cured to the semiconductor chips 20 at 25°C is more preferably set to 30 N to 180 N (1.875 to 11.25 MPa) and still more preferably set to 40 N to 160 N (2.5 to 10 MPa). Meanwhile, in a case in which the adhesive force is less than the lower limit value, there is a concern that air bubbles may easily intrude into the interfaces between the adhesive layer 601 and the semiconductor chip 20. On the other hand, in a case in which the adhesive force is more than the upper limit value, there is a concern that it becomes difficult to remove air bubbles in a case in which air bubbles intrude into the interfaces between the adhesive layer 601 and the semiconductor chip 20.

[0174]

Meanwhile, the adhesive force of the photosensitive adhesive composition which has been subjected to the etching treatment and the ashing treatment and is yet to be cured to the semiconductor chips 20 can be measured in the following manner. First, the semiconductor chips 20 are adhered together through the photosensitive adhesive composition of the present invention which has been subjected to the etching treatment and the ashing treatment and is yet to be cured, thereby obtaining a body of the adhered semiconductor chips. After that, the die

shear strength of the body of the adhered semiconductor chips is obtained using a universal bond tester Dage4000 (manufactured by Dage Japan Co., Ltd.) as the adhesive force to the semiconductor chips 20. The die shear strength is obtained from the strength at which the joining surface between the semiconductor chips 20 is broken when the semiconductor chip 20 on one side is pressed from the side (side surface) of the body of the adhered semiconductor chips in the horizontal direction (the in-plane direction of the semiconductor chip 20) using a shearing tool.

[0175]

In addition, the adhesive force of the photosensitive adhesive composition which has been subjected to the etching treatment and the ashing treatment and is yet to be cured to the semiconductor chips 20 can be obtained from the adhesive force of the coated film 601a to the semiconductor chips 20 after the treatment step and before the mounting step.

[0176]

Meanwhile, the etching treatment refers to, for example, a treatment for removing passivation films on the surface of the semiconductor chip 20 and exposing electrode pads for connecting the bonding wires 70. A specific example is an etching treatment carried out using a gas mixture of a fluorine compound gas (CF_4), an argon gas (Ar), and an oxygen gas (O_2) as gas under conditions in which the output is set to 2,500 W,

the time is set to six minutes, and the CF₄ flow rate/the Ar flow rate/the O₂ flow rate are set to 200 sccm/200 sccm/50 sccm.

[0177]

In addition, the ashing treatment refers to, for example,
5 a treatment for removing treatment residues and the like generated by the etching treatment and cleaning the adhesive layer 601 surface of the electrode pad surface. A specific example is a plasma treatment carried out using an oxygen gas (O₂) under conditions in which the output is set to 600 W, the
10 time is set to 12 minutes, and the O₂ flow rate is set to 200 sccm.

[0178]

Meanwhile, the etching treatment and the ashing treatment described above may accelerate the deterioration of organic
15 materials in some cases. Therefore, in the case of a coating (adhesive layer) having poor etching resistance and poor ashing resistance, there is a concern that it may be impossible to sufficiently adhere the semiconductor chips 20. In contrast, the coated film 601a (the adhesive layer 601) formed using the
20 photosensitive adhesive composition has sufficient etching resistance and sufficient ashing resistance. Therefore, the degradation of the adhesive force of the coated film 601a is suppressed even after the etching treatment and the ashing treatment described above, and consequently, an adhesive force
25 as described above is developed. Therefore, it is not necessary

to consider the degradation of adhesiveness in a variety of treatments in adhesion processes, and thus the above-described photosensitive adhesive composition is useful since it is possible to easily simplify the manufacturing step of the semiconductor device 10 and reduce the costs.

[0179]

In addition, the percentage of the elastic modulus of the photosensitive adhesive composition changed before and after the treatment step is preferably in a certain range. Therefore, it is preferable to appropriately set the heating conditions for the heating step which is considered to affect the resistance to the treatment step (etching resistance and ashing resistance) so that the change percentage falls into a certain range.

[0180]

Specifically, when the elastic modulus of the photosensitive adhesive composition at 25°C after the heating step and before the treatment step is represented by X [GPa], and the elastic modulus at 25°C after the treatment step is represented by Y [GPa], X and Y preferably satisfy a relationship of $0.7 \leq X/Y \leq 1.5$ and more preferably satisfy a relationship of $0.8 \leq X/Y \leq 1.3$. When the percentage of the elastic modulus changed before and after the treatment step satisfies the above-described relationship, the coated film 601a constituted of the photosensitive adhesive composition has sufficient mechanical characteristics enough to hold patterned shapes and

sufficient adhesiveness enough to adhere the semiconductor chips 20 together. That is, in the treatment step in which the etching treatment and the ashing treatment are carried out, the deterioration of the coated film 601a is accelerated; however, 5 in a case in which the percentage of the elastic modulus changed before and after the treatment step satisfies the above-described relationship, the coated film 601a sufficiently functions as the adhesive layer 601 in the mounting step while sufficiently holding patterned shapes. Therefore, when the 10 percentage of the elastic modulus changed before and after the treatment step satisfies the above-described relationship, the coated film 601a constituted of the above-described photosensitive adhesive composition are capable of satisfying a function of an etching mask and a function of the adhesive 15 layer 601.

[0181]

Meanwhile, in the treatment step, an etching treatment and an ashing treatment which satisfy the above-described treatment conditions are carried out.

20 [0182]

In addition, the minimum melt viscosity of the photosensitive adhesive composition to be cured at 100°C to 200°C is preferably 20 to 500 Pa·s. Since the above-described photosensitive adhesive composition has excellent wetting 25 properties to the semiconductor chips 20, it becomes difficult

for voids and the like to be generated in the adhesive layer 601. Therefore, it is possible to form a homogeneous adhesive layer 601 having properties varying only to a small extent. As a result, when the semiconductor chips 20 are adhered together through the adhesive layer 601, the local concentration of stress is not easily caused, and it is possible to further suppress the generation of cracks in the semiconductor chips 20, the occurrence of peeling between the semiconductor chip 20 and the adhesive layer 601, or the like. Meanwhile, the minimum melt viscosity of the photosensitive adhesive composition to be cured can be measured using a rheometer and can be obtained from the minimum melt viscosity of the coated film 601a after the treatment step and before the mounting step.

[0183]

Meanwhile, the minimum melt viscosity of the photosensitive adhesive composition to be cured is more preferably set to 25 to 400 Pa·s and still more preferably set to 30 to 300 Pa·s.

[0184]

In addition, the photosensitive adhesive composition to be cured has constant pressure-sensitive adhesiveness, but the pressure-sensitive adhesiveness can be weakened by carrying out an UV irradiation treatment on the photosensitive adhesive composition. Therefore, the pressure-sensitive adhesiveness (pressure-sensitive adhesive force) of the photosensitive

adhesive composition to be cured can be controlled depending on the presence or absence of the UV irradiation treatment.

[0185]

Specifically, the pressure-sensitive adhesive force of
5 the photosensitive adhesive composition to be cured to the back
grind film 90 will be described. First, the coated film 601a
is formed on the wafer 201 using the photosensitive adhesive
composition. Next, the coated film 601a is not cured
(completely cured), and the etching treatment and the ashing
10 treatment described above are carried out on the wafer 201
including the coated film 601a in a non-cured or semi-cured state
(the photosensitive adhesive composition to be cured). After
that, an UV peelable back grind film 90 is glued onto the coated
film 601a, and the pressure-sensitive adhesive force of the back
15 grind film 90 to the coated film 601a at 25°C is measured. Such
a pressure-sensitive adhesive force is preferably 3.0 N/25 mm
or more. The above-described photosensitive adhesive
composition is capable of developing a sufficient
pressure-sensitive adhesive force to the back grind film 90 even
20 after treatments which accelerate the deterioration of organic
materials such as the etching treatment or the ashing treatment.
Therefore, for example, when a back grinding treatment is carried
out on the wafer 201 on which the coated film 601a of the
photosensitive adhesive composition is formed, it is possible
25 to reliably fix the wafer 201 and further increase the accuracy

of the back grinding treatment.

[0186]

Meanwhile, the pressure-sensitive adhesive force is more preferably set to 3.5 N/25 mm or more and 10.0 N/25 mm or less.

5 [0187]

In addition, the pressure-sensitive adhesive force can be measured in the following manner. First, a UV peelable back grind film 90 (having a width of 25 mm and a length of 75 mm) is attached so that the pressure-sensitive adhesion surface comes into contact with the coated film 601a of the photosensitive adhesive composition. Next, the measurement temperature is set to 25°C, the peeling strength is set to 10.0±0.2 mm/s, and one end of the back grind film 90 in the longitudinal direction is pulled so that the peel angle reaches 180°, thereby peeling the back grind film 90 from the coated film 601a of the photosensitive adhesive composition. The pressure-sensitive adhesive force can be obtained by measuring the average value of loads necessary for peeling at this time (180° peeling pressure-sensitive adhesive force, unit: N/25 mm, according to JIS Z 0237).

[0188]

Meanwhile, the pressure-sensitive adhesive force of the photosensitive adhesive composition which has been subjected to the UV irradiation treatment and is to be cured to the back grind film 90 at 50°C is preferably 0.5 N/25 mm or less. In such

a case, it is possible to sufficiently decrease the pressure-sensitive adhesive force of the photosensitive adhesive composition which has been subjected to the UV irradiation treatment and is to be cured to the back grind film 90. Therefore, for example, when the back grind film 90 is peeled off from the coated film 601a of the photosensitive adhesive composition after the back grinding treatment, it is possible to smoothly peel the back grind film 90 without large loads exerting on the coated film 601a. Additionally, it is possible to peel the back grind film 90 without impairing the adhesion properties between the coated film 601a and the semiconductor chip 20. As a result, for example, when the individual pieces 21 and 22 are picked up after the dicing treatment, it is possible to prevent the generation of disadvantages such as defects in the semiconductor chips 20.

[0189]

In addition, it is possible to suppress, for example, the attachment of the photosensitive adhesive composition to the dicing blade 110 in the dicing step or the attachment of the photosensitive adhesive composition to the collet 121 in the mounting step by decreasing the pressure-sensitive adhesive force after the UV irradiation treatment. As a result, it is possible to suppress the occurrence of poor dicing or poor pickup.

[0190]

Meanwhile, the pressure-sensitive adhesive force after the UV irradiation treatment is more preferably set to 0.05 N/25 mm or more and 0.40 N/25 mm or less.

[0191]

5 In addition, in the UV irradiation treatment, the coated film 601a is irradiated with light having a wavelength of 365 nm through the back grind film 90 so that the accumulated light amount reaches 600 mJ/cm².

[0192]

10 In addition, the UV peelable back grind film 90 is made of an acrylic resin.

[0193]

Meanwhile, the pressure-sensitive adhesive force after the UV irradiation treatment can be measured using the same
15 method as the above-described method for measuring the pressure-sensitive adhesive force at 25°C of the photosensitive adhesive composition which has been subjected to the etching treatment and the ashing treatment and is yet to be cured to the back grind film 90.

20 [0194]

Hitherto, the present invention has been described, but the present invention is not limited thereto. For example, arbitrary components may be added to the photosensitive adhesive composition. In addition, arbitrary structures may be added to
25 the semiconductor device.

EXAMPLES

[0195]

Next, specific examples of the present invention will be described.

5 (Example 1)

[1] Synthesis of alkali-soluble resin (A) (cyclic olefin-based resin A-1)

A plurality of glass devices were prepared and were dried at 60°C and 0.1 Torr for 18 hours. After that, all of the glass
10 devices were put into a glove box.

[0196]

Next, toluene (992 g), dimethoxyethane (116 g), 1,1-bistrifluoromethyl-2-(bicyclo[2.2.1]hept-2-ene-5-yl)ethyl alcohol (hereinafter, HFANB) (148 g, 0.54 mol), ethyl
15 3-(bicyclo[2.2.1]hept-2-ene-2-yl)propanate (hereinafter, EPEsNB) (20.7 g, 0.107 mol), and 5-((2-(2-methoxyethoxy)ethoxy)methyl)bicyclo[2.2.1]hept-2-ene (hereinafter, NBTON) (61.9 g, 0.274 mol) were put into one glass device (glass device X), thereby obtaining a mixture
20 including the respective monomers. After that, purging (nitrogen purging) was carried out by causing nitrogen to flow for 30 minutes while heating the mixture at 45°C.

[0197]

In addition, EPEsNB (14.2 g, 0.073 mol) and NBTON (46.7
25 g, 0.159 mol) were mixed together and nitrogen purging was

carried out in another glass device (glass device Y). After the nitrogen purging ended completely,

bis(toluene)bis(perfluorophenyl) nickel (5.82 g, 0.012 mol) dissolved in 60.5 ml of toluene was injected into the glass device

5 Y. At the same time, the mixture in the above-described glass device X was added to the glass device Y for three hours at a rate so that a polymerization reaction proceeded at a certain level, thereby obtaining a reaction solution.

[0198]

10 Next, the reaction solution was dissolved in approximately 1 L of methanol/tetrahydrofuran (THF) (=4 mol/5 mol) solution, thereby removing unreacted monomers in the reaction solution. Next, esters in the reaction solution were hydrolyzed using a sodium hydroxide solution of sodium hydroxide/sodium acetate
15 (=4.8 mol/1 mol) at 60°C for four hours, thereby obtaining a solution A. After that, methanol (405 g), THF (87 g), acetic acid (67 g), formic acid (67 g), and deionized water (21 g) were added to the solution A, and were stirred at 50°C for 15 minutes. When the stirring was stopped, since the solution A was separated
20 into a water layer and an organic layer, the upper layer of the water layer was removed, and the organic layer was washed with a methanol/deionized water (=390 g/2,376 g) solution three times at 60°C for 15 minutes. In addition, the obtained polymer was diluted in propylene glycol methyl ether acetate, and the solvent
25 was substituted so that the concentration of the polymer reached

40%. In the above-described manner, a polymer in a solution state (cyclic olefin-based resin A-1), which is represented by Formula (7), was obtained.

[0199]

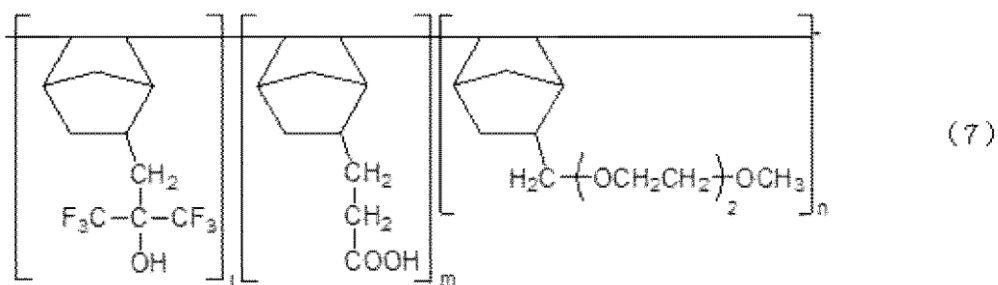
5 The yield of the cyclic olefin-based resin A-1 was 93.1%. The weight-average molecular weight (Mw) of the cyclic olefin-based resin A-1 was 85,900. The molecular weight dispersion (PD) of the cyclic olefin-based resin A-1 was 2.52.

[0200]

10 In addition, regarding the composition of the cyclic olefin-based resin A-1, in $^1\text{H-NMR}$, HFANB was 45.0 mol%, 2-(bicyclo[2.2.1]hept-2-ene-5-yl) propionate (hereinafter, EPENB) was 15.0 mol%, and NBTON was 40.0 mol%.

[0201]

「A-1」



(In Formula (7), $l:m:n=45:15:40$)

[0202]

[2] Production of photosensitive adhesive composition

20 The cyclic olefin-based resin A-1 (22.0 parts by mass in terms of the solid content) obtained in [1] as the alkali-soluble resin (A), a photo-acid-generating agent B-1 (4.0 parts by mass)

as the photo-acid-generating agent (B), an epoxy compound C-1 (5.0 parts by mass) as the epoxy compound (C), a phenolic compound D-1 (3.0 parts by mass) as the phenolic compound (D), an antioxidant E-1 (2.0 parts by mass), an antioxidant E-2 (3.0 parts by mass), and propylene glycol methyl ether acetate (61.0 parts by mass including the propylene glycol methyl ether acetate in the solution of the cyclic olefin-based resin A-1) as a solvent were mixed together, thereby obtaining a homogeneous photosensitive adhesive composition.

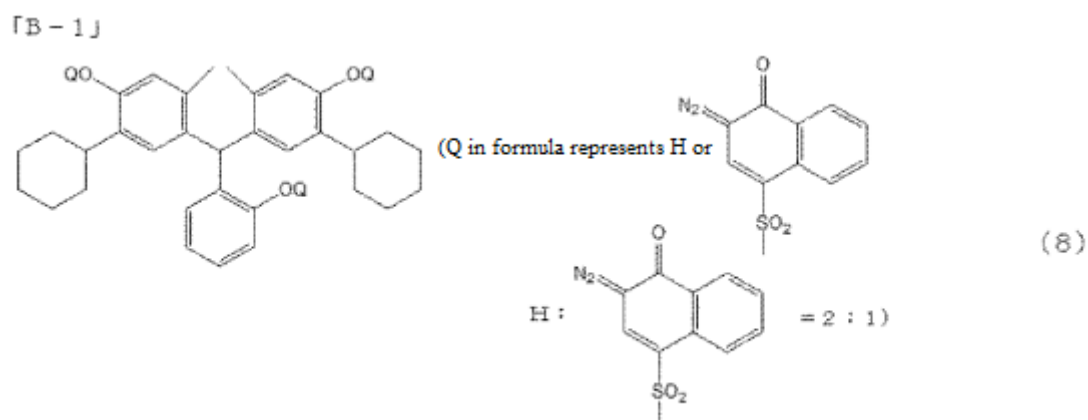
Materials used for the photosensitive adhesive composition of Example 1 will be described below.

[0203]

<Photo-acid-generating agent B-1>

As the photo-acid-generating agent B-1, a compound represented by Formula (8) was prepared.

[0204]



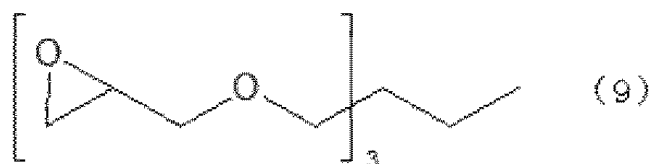
[0205]

<Epoxy compound C-1>

As the epoxy compound C-1, a compound represented by Formula (9) was prepared.

[0206]

「C-1」



5

[0207]

<Phenolic compound D-1>

As the phenolic compound D-1, a compound represented by Formula (10) (butyl 4-hydroxy benzoate) was prepared.

[0208]

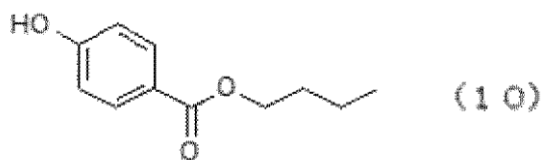
10

The melting point of the phenolic compound D-1 was 70°C.

The weight-average molecular weight (Mw) of the phenolic compound D-1 was 194. The hydroxyl group equivalent of the phenolic compound D-1 was 194 g/eq.

[0209]

「D-1」



15

[0210]

<Antioxidant E-1>

As the antioxidant E-1, a compound represented by Formula (11) (4,4'-di(α,α-dimethylbenzyl)diphenylamine) was prepared.

[0211]

「E-1」



[0212]

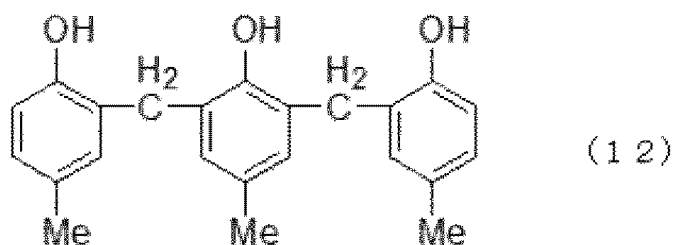
<Antioxidant E-2>

5 As the antioxidant E-2, a compound represented by Formula
(12)

(2,6-bis[(2-hydroxy-5-methylphenyl)methyl]-4-methylphenol)
was prepared.

[0213]

「E-2」



10

[0214]

(Examples 2 to 18 and Comparative Examples 1 to 4)

Photosensitive adhesive compositions were obtained in the
same manner as in Example 1 except for the fact that materials
15 constituting the photosensitive adhesive composition were
changed as shown in Tables 1 and 2 and the contents of the
respective materials were set as shown in Tables 1 and 2.

Meanwhile, materials used for the photosensitive adhesive

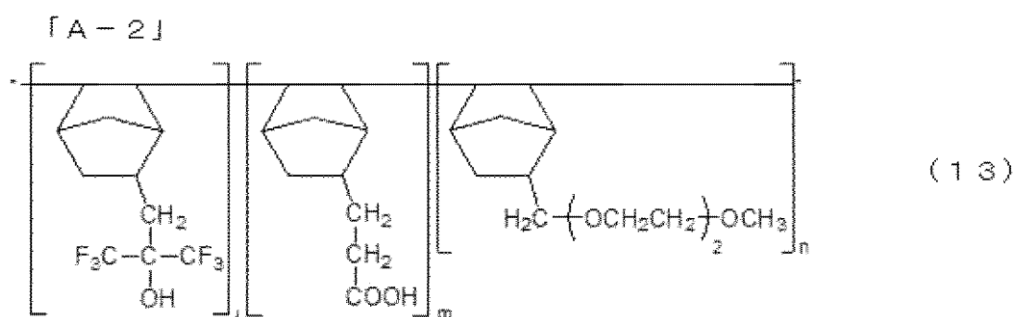
compositions of the respective examples and the respective comparative examples will be described below.

[0215]

<Cyclic olefin-based resin A-2>

5 As the cyclic olefin-based resin A-2 (the alkali-soluble resin (A)), a compound represented by Formula (13) was prepared.

[0216]



(In Formula (13), 1:m:n=25:15:60)

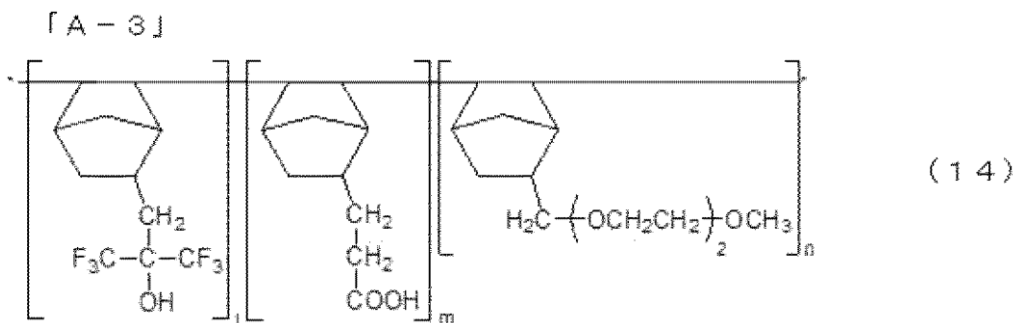
10

[0217]

<Cyclic olefin-based resin A-3>

As the cyclic olefin-based resin A-3 (the alkali-soluble resin (A)), a compound represented by Formula (14) was prepared.

[0218]



15

(In Formula (14), 1:m:n=25:35:40)

[0219]

<Phenolic compound D-2>

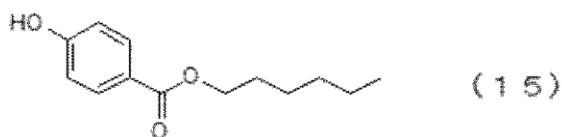
As the phenolic compound D-2 (the phenolic compound (D)),
a compound represented by Formula (15) (hexyl 4-hydroxy
benzoate) was prepared.

5 [0220]

The melting point of the phenolic compound D-2 was 53°C.
The weight-average molecular weight (Mw) of the phenolic
compound D-2 was 222. The hydroxyl group equivalent of the
phenolic compound D-2 was 222 g/eq.

10 [0221]

「D-2」



[0222]

<Phenolic compound D-3>

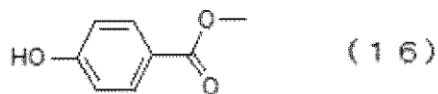
As the phenolic compound D-3 (the phenolic compound (D)),
15 a compound represented by Formula (16) (methyl 4-hydroxy
benzoate) was prepared.

[0223]

The melting point of the phenolic compound D-3 was 127°C.
The weight-average molecular weight (Mw) of the phenolic
20 compound D-3 was 152. The hydroxyl group equivalent of the
phenolic compound D-3 was 152 g/eq.

[0224]

「D-3」



[0225]

<Phenolic compound D-4>

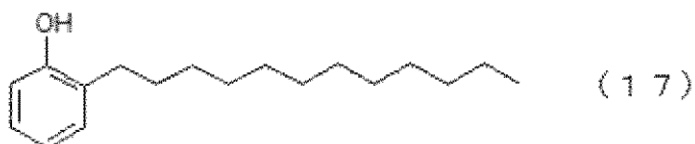
As the phenolic compound D-4 (the phenolic compound (D)),
 5 a compound represented by Formula (17) (2-dodecylphenol) was
 prepared.

[0226]

The melting point of the phenolic compound D-4 was 42°C.
 The weight-average molecular weight (Mw) of the phenolic
 10 compound D-4 was 262. The hydroxyl group equivalent of the
 phenolic compound D-4 was 262 g/eq.

[0227]

「D-4」



[0228]

15 <Phenolic compound D-5>

As the phenolic compound D-5 (the phenolic compound (D)),
 a compound represented by Formula (18)
 (1,8,9-trihydroxyanthracene) was prepared.

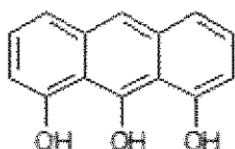
[0229]

20 The melting point of the phenolic compound D-5 was 181°C.

The weight-average molecular weight (Mw) of the phenolic compound D-5 was 226. The hydroxyl group equivalent of the phenolic compound D-5 was 113 g/eq.

[0230]

「D-5」



(18)

5

[0231]

<Phenolic compound D-6>

As the phenolic compound D-6 (the phenolic compound (D)), a compound represented by Formula (19)

10 (2,2'-dihydroxydiphenylmethane) was prepared.

[0232]

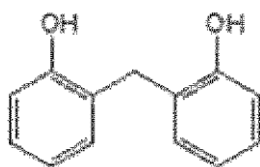
The melting point of the phenolic compound D-6 was 120°C.

The weight-average molecular weight (Mw) of the phenolic compound D-6 was 200. The hydroxyl group equivalent of the phenolic compound D-6 was 100 g/eq.

15

[0233]

「D-6」



(19)

[0234]

<Phenolic compound X-1>

20

As the phenolic compound X-1 (the phenolic compound (X)),

a compound represented by Formula (20)

(4,4'-[(2-hydroxyphenyl)methylene]bis[2-cyclohexyl-5-methylphenol]) was prepared.

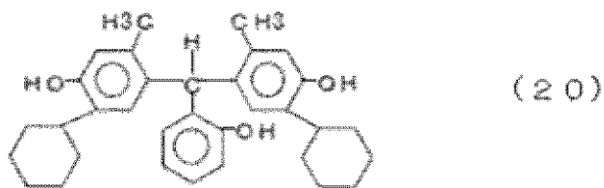
[0235]

5 The melting point of the phenolic compound X-1 was 222°C.

The weight-average molecular weight (Mw) of the phenolic compound X-1 was 484. The hydroxyl group equivalent of the phenolic compound X-1 was 161 g/eq.

[0236]

「X-1」

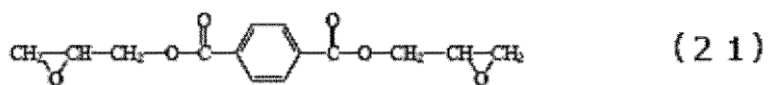


10

<Epoxy compound C-2>

As the epoxy compound C-2, an aromatic epoxy compound represented by Formula (21) was prepared.

「C-2」



15

[0237]

[3] Production of test pieces for evaluation

First, the photosensitive adhesive composition used in the respective examples and the respective comparative examples was applied onto a silicon semiconductor chip and was prebaked at 20 120°C for five minutes. Therefore, a coated film was obtained.

[0238]

Next, a heating treatment was carried out on the obtained coated film at 150°C for 40 minutes, thereby obtaining a semi-cured (to be cured) coated film.

5 Next, an etching treatment and an ashing treatment were sequentially carried out on the semiconductor chip including the coated film. The etching treatment was carried out using a gas mixture of a fluorine compound gas (CF₄), an argon gas (Ar), and an oxygen gas (O₂) as gas under conditions in which the output
10 was 2,500 W, the time was six minutes, and the CF₄ flow rate/the Ar flow rate/the O₂ flow rate were 200 sccm/200 sccm/50 sccm. In addition, the ashing treatment was carried out using a gas mixture of O₂ and Ar under conditions in which the output was 600 W, the time was 12 minutes, and the O₂ flow rate was 200 sccm.

15 [0239]

Next, another semiconductor chip was overlaid on the coated film and was pressed with a load of 10 N for five seconds while being heated at a temperature of 150°C.

[0240]

20 In the above-described manner, a test piece for evaluation in which the two semiconductor chips were adhered together through an adhesive layer was produced.

[0241]

[4] Evaluation of photosensitive adhesive composition and
25 test piece for evaluation

[4.1] Evaluation of adhesiveness

[4.1.1] Evaluation of adhesion properties during development

First, the photosensitive adhesive composition used in the
5 respective examples and the respective comparative examples was
applied onto a silicon semiconductor chip and was prebaked at
120°C for five minutes. Therefore, a 10 μm -thick coated film
was obtained.

[0242]

10 Next, an exposure treatment was carried out on the obtained
coated film through a 100 μm -wide line-and-space-pattern mask.
This exposure treatment was carried out by irradiating different
portions in one coated film for different times in the air with
light having a wavelength of 365 nm and a light intensity of
15 5 mW/cm².

[0243]

Next, the coated film on which the exposure treatment had
been carried out was developed with an alkaline developer (an
aqueous solution of 2.38% tetramethylammonium hydroxide) at 23°C
20 for 40 seconds and was then rinsed with pure water for 20 seconds.
The coated film (adhesive layer) in which 100 μm -wide opening
portions had been formed after the development was observed using
an optical microscope, and the degree of peeling of the coated
film from the semiconductor chip (the presence or absence of
25 peeling) was evaluated on the basis of the following evaluation

standards.

[0244]

<Evaluation standards>

A: All of the coated film was not peeled off from the
5 semiconductor chip.

B: Less than 30% of the coated film was peeled off from
the semiconductor chip.

C: 30% or more and less than 50% of the coated film was
peeled off from the semiconductor chip.

10 D: 50% or more of the coated film was peeled off from the
semiconductor chip.

[0245]

Meanwhile, in Comparative Examples 1, 2, and 4, it was not
possible to open a 100 μm -wide pattern, and thus the adhesion
15 properties during development could not be evaluated. In
addition, in Comparative Example 3 as well, 50% or more of the
coated film was peeled off from the semiconductor chip, and it
was not possible to open a desired pattern.

[0246]

20 [4.1.2] Evaluation of adhesion strength

For the obtained test piece for evaluation, the
semiconductor chip on one side was pressed from the side (side
surface) of the semiconductor chip in the horizontal direction
using a Dage4000 (manufactured by Dage Japan Co., Ltd.), and
25 the die shear strength per chip at which the joining surface

between the chips was broken was measured. The chip size was 4 mm×4 mm.

In addition, the measured die shear strength was evaluated on the basis of the following evaluation standards.

5 [0247]

<Evaluation standards>

A: The die shear strength is extremely high.

B: The die shear strength is high.

C: The die shear strength is low.

10 D: The die shear strength is extremely low.

[0248]

Meanwhile, in Comparative Example 4, the coted film (adhesive layer) was peeled off from the semiconductor chip, and it was not possible to evaluate the adhesion strength.

15 [0249]

[4.2] Evaluation of rework properties

First, the photosensitive adhesive composition used in the respective examples and the respective comparative examples was applied onto a silicon semiconductor chip and was prebaked at 20 120°C for five minutes. Therefore, a coated film was obtained.

[0250]

Next, a heating treatment was carried out on the obtained coated film at 150°C for 40 minutes.

Next, the semiconductor chip on which the heating-treated 25 coated film had been formed was immersed in propylene

glycol-1-monomethyl ether-2-acetate and was left to stand for 20 hours.

[0251]

Next, the semiconductor chip was removed from the
5 propylene glycol-1-monomethyl ether-2-acetate, the presence and absence of residues on the coated film was visually observed, and the rework properties were evaluated on the basis of the following evaluation standards.

[0252]

10 <Evaluation standards>

A: Residues of the coated film are not observed.

B: Residues of the coated film are slightly observed.

C: Residues of the coated film are significantly observed.

D: The coated film is rarely removed.

15 [0253]

[4.3] Evaluation of photosensitivity of photosensitive adhesive composition

First, the photosensitive adhesive composition used in the respective examples and the respective comparative examples was
20 applied onto a silicon semiconductor chip and was prebaked at 120°C for five minutes. Therefore, a 10 μm -thick coated film was obtained.

[0254]

Next, an exposure treatment was carried out on the obtained
25 coated film through a 100 μm -wide line-and-space-pattern mask.

This exposure treatment was carried out by irradiating different parts in the coated film for different times in the air with light having a wavelength of 365 nm and a light intensity of 5 mW/cm².

5 [0255]

Next, a development treatment was carried out on the coated film on which the exposure treatment had been carried out. In addition, the minimum exposure weight (unit: mJ/cm²) at which the film-remaining percentage of non-exposed portions, which
10 is defined in the following manner, was 90% or more and the film-remaining percentage of exposed portions reached 0% was obtained.

Film-remaining percentage of non-exposed
portions= $100 \times \frac{\text{film thickness after development of non-exposed}}{\text{film thickness after prebaking}}$
15

Film-remaining percentage of exposed portions= $100 \times \frac{\text{film thickness after development of exposed portions}}{\text{film thickness after prebaking}}$

The obtained exposure lights are shown in Table 1.

20 [0256]

Meanwhile, the coated films of the respective comparative examples were not reacted by light during the exposure, and the coated films could not be removed by means of the development treatment. Therefore, for the coated films of the respective
25 comparative examples, the photosensitivity could not be

evaluated (the exposure amounts could not be measured).

[0257]

[4.5] Evaluation of film-remaining percentage (residual percentage) of photosensitive adhesive composition

5 First, in the same manner as in [4.4], coated films on which the exposure treatment had been carried out in the respective examples and the respective comparative examples were prepared. Next, a development treatment was carried out on the coated films on which the exposure treatment had been carried out, and then
10 a heating treatment was carried out at 150°C for 40 minutes. In addition, the film-remaining percentages of non-exposed portions, which is defined in the following manner, were obtained.

[0258]

15 Film-remaining percentage = $100 \times \text{film thickness after development of non-exposed portions} / \text{film thickness after prebaking}$

The obtained film-remaining percentages are shown in Table 1.

20 [0259]

Meanwhile, the coated films in the respective comparative examples were not reacted by light during the exposure, and the coated films could not be removed by means of the development treatment. Therefore, for the coated films of the respective
25 comparative examples, the film-remaining percentages could not

be evaluated.

[0260]

[Table 1]

	Examp le 1	Examp le 2	Examp le 3	Examp le 4	Examp le 5	Examp le 6	Examp le 7	Examp le 8	Examp le 9	Examp le 10	Examp le 11	Examp le 12	Examp le 13	Comparat ive Example 1	Comparat ive Example 2	Comparat ive Example 3	Comparat ive Example 4
Photosensiti ve adhesive composition	Cyclic olefin-based resin A-1 [parts by mass]	22.0		22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	21.0	24.0	24.0	23.0	22.0	22.0
	Cyclic olefin-based resin A-2 [parts by mass]	22.0															
	Cyclic olefin-based resin A-3 [parts by mass]		22.0														
	Photo-acid-generati ng agent B-1 [parts by mass]	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	6.0	4.0	4.0	6.0	6.0	5.0	5.0
	Epoxy compound C-1 [parts by mass]	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	8.0	5.0	5.0		6.0	5.0	5.0
	Phenolic compound D-1 [parts by mass]	3.0	3.0	3.0	1.0	1.0					1.5	5.0		4.0			
	Phenolic compound D-2 [parts by mass]					3.0	3.0	2.0					1.0				
	Phenolic compound D-3 [parts by mass]								3.0	2.0							
	Phenolic compound D-4 [parts by mass]															3.0	
	Phenolic compound D-5 [parts by mass]																3.0
	Phenolic compound D-6 [parts by mass]			2.0	2.0		1.0	1.0		1.0			2.0				
	Phenolic compound X-1 [parts by mass]				1.0			1.0		1.0			1.0				
	Antioxidant E-1 [parts by mass]	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Antioxidant E-2 [parts by mass]	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Solvent (propylene glycol methyl ether acetate) [parts by mass]	61.0	61.0	61.0	60.0	61.0	60.0	60.0	61.0	60.0	57.5	60.0	58.0	61.0	60.0	60.0	60.0
	Characterist	70		D-1:7	D-1:7	53	D-2:5	D-2:5	127	D-3:1	70	70	D-2:5	70	-	42	181
Melting point [°C]																	

[0262]

As is clear from Tables 1 and 2, it was admitted that, in the photosensitive adhesive compositions and the test pieces for evaluation of the respective examples, air bubbles remaining in the interfaces with the semiconductor chip were suppressed, and the adhesive forces (adhering forces) were sufficient between the semiconductor chip and the adhesive layer. In addition, the coated films (adhesive layers) used in the respective examples after the predetermined heating treatment had a sufficient solubility in organic solvents and were favorable in terms of so-called rework properties. Furthermore, in the test pieces for evaluation in the respective examples, the film-remaining percentages of the non-exposed portions were admitted to be high. Meanwhile, the semiconductor devices including a laminated semiconductor element obtained by adhering semiconductor elements together through a cured substance of the photosensitive adhesive composition of each of the examples were highly reliable. On the other hand, coated films formed using the photosensitive adhesive composition of each of the comparative examples could not be removed by means of a development treatment as described in [4.3]. Therefore, it was not possible to obtain semiconductor devices including a laminated semiconductor element.

Industrial Applicability

[0263]

When used as an adhesive layer that adheres semiconductor elements together, a cured substance of the photosensitive adhesive composition of the present invention is capable of
5 reducing the generation of air bubbles (voids) in the interfaces between the semiconductor element and the adhesive layer and, even when air bubbles are generated in the interfaces, is capable of removing the generated air bubbles. As a result, it is possible to enhance the adhesiveness (adhesion properties)
10 between semiconductor elements. Therefore, the present invention has industrial applicability.

CLAIMS

1. A photosensitive adhesive composition comprising:
(A) an alkali-soluble resin;
5 (B) a photo-acid-generating agent;
(C) an epoxy compound; and
(D) a phenolic compound having a melting point of 50°C to
150°C.
- 10 2. The photosensitive adhesive composition according to
Claim 1, further comprising:
a phenolic compound (X) having a melting point higher than
that of the phenolic compound (D).
- 15 3. The photosensitive adhesive composition according to
Claim 2,
wherein the melting point of the phenolic compound (X) is
151°C to 250°C.
- 20 4. The photosensitive adhesive composition according to
Claim 2 or 3,
wherein the phenolic compound (X) includes a phenolic
compound having a plurality of phenolic skeletons.
- 25 5. The photosensitive adhesive composition according to

Claim 4,

wherein the phenolic compound having the plurality of the phenolic skeletons has a substituent which has a cyclic structure and is bonded to at least one of the phenolic skeletons.

5

6. The photosensitive adhesive composition according to any one of Claims 1 to 5,

wherein the phenolic compound (D) includes at least one of a phenolic compound having a substituent including an
10 aliphatic hydrocarbon group and a phenolic compound having a plurality of phenolic skeletons.

7. The photosensitive adhesive composition according to Claim 6,

15 wherein a hydroxyl group equivalent of the phenolic compound having the substituent including the aliphatic hydrocarbon group is 150 to 250 g/eq.

8. The photosensitive adhesive composition according to
20 Claim 6 or 7,

wherein the plurality of the phenolic skeletons of the phenolic compound (D) form a linked polycyclic structure.

9. The photosensitive adhesive composition according to
25 any one of Claims 6 to 8,

wherein a hydroxyl group equivalent of the phenolic compound having the plurality of the phenolic skeletons is 50 to 150 g/eq.

5 10. The photosensitive adhesive composition according to any one of Claims 1 to 9,

 wherein the alkali-soluble resin (A) includes a cyclic olefin-based resin.

10 11. The photosensitive adhesive composition according to Claim 10,

 wherein the cyclic olefin-based resin includes a norbornene-based resin.

15 12. The photosensitive adhesive composition according to any one of Claims 1 to 11,

 wherein the alkali-soluble resin (A) has an acidic group.

 13. The photosensitive adhesive composition according to
20 any one of Claims 1 to 12,

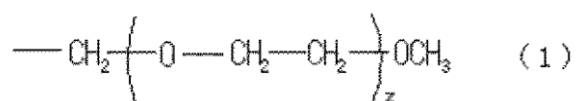
 wherein the alkali-soluble resin (A) has a linear substituent having 2 to 30 carbon atoms.

 14. The photosensitive adhesive composition according to
25 Claim 13,

wherein the linear substituent has an alkyl ether structure.

15. The photosensitive adhesive composition according to
5 Claim 13 or 14,

wherein the linear substituent is a group represented by
Formula (1) below;



(In the Formula (1), z represents an integer of 1 or more
10 and 10 or less).

16. The photosensitive adhesive composition according to
any one of Claims 13 to 15,

wherein the alkali-soluble resin (A) includes 20 to 60 mol%
15 of a repeating unit having the linear substituent.

17. The photosensitive adhesive composition according to
any one of Claims 1 to 16,

wherein the epoxy compound (C) has two or more glycidyl
20 groups.

18. A semiconductor device comprising:

a laminated semiconductor element,

wherein the laminated semiconductor element has a

plurality of semiconductor elements and a cured substance of the photosensitive adhesive composition according to any one of Claims 1 to 17 which is provided between the semiconductor elements and joins the semiconductor elements.