

## DESCRIPTION

## Title of Invention

CURABLE RESIN FILM AND SHEET FOR FORMING A FIRST PROTECTIVE  
5 FILM

## Technical Field

[0001]

The present invention relates to a curable resin film and a sheet for forming a  
10 first protective film.

Priority is claimed on Japanese Patent Application No. 2017-022165, filed on  
February 9, 2017, the content of which is incorporated herein by reference.

## Background Art

15 [0002]

In the related art, in a case in which a multi-pin LSI package, which is used in  
MPU or a gate array, is mounted on a printed wiring board, a flip chip mounting method  
in which a semiconductor chip in which convex electrodes (bumps) made of eutectic  
solder, high-temperature solder, metal, or the like are formed in connection pad portions  
20 is used, and these bumps are made to face, brought into contact with, and  
melting/diffusion-joined to the corresponding terminal portions on a chip mounting  
substrate using a so-called face down method has been employed.

[0003]

The semiconductor chip that is used in this mounting method is obtained by, for  
25 example, dividing a semiconductor wafer having bumps formed on a circuit surface by

grinding or dicing a surface opposite to the circuit surface. In the process of obtaining the above-described semiconductor chip, generally, for the purpose of protecting a circuit surface and a bump of the semiconductor wafer, a curable resin film is attached to the bump-formed surface, and this film is cured so as to form a protective film on the bump-formed surface. For example, after being attached onto the bump-formed surface, this curable resin film has an increase in fluidity by heating, and spreads between the bumps while penetrating and exposing an upper region including a top surface of the bump and the vicinity thereof, is close contact with the circuit surface, and embeds the bump while covering the surface of the bump, particularly, the surface of a portion in the vicinity of the circuit surface. The protective film formed by curing the curable resin film in such a state protects the circuit surface and the bump by being in contact with the surfaces thereof.

[0004]

Meanwhile, as such a curable resin film, one having a high visible light transmittance has been used in both a stage before curing and a stage of curing to form a protective film. When the curable resin film having such properties are used, it is possible to easily observe a semiconductor wafer of a circuit surface of a semiconductor chip through a curable resin film or a protective film. With this, it is possible to confirm a state of the circuit surface through the curable resin film or the protective film. Also, for example, when performing dicing, a position of an alignment mark (that is, a mark that positions a portion to be diced) present on the surface of a semiconductor wafer and a position of a dicing line (that is, a line indicating a position where dicing is to be performed) can be recognized, and thus it is possible to specify a cutting position on the semiconductor wafer.

[0005]

On the other hand, the curable resin film and the protective film have adverse effects resulting from high visible light transmittance. For example, even if the curable resin film or the protective film is provided on the bump-formed surface, a wiring pattern on the circuit surface can be easily read so that information on this wiring pattern can be easily obtained by a third party. Further, when attempting to bring the curable resin film into close contact with the circuit surface and the surface of the bump, an upper region including a top of the bump and the vicinity thereof does not penetrate the curable resin film and the curable resin film sometimes remains on the upper region of the bump. In this case, it is difficult to recognize a remaining state of the curable resin film. In order to solve these disadvantages, it is necessary to make it easy to recognize the curable resin film and the protective film on the bump-formed surface.

[0006]

As described above, the protective film in the related art for protecting the bump-formed surface and the curable resin film in the related art for forming the bump-formed surface have both advantages and disadvantages due to high visible light transmittance. Here, it is expected that such problems can be solved by adjusting transmission characteristics of light.

[0007]

On the other hand, when the semiconductor device is manufactured using the semiconductor wafer having the bump formed on the circuit surface as described above, a back surface on the side opposite to the circuit surface of the semiconductor chip may be exposed. Therefore, a resin film containing an organic material is formed as a protective film on the back surface of the exposed semiconductor chip, and may be taken into a semiconductor device as a semiconductor chip with a protective film. Such a protective film is used to prevent cracks from occurring in the semiconductor chip after a

dicing step and packaging.

[0008]

Such a protective film for protecting the back surface of the semiconductor chip may be required to be able to mark information relating to the semiconductor chip with a laser or to hide the back surface of the semiconductor chip. As a one capable of satisfying such requirement, there is disclosed a curable film which contains a coloring agent and thus capable of forming a protective film by adjusting transmission characteristics of light and by curing (refer to Patent Document 1).

[0009]

However, since the protective film for protecting the back surface of the semiconductor chip disclosed in Patent Document 1 is different from the protective film for protecting the bump-formed surface in the formation position on the semiconductor chip, and thus the required characteristics are also different from each other. Therefore, it is difficult to simply apply the method disclosed in Patent Document 1 to a protective film for protecting the bump-formed surface. As the protective film for protecting the bump-formed surface, there has not been known anything that has low visible light transmittance and allows observation of the circuit surface.

## Citation List

Patent Literature

[0010]

[Patent Document 1] Japanese Patent No. 5249290

## Summary of Invention

Technical Problem

[0011]

An object of the present invention is to provide a curable resin film for forming a protective film having a low visible light transmittance and capable of observing a circuit surface, as a protective film for protecting a bump-formed surface of a semiconductor wafer or a semiconductor chip.

#### Solution to Problem

[0012]

According to the present invention, there is provided a curable resin film for forming a first protective film on a surface having a bump of a semiconductor wafer by being attached to the surface, and being cured, in which a visible light transmittance of the curable resin film before curing is 45% or less, and an infrared transmittance of the curable resin film before curing is 33% or more.

In addition, according to the present invention, there is provided a sheet for forming a first protective film including a first supporting sheet, and the curable resin film on one surface of the first supporting sheet.

#### Advantageous Effects of Invention

[0013]

By using the curable resin film and the sheet for forming a first protective film of the present invention, it is possible to form a protective film having a low visible light transmittance and capable of observing a circuit surface, as a protective film for protecting a bump-formed surface of a semiconductor wafer or a semiconductor chip.

Brief Description of Drawings

[0014]

FIG. 1 is a sectional view schematically showing an example of a state in which a first protective film is formed on a bump-formed surface by using curable resin film of the present invention.

5           FIG. 2 is a cross-sectional view schematically showing an embodiment of a sheet for forming a first protective film of the present invention.

FIG. 3 is a cross-sectional view schematically showing another embodiment of the sheet for forming a first protective film of the present invention.

10           FIG. 4 is a cross-sectional view schematically showing still another embodiment of the sheet for forming a first protective film of the present invention.

#### Description of Embodiments

[0015]

##### ◇ Curable Resin Film and Sheet for Forming First Protective Film

15           The curable resin film of the present invention is for forming a first protective film on a surface having a bump of a semiconductor wafer by being attached to the surface, and being cured, in which a visible light transmittance of the curable resin film before curing is 45% or less, and an infrared transmittance of the curable resin film before curing is 33% or more.

20           [0016]

Since the visible light transmittance of the curable resin film before curing is 45% or less, both the curable resin film and the first protective film which is a cured material thereof can be easily visually recognized. Therefore, for example, in the semiconductor wafer and the semiconductor chip including the curable resin film or the first protective film on the bump-formed surface, it becomes difficult or impossible to

25

visually recognize the circuit surface due to a concealing action of the first protective film, and thus acquisition of information on a wiring pattern of the circuit surface by a three party can be suppressed. In addition, when attempting to bring the curable resin film into close contact with the circuit surface and the surface of the bump, an upper  
5 region including a top of the bump and the vicinity thereof does not penetrate the curable resin film, and even if the curable resin film remains on the upper region of the bump, the remaining curable resin film and the first protective film formed therefrom can be easily recognized.

[0017]

10 Further, since the infrared transmittance of the curable resin film before curing is 33% or more, both the curable resin film and the first protective film which is a cured material thereof can be easily transmitted. Therefore, for example, by using an infrared camera, an infrared microscope, or the like, the circuit surface of the semiconductor wafer and the semiconductor chip can be easily observed through the curable resin film  
15 or the first protective film. With this, it is possible to confirm a state of the circuit surface through the curable resin film or the first protective film. Also, for example, when performing dicing, a position of an alignment mark (a mark that positions a portion to be diced) present on the surface of a semiconductor wafer and a position of a dicing line (a line indicating a position where dicing is to be performed) can be recognized, and  
20 thus it is possible to specify a cutting position on the semiconductor wafer.

[0018]

As described above, the curable resin film has the transmission characteristics of light adjusted, so that the curable resin film and the first protective film can be visually easily observed in general, and the circuit surface is not possible to be visually  
25 recognized. Also, if necessary, the circuit surface can be observed by an appropriate

means such as an infrared camera, an infrared microscope, or the like.

[0019]

In the semiconductor wafer and a semiconductor chip having bumps on the circuit surface, a surface (back surface) on the side opposite to the circuit surface may be exposed. Therefore, a protective film containing an organic material (sometimes referred to as a “second protective film” in this specification in order to distinguish it from the first protective film) may be formed on the back surface. The second protective film is used to prevent cracks from occurring in the semiconductor chip after a dicing step and packaging. The semiconductor chip with the second protective film, which is provided with the second protective film on the back surface, is ultimately taken into the semiconductor device.

On the other hand, in the second protective film, a function of marking information relating to the semiconductor chip with a laser, or concealing the back surface of the semiconductor chip is sometimes required in some cases. A curable film capable of forming a second protective film by curing and having adjusted transmission characteristics of light has been known as one satisfying such a requirement.

However, since the formation positions of the second protective film for protecting the back surface of the semiconductor chip and the first protective film for protecting the bump-formed surface of the semiconductor chip are different from each other on the semiconductor chip, the characteristics thereof are also different from each other. Therefore, it is generally difficult to immediately use a curable film, which is capable of forming the second protective film, and has the adjusted transmission characteristics of light, for forming the first protective film.

On the other hand, the curable resin film of the present invention is a novel film which is capable of forming the first protective film and has the adjusted transmission

characteristics of light.

[0020]

The sheet for forming a first protective film of the present invention is provided with a first supporting sheet, and the curable resin film of the present invention on one  
5 surface of the first supporting sheet. In the sheet for forming a first protective film, the “curable resin film” may be referred to as a “curable resin layer”.

[0021]

The sheet for forming a first protective film of the present invention is used by being attached to the surface having the bump of the semiconductor wafer (that is, a  
10 circuit surface) through the curable resin layer (a curable resin film). Then, the curable resin layer after attachment has an increase in fluidity by heating, spreads between the bumps so as to cover the bumps, is close contact with the circuit surface, and embeds the bump while covering the surface of the bump, particularly, the surface of the portion in the vicinity of the circuit surface.

15 The curable resin layer in such a state is further heated or cured by irradiation with energy ray so as to finally form the first protective film and protects the circuit surface and the bump in a state of being in close contact with the surfaces thereof. As such, when the curable resin film of the present invention is used, the circuit surface of the semiconductor wafer, a portion in the vicinity of the circuit surface of the bump, that  
20 is, a base portion, is sufficiently protected by the first protective film.

[0022]

After the surface of the semiconductor wafer, on which the sheet for forming a first protective film, attached, for example, onto the surface opposite to the circuit surface is ground, the first supporting sheet is removed, and then embedding of the bump by  
25 heating of the curable resin layer and forming of the first protective film are performed,

and finally, the semiconductor wafer is incorporated into the semiconductor device in a state of being provided with this first protective film.

In this specification, the bump surface and the circuit surface of the semiconductor wafer are collectively referred to as “bump-formed surface” in some cases.

Unless otherwise specified, the expression of mere “curable resin layer” means “curable resin layer before curing”.

[0023]

FIG. 1 is a sectional view schematically showing an example of a state in which a first protective film is formed on a bump-formed surface by using curable resin film of the present invention. Note that, in the drawings used in the following description, for the sake of easy understanding of the features of the present invention, and for the sake of convenience, a portion serving as a main part is sometimes enlarged and the dimensional ratio and the like of each component is not necessarily the same as the actual one.

[0024]

On a circuit surface 90a of the semiconductor wafer 90 shown in the drawing, a plurality of the bumps 91 is provided. The bump 91 has, for example, a shape of a sphere a part of which is cut out along a flat surface, and a flat surface corresponding to a portion exposed by cutting out the above-described part is in contact with the circuit surface 90a of the semiconductor wafer 90.

The first protective film 12' is formed with the curable resin film of the present invention, covers the circuit surface 90a of the semiconductor wafer 90, and further covers an area of the surface 91a of the bump 91 other than the top of the bump 91 and the vicinity thereof. In this way, the first protective film 12' is close contact with the surface 91a of the bump 91 other than the top of the bump 91 and the vicinity thereof,

and is also close contact with the circuit surface 90a of the semiconductor wafer 90 so as to embed the bump 91.

The substantially spherical shape of the bump 91 as described above is also particularly advantageous for forming the first protective film using the curable resin film  
5 of the present invention.

[0025]

Note that, the semiconductor wafer to be used for the curable resin film of the present invention is not limited to that shown in FIG. 1, and a configuration in which a part of the configuration is changed, deleted, or added within a range that does not impair  
10 the effect of the present invention may be used. For example, FIG. 1 illustrates a bump having a substantially spherical shape (a shape in which a part of a sphere is cut out by a plane) as described above, and examples of preferred bumps include a bump having a shape obtained by stretching the bump having a substantially spherical shape in a height direction (direction orthogonal to the circuit surface 90a of the semiconductor wafer 90 in  
15 FIG. 1), that is, a shape of a spheroid which is substantially long spherical (a shape in which a portion including one end in the major axis direction of a spheroid which is long spherical is cut out by a plane), and a bump having a shape obtained by crushing the bump having a substantially spherical shape in a height direction, that is, a shape of a spheroid which is substantially oblate (a shape in which a portion including one end in  
20 the minor axis direction of a spheroid which is substantially oblate is cut out by a plane). Such a bump having a substantially spheroidal shape is also particularly advantageous for forming the first protective film using the curable resin film of the present invention, similar to the substantially spherical bump.

Note that, the shape of the bump described so far is merely an example of a  
25 preferable example in applying the curable resin film of the present invention, and the

shape of the bump is not limited to these in the present invention.

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

[0026]

5     • First Supporting sheet

The first supporting sheet may be a sheet made of a single layer (monolayer) or a sheet made of a plurality of layers (two or more layers). In a case in which the supporting sheet is made of a plurality of layers, the constituent materials and the thicknesses of the plurality of layers may be identical to or different from one another, and the combination of the plurality of layers is not particularly limited as long as the effects of the present invention are not impaired.

Meanwhile, in the present specification, the sentence “the plurality of layers may be identical to or different from one another” means that “all of the layers may be identical to one another, all of the layers may be different from one another, or only some of the layers may be identical to one another”, which will be true not only for the first supporting sheet but also for other elements. Furthermore, the sentence “a plurality of layers is different from one another” means that “at least one of the constituent materials and the thicknesses of the respective layers are different from one another”.

[0027]

Examples of a preferred the first supporting sheet include a structure formed by stacking a first pressure-sensitive adhesive layer on a first base material, a structure formed by stacking a first interlayer on the first base material and stacking the first pressure-sensitive adhesive layer on the first interlayer, and a structure formed of the first base material.

[0028]

An example of the sheet for forming a first protective film of the present invention will be described with reference to the following drawings for each kind of such first supporting sheet.

[0029]

5           FIG. 2 is a cross-sectional view schematically showing an embodiment of the sheet for forming a first protective film of the present invention.

          The sheet for forming a first protective film 1 as shown in FIG. 2 uses the first supporting sheet obtained by stacking the first pressure-sensitive adhesive layer on the first base material. That is, the sheet for forming a first protective film 1 is configured  
10   to include a first base material 11, a first pressure-sensitive adhesive layer 13 on the first base material 11, and a curable resin layer (curable resin film) 12 on the first pressure-sensitive adhesive layer 13. The first supporting sheet 101 is a stacked body of the first base material 11 and the first pressure-sensitive adhesive layer 13, in which curable resin layer 12 is provided on one surface 101a of the first supporting sheet 101,  
15   that is, on one surface 13a of the first pressure-sensitive adhesive layer 13.

          In the sheet for forming a first protective film 1, the visible light transmittance of the curable resin layer 12 is 45% or less, and the infrared transmittance is 33% or more. By curing the curable resin layer 12, similarly, the first protective film having sufficiently low visible light transmittance and sufficiently high infrared transmittance is formed.

20           [0030]

          FIG. 3 is a cross-sectional view schematically showing another embodiment of the sheet for forming a first protective film of the present invention.

          In the figures after FIG. 3, the same reference numerals are given to the same constituent elements as those shown in the already described figures, and a detailed  
25   description thereof will be not be repeated.

[0031]

The sheet for forming a first protective film 2 as shown in FIG. 3 uses the first supporting sheet obtained by stacking the first interlayer on the first base material, and stacking the first pressure-sensitive adhesive layer on the first interlayer. That is, the sheet for forming a first protective film 2 is configured to include a first base material 11, a first interlayer 14 on the first base material 11, a first pressure-sensitive adhesive layer 13 on the first interlayer 14, and the curable resin layer (curable resin film) 12 on the first pressure-sensitive adhesive layer 13. The first supporting sheet 102 is a stacked body obtained by stacking the first base material 11, the first interlayer 14, and the first pressure-sensitive adhesive layer 13 in this order, in which the curable resin layer 12 is provided on one surface 102a of the first supporting sheet 102, that is, on one surface 13a of the first pressure-sensitive adhesive layer 13.

In other words, the sheet for forming a first protective film 2 is further provided with the first interlayer 14 between the first base material 11 and the first pressure-sensitive adhesive layer 13 in the sheet for forming a first protective film 1 as shown in FIG. 2.

In the sheet for forming a first protective film 2, the visible light transmittance of the curable resin layer 12 is 45% or less, and the infrared transmittance is 33% or more. By curing the curable resin layer 12, similarly, the first protective film having sufficiently low visible light transmittance and sufficiently high infrared transmittance is formed.

[0032]

FIG. 4 is a cross-sectional view schematically showing still another embodiment of the sheet for forming a first protective film of the present invention.

In the sheet for forming a first protective film 3 as shown in FIG. 4, the first supporting sheet is formed of only the first base material. That is, the sheet for forming

a first protective film 3 is configured to include a first base material 11 and a curable resin layer (curable resin film) 12 on the first base material 11.

The first supporting sheet 103 is formed of only the first base material 11, curable resin film 12 is provided in direct contact with on one surface 103a of the first supporting sheet 103, that is, one surface 11a of the first base material 11.

In other words, the sheet for forming a first protective film 3 is formed by removing the first pressure-sensitive adhesive layer 13 in the sheet for forming a first protective film 1 as shown in FIG. 2.

In the sheet for forming a first protective film 3, the visible light transmittance of the curable resin layer 12 is 45% or less, and the infrared transmittance is 33% or more. By curing the curable resin layer 12, similarly, the first protective film having sufficiently low visible light transmittance and sufficiently high infrared transmittance is formed.

Next, the configuration of the first supporting sheet will be described in detail.

[0033]

#### ○ First Base Material

The first base material is a sheet-form or film-form base material, and examples of a constituent material thereof include a variety of resins.

Examples of the resins include polyethylene such as low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE); polyolefin other than polyethylene such as polypropylene, polybutene, polybutadiene, polymethylpentene, and norbornene resins; ethylene-based copolymers (copolymers obtained using ethylene as monomers) such as ethylene-vinyl acetate copolymers, ethylene-(meth)acrylic acid copolymers, ethylene-(meth)acrylic acid ester copolymers, and ethylene-norbornene copolymers; vinyl chloride-based resins (resins obtained using vinyl chloride as monomers) such as polyvinyl chloride and vinyl chloride

copolymers; polystyrene; polycycloolefin; polyesters such as polyethylene terephthalate, polyethylene naphthalate, polybutylene terephthalate, polyethylene isophthalate, polyethylene-2,6-naphthalene dicarboxylate, and wholly aromatic polyesters in which all constituent units have an aromatic cyclic group; copolymers of two or more polyester  
5 described above; poly(meth)acrylic acid esters; polyurethane; polyurethane acrylate; polyimide; polyamide; polycarbonate; fluororesin; polyacetal; modified polyphenylene oxides; polyphenylene sulfides; polysulfone; and polyether ketones.

In addition, examples of the resins also include polymer alloys such as mixtures of the polyester and other resin. The polymer alloys of the polyester and other resin are  
10 preferably polymer alloys in which the amount of the resin other than the polyester is relatively small.

In addition, examples of the resins material also include crosslinked resins in which one or more exemplary resins above are crosslinked with each other; modified resins such as ionomers for which one or more resins exemplified above are used; and the  
15 like.

[0034]

Meanwhile, in the present specification, “(meth)acrylic acid” refers to both “acrylic acid” and “methacrylic acid”. What has been described above is also true for terminologies similar to (meth)acrylic acid, for example, “(meth)acrylate” refers to both  
20 “acrylate” and “methacrylate”, and “a (meth)acryloyl group” refers to both “an acryloyl group” and “a methacryloyl group”.

[0035]

Only one kind or two or more kinds of resins may constitute the first base material, and in a case in which two or more kinds of resins constitute the first base  
25 material, the combination and ratio thereof can be optionally selected.

[0036]

The first base material may be a single layer (monolayer) or a plurality of layers (two or more layers), and in a case in which the first base material is a plurality of layers, the respective layers in the plurality of layers may be identical to or different from one another, and the combination of the plurality of layers is not particularly limited.

[0037]

The thickness of the first base material is preferably 5 to 1,000  $\mu\text{m}$ , more preferably 10 to 500  $\mu\text{m}$ , still more preferably 15 to 300  $\mu\text{m}$ , and particularly preferably 20 to 150  $\mu\text{m}$ .

Here, “the thickness of the first base material” refers to the thickness of the entire first base material, and for example, the thickness of the first base material made up of a plurality of layers refers to the total thickness of all of the layers constituting the first base material.

[0038]

The first base material is preferably a first base material having a high accuracy in thickness, that is, a first base material in which the variation of the thickness is suppressed throughout the entire portion. Among the above-described constituent materials, examples of materials having a high accuracy in thickness that can be used to constitute the above-described first base material include polyethylene, polyolefin other than polyethylene, polyethylene terephthalate, ethylene-vinyl acetate copolymers, and the like.

[0039]

The first base material may also contain, in addition to the main constituent material such as the resin, a variety of well-known additives such as a filler, a colorant, an antistatic agent, an antioxidant, an organic lubricant, a catalyst, and a softening agent

(plasticizer).

[0040]

The first base material may be transparent or opaque and may be colored depending on the purpose. In addition, other layers may be deposited on the first base material.

In a case in which the first pressure-sensitive adhesive layer described below or the curable resin layer is energy ray-curable, the first base material preferably transmits energy rays.

[0041]

For example, the first base material may be a peeling film obtained by peeling one surface of a resin film by a silicone treatment or the like as described later in the examples.

[0042]

The first base material can be manufactured using a well-known method. For example, the first base material containing the resin can be manufactured by forming a resin composition containing the resin.

[0043]

#### o First Pressure-Sensitive Adhesive Layer

The first pressure-sensitive adhesive layer has a sheet form or a film form and contains a pressure-sensitive adhesive.

Examples of the pressure-sensitive adhesive include a pressure-sensitive adhesive resin such as an acrylic resin, a urethane resin, a rubber resin, a silicone resin, an epoxy resin, polyvinyl ether, and polycarbonate, and an acrylic resin is preferable.

[0044]

Meanwhile, in the present invention, “pressure-sensitive adhesive resins” refer

to both resins having an adhesiveness and resins having an adhesive property, and examples thereof include not only resins having an adhesive property for themselves but also resins exhibiting the adhesiveness when jointly used with other components such as additives, resins exhibiting an adhesive property due to the presence of a trigger such as heat or water, and the like.

[0045]

The first pressure-sensitive adhesive layer may be a single layer (monolayer) or a plurality of layers of two or more layers, and in a case in which the first pressure-sensitive adhesive layer is a plurality of layers, the respective layers in the plurality of layers may be identical to or different from one another, and the combination of the plurality of layers is not particularly limited.

[0046]

The thickness of the first pressure-sensitive adhesive layer is preferably 1 to 1,000  $\mu\text{m}$ , more preferably 5 to 500  $\mu\text{m}$ , and particularly preferably 10 to 100  $\mu\text{m}$ .

Here, “the thickness of the first pressure-sensitive adhesive layer” refers to the thickness of the entire first pressure-sensitive adhesive layer, and for example, the thickness of the first pressure-sensitive adhesive layer made up of a plurality of layers refers to the total thickness of all of the layers constituting the first pressure-sensitive adhesive layer.

[0047]

The first pressure-sensitive adhesive layer may be a first pressure-sensitive adhesive layer formed using an energy ray-curable pressure-sensitive adhesive or a first pressure-sensitive adhesive layer formed using a non-energy ray-curable pressure-sensitive adhesive. For the first pressure-sensitive adhesive layer formed using an energy ray-curable pressure-sensitive adhesive, it is possible to easily adjust the

properties before curing and after curing.

In the present invention, “energy rays” refer to rays having energy quanta in electromagnetic waves or charged particle radiation, and examples thereof include ultraviolet rays, radiations, electron beams, and the like.

5           Ultraviolet rays can be irradiated using, for example, a high-pressure mercury lamp, a fusion H lamp, a xenon lamp, black light, a LED lamp, or the like as an ultraviolet ray source. As the electron beams, electron beams generated using an electron beam accelerator or the like can be irradiated.

In the present invention, “being energy ray-curable” refers to a property of being  
10   cured by being irradiated with energy rays, and “being non-energy ray-curable” refers to a property of not being cured by being irradiated with energy rays.

[0048]

<<First Pressure-Sensitive Adhesive Composition>>

The first pressure-sensitive adhesive layer can be formed using a first  
15   pressure-sensitive adhesive composition containing a pressure-sensitive adhesive. For example, the first pressure-sensitive adhesive layer can be formed at an intended portion by applying the first pressure-sensitive adhesive composition to a target surface on which the first pressure-sensitive adhesive layer is to be formed and drying the first pressure-sensitive adhesive composition as necessary. A more specific method for  
20   forming the first pressure-sensitive adhesive layer will be described below in detail together with methods for forming other layers.

[0049]

The first pressure-sensitive adhesive composition may be applied using a well-known method, and examples thereof include methods in which a variety of coaters  
25   such as an air knife coater, a blade coater, a bar coater, a gravure coater, a roll coater, a

roll knife coater, a curtain coater, a die coater, a knife coater, a screen coater, a Mayer bar coater, and a kiss coater are used.

[0050]

The drying conditions of the first pressure-sensitive adhesive composition are not particularly limited; however, in a case in which the first pressure-sensitive adhesive composition contains a solvent described below, the first pressure-sensitive adhesive composition is preferably heated and dried. The first pressure-sensitive adhesive composition containing a solvent is preferably dried at 70°C to 130°C for 10 seconds to 5 minutes.

10 [0051]

In a case in which the first pressure-sensitive adhesive layer is energy ray-curable, examples of the first pressure-sensitive adhesive composition containing an energy ray-curable pressure-sensitive adhesive, that is, an energy ray-curable first pressure-sensitive adhesive composition include a first pressure-sensitive adhesive composition (I-1) containing a non-energy ray-curable pressure-sensitive adhesive resin (I-1a) (hereinafter, in some cases, abbreviated as “the pressure-sensitive adhesive resin (I-1a)”) and an energy ray-curable compound; a first pressure-sensitive adhesive composition (I-2) containing an energy ray-curable pressure-sensitive adhesive resin (I-2a) in which an unsaturated group is introduced into a side chain of the non-energy ray-curable pressure-sensitive adhesive resin (I-1a) (hereinafter, in some cases, abbreviated as “the pressure-sensitive adhesive resin (I-2a)”); a first pressure-sensitive adhesive composition (I-3) containing the pressure-sensitive adhesive resin (I-2a) and an energy ray-curable low-molecular-weight compound; and the like.

[0052]

25 <First Pressure-Sensitive Adhesive Composition (I-1)>

As described above, the first pressure-sensitive adhesive composition (I-1) contains the non-energy ray-curable pressure-sensitive adhesive resin (I-1a) and an energy ray-curable compound.

[0053]

#### 5 [Pressure-Sensitive Adhesive Resin (I-1a)]

The pressure-sensitive adhesive resin (I-1a) is preferably an acrylic resin.

Examples of the acrylic resin include acrylic polymers having at least a constituent unit derived from an alkyl (meth)acrylate.

The acrylic resin may have only one type or two or more kinds of constituent  
10 units, and in a case in which the acrylic resin has two or more kinds of constituent units, the combination and ratio thereof can be arbitrarily selected.

[0054]

Examples of the alkyl (meth)acrylate include alkyl (meth)acrylates in which the number of carbon atoms in an alkyl group constituting the alkyl ester is 1 to 20, and the  
15 alkyl group is preferably a linear alkyl group or a branched alkyl group.

More specific examples of the alkyl (meth)acrylate include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate,  
20 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (also referred to as lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (also referred to as palmityl (meth)acrylate), heptadecyl (meth)acrylate,  
25 octadecyl (meth)acrylate (also referred to as stearyl (meth)acrylate), nonadecyl

(meth)acrylate, icosyl (meth)acrylate, and the like.

[0055]

Since the pressure-sensitive adhesive force of the first pressure-sensitive adhesive layer improves, the acrylic polymer preferably has a constituent unit derived from an alkyl (meth)acrylate in which the number of carbon atoms in the alkyl group is four or more. In addition, since the pressure-sensitive adhesive force of the first pressure-sensitive adhesive layer further improves, the number of carbon atoms in the alkyl group is preferably 4 to 12 and more preferably 4 to 8. In addition, the alkyl (meth)acrylate in which the number of carbon atoms in the alkyl group is four is preferably alkyl acrylate.

[0056]

The acrylic polymer preferably further has, in addition to the constituent unit derived from the alkyl (meth)acrylate, a constituent unit derived from a functional group-containing monomer.

Examples of the functional group-containing monomer include monomers in which the functional group reacts with a crosslinking agent described below and thus serves as a starting point of crosslinking or the functional group reacts with an unsaturated group in an unsaturated group-containing compound and thus enables the introduction of the unsaturated group into a side chain of the acrylic polymer.

[0057]

Examples of the functional group in the functional group-containing monomer include a hydroxyl group, a carboxy group, an amino group, an epoxy group, and the like.

That is, examples of the functional group-containing monomer include hydroxyl group-containing monomers, carboxy group-containing monomers, amino

group-containing monomers, epoxy group-containing monomers, and the like.

[0058]

Examples of the hydroxyl group-containing monomers include hydroxyalkyl (meth)acrylates such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 5 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, and 4-hydroxybutyl (meth)acrylate; non-(meth)acrylic unsaturated alcohols such as vinyl alcohol and allyl alcohol (unsaturated alcohols not having a (meth)acryloyl skeleton); and the like.

[0059]

10 Examples of the carboxy group-containing monomers include ethylenic unsaturated monocarboxylic acids such as (meth)acrylic acid and crotonic acid (monocarboxylic acids having an ethylenic unsaturated bond); ethylenic unsaturated dicarboxylic acids such as fumaric acid, itaconic acid, maleic acid, and citraconic acid (dicarboxylic acids having an ethylenic unsaturated bond); anhydrides of the ethylenic 15 unsaturated dicarboxylic acid; carboxyalkyl (meth)acrylates such as 2-carboxyethyl methacrylate; and the like.

[0060]

The functional group-containing monomer is preferably the hydroxyl group-containing monomer or the carboxy group-containing monomer and more 20 preferably the hydroxyl group-containing monomer.

[0061]

The acrylic polymer may be constituted of only one type or two or more kinds of the functional group-containing monomers, and in a case in which the acrylic polymer is constituted of two or more kinds of the functional group-containing monomers, the 25 combination and ratio thereof can be arbitrarily selected.

[0062]

In the acrylic polymer, the amount of the constituent unit derived from the functional group-containing monomer is preferably 1% to 35% by mass, more preferably 3% to 32% by mass, and particularly preferably 5% to 30% by mass of the mass of the constituent units.

[0063]

The acrylic polymer may further have, in addition to the constituent unit derived from the alkyl (meth)acrylate and the constituent unit derived from the functional group-containing monomer, a constituent unit derived from a different monomer.

The different monomer is not particularly limited as long as the monomer can be copolymerized with the alkyl (meth)acrylate or the like.

Examples of the different monomer include styrene,  $\alpha$ -methylstyrene, vinyl toluene, vinyl formate, vinyl acetate, acrylonitrile, acrylamide, and the like.

[0064]

The acrylic polymer may be constituted of only one type or two or more kinds of the different monomers, and in a case in which the acrylic polymer is constituted of two or more kinds of the different monomers, the connection and ratio thereof can be arbitrarily selected.

[0065]

The acrylic polymer can be used as the non-energy ray-curable pressure-sensitive adhesive resin (I-1a).

Meanwhile, a substance obtained by causing an unsaturated group-containing compound having an energy ray-polymerizable unsaturated group (energy ray-polymerizable group) to react with the functional group in the acrylic polymer can be used as the energy ray-curable pressure-sensitive adhesive resin (I-2a).

Meanwhile, in the present invention, “being energy ray-polymerizable” refers to a property of being polymerized by being irradiated with energy rays.

[0066]

The first pressure-sensitive adhesive composition (I-1) may contain only one  
5 type or two or more kinds of the pressure-sensitive adhesive resins (I-1a), and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the pressure-sensitive adhesive resins, the combination and ratio thereof can be arbitrarily selected.

[0067]

10 In the first pressure-sensitive adhesive composition (I-1), the amount of the pressure-sensitive adhesive resin (I-1a) is preferably 5% to 99% by mass, more preferably 10% to 95% by mass, and particularly preferably 15% to 90% by mass.

[0068]

[Energy Ray-Curable Compounds]

15 Examples of the energy ray-curable compound contained in the first pressure-sensitive adhesive composition (I-1) include monomers or oligomers which have an energy ray-polymerizable unsaturated group and can be cured by being irradiated with energy rays.

Among the energy ray-curable compounds, examples of monomers include  
20 polyhydric (meth)acrylates such as trimethylol propane tri(meth)acrylate, pentaerythritol (meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, 1,4-butylene glycol di(meth)acrylate, and 1,6-hexanediol (meth)acrylate; urethane (meth)acrylate; polyester (meth)acrylate; polyether (meth)acrylate; epoxy (meth)acrylate; and the like.

25 Among the energy ray-curable compounds, examples of oligomers include

oligomers obtained by polymerizing the exemplary examples of monomers above.

The energy ray-curable compound is preferably urethane (meth)acrylate or a urethane (meth)acrylate oligomer since the molecular weight is relatively great and the storage elastic modulus of the first pressure-sensitive adhesive layer is not easily  
5 decreased.

[0069]

The first pressure-sensitive adhesive composition (I-1) may contain only one type or two or more kinds of the energy ray-curable compounds, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the  
10 energy ray-curable compounds, the combination and ratio thereof can be arbitrarily selected.

[0070]

In the first pressure-sensitive adhesive composition (I-1), the amount of the energy ray-curable compound is preferably 1% to 95% by mass, more preferably 5% to  
15 90% by mass, and particularly preferably 10% to 85% by mass.

[0071]

[Crosslinking Agent]

In a case in which the acrylic polymer further having, in addition to the constituent unit derived from the alkyl (meth)acrylate, the constituent unit derived from  
20 the functional group-containing monomer as the pressure-sensitive adhesive resin (I-1a), the first pressure-sensitive adhesive composition (I-1) preferably further contains a crosslinking agent.

[0072]

The crosslinking agent is, for example, a substance that reacts with the  
25 functional group and thus crosslinks the pressure-sensitive adhesive resins (I-1a).

Examples of the crosslinking agent include isocyanate-based crosslinking agents (crosslinking agents having an isocyanate group) such as tolylene diisocyanate, hexamethylene diisocyanate, xylene diisocyanate, and adduct bodies of the above-described diisocyanate; epoxy-based crosslinking agents (crosslinking agents having a glycidyl group) such as ethylene glycol glycidyl ether; aziridine-based crosslinking agents (crosslinking agents having an aziridinly group) such as hexa[1-(2-methyl)-aziridinyl]triphosphatriazine; metal chelate-based crosslinking agents (crosslinking agents having a metal chelate structure) such as aluminum chelates; isocyanurate-based crosslinking agents (crosslinking agents having an isocyanuric acid skeleton); and the like.

The crosslinking agent is preferably the isocyanate-based crosslinking agent since the isocyanate-based crosslinking agent improves the cohesive force of the pressure-sensitive adhesive so as to improve the pressure-sensitive adhesive force of the first pressure-sensitive adhesive layer, is easily procurable, and the like.

[0073]

The first pressure-sensitive adhesive composition (I-1) may contain only one type or two or more kinds of the crosslinking agents, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the crosslinking agents, the combination and ratio thereof can be arbitrarily selected.

[0074]

In the first pressure-sensitive adhesive composition (I-1), the amount of the crosslinking agent is preferably 0.01 to 50 parts by mass, more preferably 0.1 to 20 parts by mass, and particularly preferably 1 to 10 parts by mass of the amount (100 parts by mass) of the pressure-sensitive adhesive resin (I-1a).

[0075]

## [Photopolymerization Initiator]

The first pressure-sensitive adhesive composition (I-1) may also further contain a photopolymerization initiator. The first pressure-sensitive adhesive composition (I-1) containing the photopolymerization initiator sufficiently proceeds with a curing reaction even when irradiated with energy rays having a relatively low energy such as ultraviolet rays.

[0076]

Examples of the photopolymerization initiator include benzoin compounds such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin benzoate, methyl benzoin benzoate, and benzoin dimethyl ketal; acetophenone compounds such as acetophenone, 2-hydroxy-2-methyl-1-phenyl-propane-1-one, and 2,2-dimethoxy-1,2-diphenylethane-1-one; acylphosphine oxide compounds such as bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide and 2,4,6-trimethylbenzoyldiphenylphosphine oxide; sulfide compounds such as benzylphenyl sulfide and tetramethylthiuram monosulfide;  $\alpha$ -ketol compounds such as 1-hydroxycyclohexyl phenyl ketone; azo compounds such as azobisisobutyronitrile; titanocene compounds such as titanocene; thioxanthone compounds such as thioxanthone; peroxide compounds; diketone compounds such as diacetyl; benzyl, dibenzyl, benzophenone, 2,4-diethylthioxanthone, 1,2-diphenylmethane, 2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone, 2-chloroanthraquinone, and the like.

In addition, as the photopolymerization initiator, for example, a quinone compound such as 1-chloroanthraquinone; a photosensitizer such as amine; or the like can also be used.

[0077]

The first pressure-sensitive adhesive composition (I-1) may contain only one type or two or more kinds of the photopolymerization initiators, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the photopolymerization initiators, the combination and ratio thereof can be arbitrarily selected.

[0078]

In the first pressure-sensitive adhesive composition (I-1), the amount of the photopolymerization initiator is preferably 0.01 to 20 parts by mass, more preferably 0.03 to 10 parts by mass, and particularly preferably 0.05 to 5 parts by mass of the amount (100 parts by mass) of the energy ray-curable compound.

[0079]

[Other Additives]

The first pressure-sensitive adhesive composition (I-1) may also contain other additives which do not correspond to any of the above-described components as long as the effects of the present invention are not impaired.

Examples of the other additives include known additives such as an antistatic agent, an antioxidant, a softening agent (plasticizer), a filler (filler), an antirust agent, a colorant (a pigment or a dye), a sensitizer, a tackifier, a reaction retardant, and a crosslinking accelerator (catalyst).

Meanwhile, the reaction retardant is a substance that suppresses the progress of an unintended crosslinking reaction in the first pressure-sensitive adhesive composition (I-1) under storage due to, for example, the action of the catalyst mixed into the first pressure-sensitive adhesive composition (I-1). Examples of the reaction retardant include reaction retardants that form a chelate complex due to a chelate with respect to

the catalyst, and more specific examples thereof include substances having two or more carbonyl groups ( $-\text{C}(=\text{O})-$ ) in one molecule.

[0080]

The first pressure-sensitive adhesive composition (I-1) may contain only one  
5 type or two or more kinds of the other additives, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the other additives, the combination and ratio thereof can be arbitrarily selected.

[0081]

In the first pressure-sensitive adhesive composition (I-1), the amount of the  
10 other additives is not particularly limited and may be appropriately selected depending on the type of the additives.

[0082]

[Solvent]

The first pressure-sensitive adhesive composition (I-1) may also contain a  
15 solvent. When the first pressure-sensitive adhesive composition (I-1) contains a solvent, the coating aptitude to a coating target surface improves.

[0083]

The solvent is preferably an organic solvent, and examples of the organic solvent include ketones such as methyl ethyl ketone and acetone; esters (carboxylic acid  
20 esters) such as ethyl acetate; ethers such as tetrahydrofuran and dioxane; aliphatic hydrocarbons such as cyclohexane and n-hexane; aromatic hydrocarbons such as toluene and xylene; alcohols such as 1-propanol and 2-propanol; and the like.

[0084]

As the solvent, a solvent used during the manufacturing of the pressure-sensitive  
25 adhesive resin (I-1a) may be continuously used in the first pressure-sensitive adhesive

composition (I-1) without being removed from the pressure-sensitive adhesive resin (I-1a) or a solvent of the same type as or a different type from the solvent used during the manufacturing of the pressure-sensitive adhesive resin (I-1a) may be separately added during the manufacturing of the first pressure-sensitive adhesive composition (I-1).

5 [0085]

The first pressure-sensitive adhesive composition (I-1) may contain only one type or two or more kinds of the solvents, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the solvents, the combination and ratio thereof can be arbitrarily selected.

10 [0086]

In the first pressure-sensitive adhesive composition (I-1), the amount of the solvent is not particularly limited and may be appropriately adjusted.

[0087]

<First Pressure-Sensitive Adhesive Composition (I-2)>

15 As described above, the first pressure-sensitive adhesive composition (I-2) contains an energy ray-curable pressure-sensitive adhesive resin (I-2a) in which an unsaturated group is introduced into a side chain of the non-energy ray-curable pressure-sensitive adhesive resin (I-1a).

[0088]

20 [Pressure-Sensitive Adhesive Resin (I-2a)]

The pressure-sensitive adhesive resin (I-2a) can be obtained by, for example, causing an unsaturated group-containing compound having an energy ray-polymerizable unsaturated group to react with the functional group in the pressure-sensitive adhesive resin (I-1a).

25 [0089]

The unsaturated group-containing compound is a compound further having, in addition to the energy ray-polymerizable unsaturated group, a group that can be bonded with the pressure-sensitive adhesive resin (I-1a) by reacting with the functional group in the pressure-sensitive adhesive resin (I-1a).

5           Examples of the energy ray-polymerizable unsaturated group include a (meth)acryloyl group, a vinyl group (ethenyl group), an allyl group (2-propenyl group), and the like, and a (meth)acryloyl group is preferred.

          Examples of the group that can be bonded with the functional group in the pressure-sensitive adhesive resin (I-1a) include isocyanate groups and glycidyl groups  
10       that can be bonded with a hydroxyl group or an amino group, hydroxyl groups and amino groups that can be bonded with a carboxy group or an epoxy group, and the like.

[0090]

          Examples of the unsaturated group-containing compound include (meth)acryloyloxyethyl isocyanate, (meth)acryloyl isocyanate, glycidyl (meth)acrylate,  
15       and the like.

[0091]

          The first pressure-sensitive adhesive composition (I-2) may contain only one type or two or more kinds of the pressure-sensitive adhesive resins (I-2a), and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the  
20       pressure-sensitive adhesive resins, the combination and ratio thereof can be arbitrarily selected.

[0092]

          In the first pressure-sensitive adhesive composition (I-2), the amount of the pressure-sensitive adhesive resin (I-2a) is preferably 5% to 99% by mass, more  
25       preferably 10% to 95% by mass, and particularly preferably 10% to 90% by mass.

[0093]

[Crosslinking Agent]

In a case in which, as the pressure-sensitive adhesive resin (I-2a), for example, the acrylic polymer having the constituent unit derived from the functional  
5 group-containing monomer, which is the same as that in the pressure-sensitive adhesive resin (I-1a) is used, the first pressure-sensitive adhesive composition (I-2) further contains a crosslinking agent.

[0094]

Examples of the crosslinking agent in the first pressure-sensitive adhesive  
10 composition (I-2) include the same crosslinking agents as those in the first pressure-sensitive adhesive composition (I-1).

The first pressure-sensitive adhesive composition (I-2) may contain only one type or two or more kinds of the crosslinking agents, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the crosslinking  
15 agents, the combination and ratio thereof can be arbitrarily selected.

[0095]

In the first pressure-sensitive adhesive composition (I-2), the amount of the crosslinking agent is preferably 0.01 to 50 parts by mass, more preferably 0.1 to 20 parts by mass, and particularly preferably 1 to 10 parts by mass of the amount (100 parts by  
20 mass) of the pressure-sensitive adhesive resin (I-2a).

[0096]

[Photopolymerization Initiator]

The first pressure-sensitive adhesive composition (I-2) may also further contain a photopolymerization initiator. The first pressure-sensitive adhesive composition (I-2)  
25 containing the photopolymerization initiator sufficiently proceeds with a curing reaction

even when irradiated with energy rays having a relatively low energy such as ultraviolet rays.

[0097]

Examples of the photopolymerization initiator in the first pressure-sensitive  
5 adhesive composition (I-2) include the same photopolymerization initiators as those in  
the first pressure-sensitive adhesive composition (I-1).

The first pressure-sensitive adhesive composition (I-2) may contain only one  
type or two or more kinds of the photopolymerization initiators, and in a case in which  
the first pressure-sensitive adhesive composition contains two or more kinds of the  
10 photopolymerization initiators, the combination and ratio thereof can be arbitrarily  
selected.

[0098]

In the first pressure-sensitive adhesive composition (I-2), the amount of the  
photopolymerization initiator is preferably 0.01 to 20 parts by mass, more preferably 0.03  
15 to 10 parts by mass, and particularly preferably 0.05 to 5 parts by mass of the amount  
(100 parts by mass) of the pressure-sensitive adhesive resin (I-2a).

[0099]

[Other Additives]

The first pressure-sensitive adhesive composition (I-2) may also contain other  
20 additives which do not correspond to any of the above-described components as long as  
the effects of the present invention are not impaired.

Examples of the other additives in the first pressure-sensitive adhesive  
composition (I-2) include the same other additives as those in the first pressure-sensitive  
adhesive composition (I-1).

25 The first pressure-sensitive adhesive composition (I-2) may contain only one

type or two or more kinds of the other additives, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the other additives, the combination and ratio thereof can be arbitrarily selected.

[0100]

5           In the first pressure-sensitive adhesive composition (I-2), the amount of the other additives is not particularly limited and may be appropriately selected depending on the type of the additives.

[0101]

[Solvent]

10           The first pressure-sensitive adhesive composition (I-2) may also contain a solvent for the same purpose as in the case of the first pressure-sensitive adhesive composition (I-1).

Examples of the solvent in the first pressure-sensitive adhesive composition (I-2) include the same solvents as those in the first pressure-sensitive adhesive  
15   composition (I-1).

The first pressure-sensitive adhesive composition (I-2) may contain only one type or two or more kinds of the solvents, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the solvents, the combination and ratio thereof can be arbitrarily selected.

20           In the first pressure-sensitive adhesive composition (I-2), the amount of the solvent is not particularly limited and may be appropriately adjusted.

[0102]

<First Pressure-Sensitive Adhesive Composition (I-3)>

As described above, the first pressure-sensitive adhesive composition (I-3)  
25   contains the pressure-sensitive adhesive resin (I-2a) and an energy ray-curable

low-molecular-weight compound.

[0103]

In the first pressure-sensitive adhesive composition (I-3), the amount of the pressure-sensitive adhesive resin (I-2a) is preferably 5% to 99% by mass, more  
5 preferably 10% to 95% by mass, and particularly preferably 15% to 90% by mass.

[0104]

[Energy Ray-Curable Low-Molecular-Weight Compound]

Examples of the energy ray-curable low-molecular-weight compound contained in the first pressure-sensitive adhesive composition (I-3) include monomers or oligomers  
10 which have an energy ray-polymerizable unsaturated group and can be cured by being irradiated with energy rays and include the same energy ray-curable compounds as that in the first pressure-sensitive adhesive composition (I-1).

The first pressure-sensitive adhesive composition (I-3) may contain only one type or two or more kinds of the energy ray-curable low-molecular-weight compounds,  
15 and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the energy ray-curable low-molecular-weight compounds, the combination and ratio thereof can be arbitrarily selected.

[0105]

In the first pressure-sensitive adhesive composition (I-3), the amount of the  
20 energy ray-curable low-molecular-weight compound is preferably 0.01 to 300 parts by mass, more preferably 0.03 to 200 parts by mass, and particularly preferably 0.05 to 100 parts by mass of the amount (100 parts by mass) of the pressure-sensitive adhesive resin (I-2a).

[0106]

25 [Photopolymerization Initiator]

The first pressure-sensitive adhesive composition (I-3) may also further contain a photopolymerization initiator. The first pressure-sensitive adhesive composition (I-3) containing the photopolymerization initiator sufficiently proceeds with a curing reaction even when irradiated with energy rays having a relatively low energy such as ultraviolet rays.

[0107]

Examples of the photopolymerization initiator in the first pressure-sensitive adhesive composition (I-3) include the same photopolymerization initiators as those in the first pressure-sensitive adhesive composition (I-1).

The first pressure-sensitive adhesive composition (I-3) may contain only one type or two or more kinds of the photopolymerization initiators, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the photopolymerization initiators, the combination and ratio thereof can be arbitrarily selected.

[0108]

In the first pressure-sensitive adhesive composition (I-3), the amount of the photopolymerization initiator is preferably 0.01 to 20 parts by mass, more preferably 0.03 to 10 parts by mass, and particularly preferably 0.05 to 5 parts by mass of the total amount (100 parts by mass) of the pressure-sensitive adhesive resin (I-2a) and the energy ray-curable low-molecular-weight compound.

[0109]

[Other Additives]

The first pressure-sensitive adhesive composition (I-3) may also contain other additives which do not correspond to any of the above-described components as long as the effects of the present invention are not impaired.

Examples of the other additives include the same other additives as those in the first pressure-sensitive adhesive composition (I-1).

The first pressure-sensitive adhesive composition (I-3) may contain only one type or two or more kinds of the other additives, and in a case in which the first  
5 pressure-sensitive adhesive composition contains two or more kinds of the other additives, the combination and ratio thereof can be arbitrarily selected.

[0110]

In the first pressure-sensitive adhesive composition (I-3), the amount of the other additives is not particularly limited and may be appropriately selected depending on  
10 the type of the additives.

[0111]

[Solvent]

The first pressure-sensitive adhesive composition (I-3) may also contain a solvent for the same purpose as in the case of the first pressure-sensitive adhesive  
15 composition (I-1).

Examples of the solvent in the first pressure-sensitive adhesive composition (I-3) include the same solvents as those in the first pressure-sensitive adhesive composition (I-1).

The first pressure-sensitive adhesive composition (I-3) may contain only one  
20 type or two or more kinds of the solvents, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the solvents, the combination and ratio thereof can be arbitrarily selected.

In the first pressure-sensitive adhesive composition (I-3), the amount of the solvent is not particularly limited and may be appropriately adjusted.

25 [0112]

<First Pressure-Sensitive Adhesive Compositions Other Than First Pressure-Sensitive Adhesive Compositions (I-1) to (I-3)>

Hitherto, the first pressure-sensitive adhesive composition (I-1), the first pressure-sensitive adhesive composition (I-2), and the first pressure-sensitive adhesive composition (I-3) have been mainly described, but the substances described as the contained components thereof can also be used in the same manner in general first pressure-sensitive adhesive compositions other than the above-described three kinds of first pressure-sensitive adhesive compositions (in the present specification, referred to as the first pressure-sensitive adhesive compositions other than the first pressure-sensitive adhesive compositions (I-1) to (I-3)).

[0113]

Examples of the first pressure-sensitive adhesive compositions other than the first pressure-sensitive adhesive compositions (I-1) to (I-3) include, in addition to, the energy ray-curable pressure-sensitive adhesive compositions, non-energy ray-curable pressure-sensitive adhesive compositions.

Examples of the first non-energy ray-curable pressure-sensitive adhesive compositions include first pressure-sensitive adhesive composition (I-4) containing a non-energy ray-curable pressure-sensitive adhesive resin (I-1a) such as an acrylic resin, a urethane resin, a rubber resin, a silicone resin, an epoxy resin, a polyvinyl ether, a polycarbonate, an ester resin, and one containing an acrylic resin is preferable.

[0114]

The first pressure-sensitive adhesive compositions other than the first pressure-sensitive adhesive compositions (I-1) to (I-3) preferably contain one or more kinds of crosslinking agents, and the amount thereof can be set to be the same as that in the case of the above-described first pressure-sensitive adhesive composition (I-1) or the

like.

[0115]

<First Pressure-Sensitive Adhesive Composition (I-4)>

Examples of the preferable first pressure-sensitive adhesive composition (I-4)  
5 include those containing the pressure-sensitive adhesive resin (I-1a) and a crosslinking agent.

[0116]

[Pressure-Sensitive Adhesive Resin (I-1a)]

Examples of the pressure-sensitive adhesive resin (I-1a) in the first  
10 pressure-sensitive adhesive composition (I-4) include the same pressure-sensitive adhesive resin (I-1a) as those in the first pressure-sensitive adhesive resins (I-1).

The first pressure-sensitive adhesive composition (I-4) may contain only one type or two or more kinds of the pressure-sensitive adhesive resins (I-1a), and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the  
15 pressure-sensitive adhesive compositions, the combination and ratio thereof can be arbitrarily selected.

[0117]

In the first pressure-sensitive adhesive composition (I-4), the amount of the pressure-sensitive adhesive resin (I-1a) (that is, the amount of the pressure-sensitive  
20 adhesive resin (I-1a) of the first pressure-sensitive adhesive layer) is preferably 5% to 99% by mass, more preferably 10% to 95% by mass, and particularly preferably 15% to 90% by mass of the total amount of components other than solvent.

[0118]

[Crosslinking Agent]

25 In a case in which the acrylic polymer further having, in addition to the

constituent unit derived from the alkyl (meth)acrylate, the constituent unit derived from the functional group-containing monomer as the pressure-sensitive adhesive resin (I-1a), the first pressure-sensitive adhesive composition (I-4) preferably further contains a crosslinking agent.

5 [0119]

Examples of the crosslinking agent in the first pressure-sensitive adhesive composition (I-4) include the same crosslinking agents as those in the first pressure-sensitive adhesive composition (I-1).

The first pressure-sensitive adhesive composition (I-4) may contain only one  
10 type or two or more kinds of the crosslinking agents, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the crosslinking agents, the combination and ratio thereof can be arbitrarily selected.

[0120]

In the first pressure-sensitive adhesive composition (I-4), the amount of the  
15 crosslinking agent is preferably 0.01 to 50 parts by mass, more preferably 0.1 to 20 parts by mass, and particularly preferably 0.3 to 15 parts by mass of the amount (100 parts by mass) of the pressure-sensitive adhesive resin (I-1a).

[0121]

[Other Additives]

20 The first pressure-sensitive adhesive composition (I-4) may also contain other additives which do not correspond to any of the above-described components as long as the effects of the present invention are not impaired.

Examples of the other additives include the same other additives as those in the first pressure-sensitive adhesive composition (I-1).

25 The first pressure-sensitive adhesive composition (I-4) may contain only one

type or two or more kinds of the other additives, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the other additives, the combination and ratio thereof can be arbitrarily selected.

[0122]

5           In the first pressure-sensitive adhesive composition (I-4), the amount of the other additives is not particularly limited and may be appropriately selected depending on the type of the additives.

[0123]

[Solvent]

10           The first pressure-sensitive adhesive composition (I-4) may also contain a solvent for the same purpose as in the case of the first pressure-sensitive adhesive composition (I-1).

Examples of the solvent in the first pressure-sensitive adhesive composition (I-4) include the same solvents as those in the first pressure-sensitive adhesive  
15   composition (I-1).

The first pressure-sensitive adhesive composition (I-4) may contain only one type or two or more kinds of the solvents, and in a case in which the first pressure-sensitive adhesive composition contains two or more kinds of the solvents, the combination and ratio thereof can be arbitrarily selected.

20           In the first pressure-sensitive adhesive composition (I-4), the amount of the solvent is not particularly limited and may be appropriately adjusted.

[0124]

<<Method for Manufacturing First Pressure-Sensitive Adhesive Composition>>

The first pressure-sensitive adhesive compositions such as the first  
25   pressure-sensitive adhesive compositions (I-1) to (I-4) can be obtained by blending

individual components for constituting the first pressure-sensitive adhesive compositions such as the pressure-sensitive adhesive, components other than the pressure-sensitive adhesive as necessary, and the like.

The addition order during the blending of the respective components is not particularly limited, and two or more kinds of components may be added at the same time.

In a case in which the solvent is used, the solvent may be used by mixing the solvent with all of the blending components other than the solvent so as to dilute these blending components in advance or may be used by mixing the solvent with the blending components without diluting all of the blending components other than the solvent in advance.

A method for mixing the respective components during blending is not particularly limited and may be appropriately selected from well-known methods such as a method in which the components are mixed together by rotating a stirring stick, a stirring blade, or the like; a method in which the components are mixed together using a mixer, and a method in which the components are mixed together by applying ultrasonic waves thereto.

The temperature and the time during the addition and mixing of the respective components are not particularly limited as long as the respective blending components do not deteriorate and may be appropriately adjusted, but the temperature is preferably 15°C to 30°C.

[0125]

#### o First Interlayer

The first interlayer has a sheet form or a film form, and a constituent material thereof may be appropriately selected depending on the purpose and is not particularly

limited.

For example, in a case in which the purpose is to suppress the deformation of the first protective film by reflecting the shape of bumps present on the circuit surface in the first protective film that is formed on the bump-formed surface, examples of a preferred  
5 constituent material of the first interlayer include urethane (meth)acrylate and the like from the viewpoint of further improving the attachment property of the first interlayer.

[0126]

The first interlayer may be a single layer (monolayer) or a plurality of layers of two or more layers, and in a case in which the first interlayer is a plurality of layers, the  
10 respective layers in the plurality of layers may be identical to or different from one another, and the combination of the plurality of layers is not particularly limited.

[0127]

The thickness of the first interlayer can be appropriately adjusted depending on the height of bumps on the semiconductor surface which is a protection target, but is  
15 preferably 50 to 600  $\mu\text{m}$ , more preferably 70 to 500  $\mu\text{m}$ , and particularly preferably 80 to 400  $\mu\text{m}$  since it is possible to relatively easily absorb the influence of bumps having a relatively high height.

Here, “the thickness of the first interlayer” refers to the thickness of the entire first interlayer, and for example, the thickness of the first interlayer made up of a  
20 plurality of layers refers to the total thickness of all of the layers constituting the first interlayer.

[0128]

<<First Interlayer Forming Composition>>

The first interlayer can be formed using a first interlayer forming composition  
25 containing the constituent material.

For example, the first interlayer can be formed at an intended portion by applying the first interlayer forming composition to a target surface on which the first interlayer is to be formed and drying the first interlayer forming composition or curing the first interlayer forming composition by being irradiated with energy rays as necessary.

5 A more specific method for forming the first interlayer will be described below in detail together with methods for forming other layers.

[0129]

The first interlayer forming composition may be applied using a well-known method, and examples thereof include methods in which a variety of coaters such as an  
10 air knife coater, a blade coater, a bar coater, a gravure coater, a roll coater, a roll knife coater, a curtain coater, a die coater, a knife coater, a screen coater, a Mayer bar coater, and a kiss coater are used.

[0130]

The drying conditions of the first interlayer forming composition are not  
15 particularly limited. For example, it is preferable that the first interlayer forming composition containing a solvent described later is dried by heating. The first interlayer forming composition containing a solvent is preferably dried at 70°C to 130°C for 10 seconds to 5 minutes.

In a case in which the first interlayer forming composition is energy ray-curable,  
20 the first interlayer forming composition is preferably further cured by being irradiated with energy rays after drying.

[0131]

Examples of the first interlayer forming composition include a first interlayer forming composition containing urethane (meth)acrylate (II-1) and the like.

25 [0132]

## &lt;First Interlayer Forming Composition (II-1)&gt;

As described above, the first interlayer forming composition (II-1) contains urethane (meth)acrylate.

[0133]

## 5 [Urethane (Meth)acrylate]

The urethane (meth)acrylate is a compound having at least a (meth)acryloyl group and a urethane bond in one molecule and is energy ray-polymerizable.

The urethane (meth)acrylate may be a monofunctional urethane (meth)acrylate (urethane (meth)acrylate having only one (meth)acryloyl group in one molecule) or may  
10 be a di- or higher-functional urethane (meth)acrylate (urethane (meth)acrylate having two or more (meth)acryloyl groups in one molecule), that is, a multifunctional urethane (meth)acrylate. However, in the present invention, it is preferable to use at least monofunctional urethane (meth) acrylate.

[0134]

15 Examples of the urethane (meth)acrylate contained in the first interlayer forming composition include urethane (meth)acrylate obtained by further causing a (meth)acrylic compound having a hydroxyl group and a (meth)acryloyl group to react with a terminal isocyanate urethane prepolymer obtained by reacting a polyol compound and a polyhydric isocyanate compound. Here, “the terminal isocyanate urethane prepolymer”  
20 refers to a prepolymer having a urethane bond and having an isocyanate group at a terminal portion of the molecule.

[0135]

The first interlayer forming composition (II-1) may contain only one type or two or more kinds of the urethane (meth)acrylate, and in a case in which the first interlayer  
25 forming composition contains two or more kinds of the urethane (meth)acrylate, the

combination and ratio thereof can be arbitrarily selected.

[0136]

(Polyol Compound)

The polyol compound is not particularly limited as long as the compound has  
5 two or more hydroxyl groups in one molecule.

One type of the polyol compound may be used singly or two or more kinds of  
the polyol compounds may be jointly used; however, in a case in which two or more  
kinds of the polyol compounds are jointly used, the combination and ratio thereof can be  
arbitrarily selected.

10 [0137]

Examples of the polyol compound include alkylenediol, polyether-type polyols,  
polyester-type polyols, polycarbonate-type polyols, and the like.

The polyol compound may be any one of a difunctional diol, a trifunctional triol,  
and tetra- or higher-functional polyols, but a diol is preferred since the diol can be easily  
15 procured and is excellent in terms of versatility, reactivity, and the like.

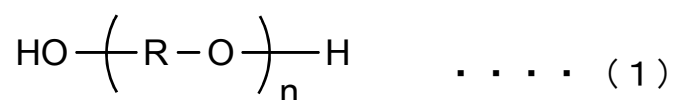
[0138]

· Polyether-Type Polyol

The polyether-type polyol is not particularly limited, and is preferably a  
polyether-type diol. Examples of the polyether-type diol include a compound  
20 represented by General Formula (1).

[0139]

[Chem. 1]



(In the formula, n represents an integer of 2 or more; R represents a divalent

hydrocarbon group, and a plurality of R's may be identical to or different from one another)

[0140]

In the formula, n represents the number of repeating units of a group represented by General Formula “-R-O-” and is not particularly limited as long as n is an integer of 2 or more. Among these, n is preferably 10 to 250, more preferably 25 to 205, and particularly preferably 40 to 185.

[0141]

In the formula, R is not particularly limited as long as R is a divalent hydrocarbon group, but is preferably an alkylene group, more preferably an alkylene group having 1 to 6 carbon atoms, still more preferably an ethylene group, a propylene group, or a tetramethylene group, and particularly preferably a propylene group or a tetramethylene group.

[0142]

The compound represented by General Formula (1) is preferably polyethylene glycol, polypropylene glycol or polytetramethylene glycol and more preferably polypropylene glycol or polytetramethylene glycol.

[0143]

When the polyether-type diol and the polyhydric isocyanate compound are reacted with each other, urethane (meth)acrylate having an ether bond portion represented by General Formula (1a) as the terminal isocyanate urethane prepolymer can be obtained. In addition, when the above-described terminal isocyanate urethane prepolymer is used, the urethane (meth)acrylate has the ether bond portion, that is, has a constituent unit derived from the polyether-type diol.

[0144]

[Chem. 2]



(In the formula, R and n are the same as described above)

[0145]

## 5        · Polyester-Type Polyol

The polyester-type polyol is not particularly limited, and examples thereof include polyols obtained by causing an esterification reaction using a polybasic acid or a derivative thereof, and the like. Meanwhile, in the present specification, unless particularly otherwise described, “a derivative” refers to a compound in which one or more groups are substituted with other groups (substituents). Here, “a group” refers not only to an atomic group formed by bonding a plurality of atoms but also to one atom.

[0146]

Examples of the polybasic acid or the derivative thereof include polybasic acids that are ordinarily used as a manufacturing raw material of polyesters and derivatives thereof.

Examples of the polybasic acids include saturated aliphatic polybasic acids, unsaturated aliphatic polybasic acids, aromatic polybasic acids, and the like, and dimers corresponding to any of the above-described polybasic acids may also be used.

[0147]

Examples of the saturated aliphatic polybasic acids include saturated aliphatic dibasic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid, and the like.

Examples of the unsaturated aliphatic polybasic acids include unsaturated aliphatic dibasic acids such as maleic acid and fumaric acid.

Examples of the aromatic polybasic acids include aromatic dibasic acids such as phthalic acid, isophthalic acid, terephthalic acid, and 2,6-naphthalenedicarboxylic acid; aromatic tribasic acids such as trimellitic acid; aromatic tetrabasic acids such as pyromellitic acid; and the like.

5 [0148]

Examples of the derivatives of the polybasic acids include acid anhydrides of the saturated aliphatic polybasic acids, the unsaturated aliphatic polybasic acids, and the aromatic polybasic acids described above, hydrogenated dimer acids, and the like.

[0149]

10 One type of any of the polybasic acids or the derivatives thereof may be used singly or two or more kinds of any of the polybasic acids or the derivatives thereof may be jointly used, and in a case in which two or more kinds of any of the polybasic acids or the derivatives thereof are jointly used, the combination and ratio thereof can be arbitrarily selected.

15 [0150]

The polybasic acid is preferably the aromatic polybasic acid since the aromatic polybasic acid is suitable for the formation of coated films having an appropriate hardness.

[0151]

20 In the esterification reaction for obtaining the polyester-type polyol, a well-known catalyst may also be used as necessary.

Examples of the catalyst include tin compounds such as dibutyltin oxide and stannous octanoate; alkoxy titanium such as tetrapropyl titanate; and the like.

[0152]

25 · Polycarbonate-Type Polyol

The polycarbonate-type polyol is not particularly limited, and examples thereof include polycarbonates obtained by reacting the same glycol as the compound represented by General Formula (1) and alkylene carbonate, and the like.

Here, one type of any of the glycol and the alkylene carbonate may be used  
5 singly or two or more kinds of any of the glycol and the alkylene carbonate may be jointly used, and in a case in which two or more kinds of any of the glycol and the alkylene carbonate are jointly used, the combination and ratio thereof can be arbitrarily selected.

[0153]

10 The number-average molecular weight computed from the hydroxyl value of the polyol compound is preferably 1,000 to 10,000, more preferably 2,000 to 9,000, and particularly preferably 3,000 to 7,000. When the number-average molecular weight is 1,000 or more, the excess generation of urethane bonds is suppressed, and it becomes easier to control the viscoelastic characteristic of the first interlayer. In addition, when  
15 the number-average molecular weight is 10,000 or less, the excess softening of the first interlayer is suppressed.

The number-average molecular weight computed from the hydroxyl value of the polyol compound refers to a value computed from the following expression.

[The number-average molecular weight of the polyol compound]=[the number  
20 of functional groups in the polyol compound] $\times 56.11 \times 1,000$ /[the hydroxyl value of the polyol compound (unit: mgKOH/g)]

[0154]

The polyol compound is preferably the polyether-type polyol and more preferably a polyether-type diol.

25 [0155]

(Polyhydric Isocyanate Compound)

The polyhydric isocyanate compound that is reacted with the polyol compound is not particularly limited as long as the polyhydric isocyanate compound has two or more isocyanate groups.

- 5           One type of the polyhydric isocyanate compound may be used singly or two or more kinds of the polyhydric isocyanate compounds may be jointly used, and in a case in which two or more kinds of the polyhydric isocyanate compounds are jointly used, the combination and ratio thereof can be arbitrarily selected.

[0156]

- 10           Examples of the polyhydric isocyanate compound include chain-like aliphatic diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate, and trimethylhexamethylene diisocyanate; cyclic aliphatic diisocyanates such as isophorone diisocyanate, norbornane diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, dicyclohexylmethane-2,4'-diisocyanate, and  $\omega,\omega'$ -diisocyanate dimethylcyclohexane;
- 15           aromatic diisocyanates such as 4,4'-diphenylmethane diisocyanate, tolylene diisocyanate, tetramethylene xylylene diisocyanate, and naphthalene-1,5-diisocyanate; and the like.

Among these, the polyhydric isocyanate compound is preferably isophorone diisocyanate, hexamethylene diisocyanate, or xylylene diisocyanate from the viewpoint of the handling property.

- 20           [0157]

((Meth)acrylic Compound)

The (meth)acrylic compound that is reacted with the terminal isocyanate urethane prepolymer is not particularly limited as long as the compound has at least a hydroxyl group and a (meth)acryloyl group in one molecule.

- 25           One type of the (meth)acrylic compound may be used singly or two or more

kinds of the (meth)acrylic compounds may be jointly used, and in a case in which two or more kinds of the (meth)acrylic compounds are jointly used, the combination and ratio thereof can be arbitrarily selected.

[0158]

5           Examples of the (meth)acrylic compound include hydroxyl group-containing (meth)acrylic acid esters such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 4-hydroxycyclohexyl (meth)acrylate, 5-hydroxycyclooctyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, pentaerythritol tri(meth)acrylate, polyethylene glycol mono(meth)acrylate, and polypropylene glycol mono(meth)acrylate; hydroxyl group-containing (meth)acrylamides such as N-methylol (meth)acrylamide; reactants obtained by reacting (meth)acrylic acid with vinyl alcohol, vinyl phenol, or bisphenol A diglycidyl ether; and the like.

15           Among these, the (meth)acrylic compound is preferably the hydroxyl group-containing (meth)acrylic acid ester, more preferably a hydroxyl group-containing alkyl (meth)acrylate, and particularly preferably 2-hydroxyethyl (meth)acrylate.

[0159]

20           The reaction between the terminal isocyanate urethane prepolymer and the (meth)acrylic compound may be caused using a solvent, a catalyst, and the like as necessary.

[0160]

25           Conditions during the reaction between the terminal isocyanate urethane prepolymer and the (meth)acrylic compound may be appropriately adjusted, and for example, the reaction temperature is preferably 60°C to 100°C, and the reaction time is

preferably one to four hours.

[0161]

The urethane (meth)acrylate may be any of an oligomer, a polymer and a mixture of an oligomer and a polymer and is preferably an oligomer.

5 For example, the weight-average molecular weight of the urethane (meth)acrylate is preferably 1,000 to 100,000, more preferably 3,000 to 80,000, and particularly preferably 5,000 to 65,000. When the weight-average molecular weight is 1,000 or more, it becomes easy to optimize the hardness of the first interlayer due to the intermolecular force between structures derived from the urethane (meth)acrylate in  
10 polymers of the urethane (meth)acrylate and a polymerizable monomer described below.

In the present specification, unless particularly otherwise described, the weight-average molecular weight refers to a polystyrene-equivalent value measured using gel permeation chromatography (GPC).

[0162]

15 [Polymerizable Monomer]

The first interlayer forming composition (II-1) may also contain, in addition to the urethane (meth)acrylate, a polymerizable monomer from the viewpoint of further improving the film-forming property.

The polymerizable monomer refers to polymerizable monomers except for  
20 oligomers and polymers which are energy ray-polymerizable and have a weight-average molecular weight of 1,000 or more and is preferably a compound having at least one (meth)acryloyl group in one molecule.

[0163]

Examples of the polymerizable monomer include alkyl (meth)acrylates in which  
25 an alkyl group constituting the alkyl ester has 1 to 30 carbon atoms and has a chain-like

shape; functional group-containing (meth)acrylic compounds having a functional group such as a hydroxyl group, an amide group, an amino group, or an epoxy group; (meth)acrylic acid esters having an aliphatic cyclic group; (meth)acrylic acid esters having an aromatic hydrocarbon group; (meth)acrylic acid esters having a heterocyclic group; compounds having a vinyl group; compounds having an allyl group; and the like.

[0164]

Examples of the alkyl (meth)acrylates having a chain-like alkyl group having 1 to 30 carbon atoms include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, n-octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), a pentadecyl (meth)acrylate group, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, octadecyl (meth)acrylate (stearyl (meth)acrylate), isooctadecyl (meth)acrylate (isostearyl (meth)acrylate), nonadecyl (meth)acrylate, icosyl (meth)acrylate, and the like.

[0165]

Examples of functional group-containing (meth)acrylic derivatives include hydroxyl group-containing (meth)acrylic acid esters such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, and 4-hydroxybutyl (meth)acrylate; (meth)acrylamides such as (meth)acrylamide, N,N-dimethyl (meth)acrylamide, N-butyl (meth)acrylamide, N-methylol (meth)acrylamide,

N-methylolpropane (meth)acrylamide, N-methoxymethyl (meth)acrylamide, and N-butoxymethyl (meth)acrylamide and derivatives thereof; (meth)acrylic acid esters having an amino group (hereinafter, in some cases, referred to as “the amino group-containing (meth)acrylic acid esters”); (meth)acrylic acid esters having a

5 monosubstituted amino group which are formed by substituting one hydrogen atom in an amino group with a group other than a hydrogen atom (hereinafter, in some cases, referred to as “the monosubstituted amino group-containing (meth)acrylic acid esters”); (meth)acrylic acid esters having a disubstituted amino group which are formed by substituting two hydrogen atoms in an amino group with groups other than a hydrogen

10 atom (hereinafter, in some cases, referred to as “the disubstituted amino group-containing (meth)acrylic acid esters”); (meth)acrylic acid esters having an epoxy group such as glycidyl (meth)acrylate and methyl glycidyl (meth)acrylate (hereinafter, in some cases, referred to as “the epoxy group-containing (meth)acrylic acid esters”); and the like.

[0166]

15 Here, “the amino group-containing (meth)acrylic acid ester” refers to a compound formed by substituting one or more hydrogen atoms in a (meth)acrylic acid ester with an amino group ( $\text{-NH}_2$ ). Similarly, “the monosubstituted amino group-containing (meth)acrylic acid ester” refers to a compound formed by substituting one or more hydrogen atoms in a (meth)acrylic acid ester with a monosubstituted amino

20 group, and “the disubstituted amino group-containing (meth)acrylic acid ester” refers to a compound formed by substituting one or more hydrogen atoms in a (meth)acrylic acid ester with a disubstituted amino group.

Examples of the group other than a hydrogen atom which substitutes the hydrogen atom (that is, the substituent) in “the monosubstituted amino group” and “the

25 disubstituted amino group” include alkyl groups and the like.

[0167]

Examples of the (meth)acrylic acid esters having an aliphatic cyclic group include isobornyl (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, cyclohexyl (meth)acrylate,  
5 adamantyl (meth)acrylate, and the like.

[0168]

Examples of the (meth)acrylic acid esters having an aromatic hydrocarbon group include phenyl hydroxypropyl (meth)acrylate, benzyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, and the like.

10 [0169]

The heterocyclic group in the (meth)acrylic acid ester having a heterocyclic group may be any of an aromatic heterocyclic group and an aliphatic heterocyclic group.

Examples of the (meth)acrylic acid esters having the heterocyclic group include tetrahydrofurfuryl (meth)acrylate, (meth)acryloyl morpholine, and the like.

15 [0170]

Examples of the compounds having a vinyl group include styrene, hydroxyethyl vinyl ether, hydroxybutyl vinyl ether, N-vinylformamide, N-vinylpyrrolidone, N-vinylcaprolactam, and the like.

[0171]

20 Examples of the compounds having an allyl group include allyl glycidyl ethers and the like.

[0172]

From the viewpoint of good compatibility with the urethane (meth)acrylate, the polymerizable monomer preferably has a relatively bulky group.

25 Examples of the polymerizable monomer include (meth)acrylic acid esters

having an aliphatic cyclic group, (meth)acrylic acid esters having an aromatic hydrocarbon group, and (meth)acrylic acid esters having a heterocyclic group, and (meth)acrylic acid esters having an aliphatic cyclic group are more preferred.

[0173]

5           The first interlayer forming composition (II-1) may contain only one type or two or more kinds of the polymerizable monomers, and in a case in which the first interlayer forming composition contains two or more kinds of the polymerizable monomers, the combination and ratio thereof can be arbitrarily selected.

[0174]

10           In the first interlayer forming composition (II-1), the amount of the polymerizable monomer is preferably 10% to 99% by mass, more preferably 15% to 95% by mass, still more preferably 20% to 90% by mass, and particularly preferably 25% to 80% by mass.

[0175]

15   [Photopolymerization Initiator]

          The first interlayer forming composition (II-1) may also contain, in addition to the urethane (meth)acrylate and the polymerizable monomer, a photopolymerization initiator. The first interlayer forming composition (II-1) containing the photopolymerization initiator sufficiently proceeds with a curing reaction even when  
20   irradiated with energy rays having a relatively low energy such as ultraviolet rays.

[0176]

          Examples of the photopolymerization initiator in the first interlayer forming composition (II-1) include the same photopolymerization initiators as those in the first pressure-sensitive adhesive composition (I-1).

25           [0177]

The first interlayer forming composition (II-1) may contain only one type or two or more kinds of the photopolymerization initiators, and in a case in which the first interlayer forming composition contains two or more kinds of the photopolymerization initiators, the combination and ratio thereof can be arbitrarily selected.

5 [0178]

In the first interlayer forming composition (II-1), the amount of the photopolymerization initiator is preferably 0.01 to 20 parts by mass, more preferably 0.03 to 10 parts by mass, and particularly preferably 0.05 to 5 parts by mass with respect to the total amount (100 parts by mass) of the urethane (meth)acrylate and the  
10 polymerizable monomer.

[0179]

[Resin Components Other Than Urethane (Meth)acrylate]

The first interlayer forming composition (II-1) may also contain resin components other than the urethane (meth)acrylate as long as the effects of the present  
15 invention are not impaired.

The kinds of the resin components and the amount thereof in the first interlayer forming composition (II-1) may be appropriately selected depending on the purpose and are not particularly limited.

[0180]

20 [Other Additives]

The first interlayer forming composition (II-1) may also contain other additives which do not correspond to any of the above-described components as long as the effects of the present invention are not impaired.

Examples of the other additives include a variety of additives such as a  
25 crosslinking agent, an antistatic agent, an antioxidant, a chain transfer, a softening agent

(plasticizer), a filler, an antirust agent, and a colorant (a pigment or a dye).

Examples of the chain transfer include thiol compounds having at least one thiol group (mercapto group) in one molecule.

[0181]

5           Examples of the thiol compounds include nonyl mercaptan, 1-dodecanethiol, 1,2-ethanedithiol, 1,3-propandithiol, triazinethiol, triazinedithiol, triazinetrithiol, 1,2,3-propanetrithiol, tetraethylene glycol bis(3-mercaptopropionate), trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakisthioglycolate, dipentaerythritol hexakis(3-mercaptopropionate),  
10       tris[(3-mercaptopropioniloxy)-ethyl]-isocyanurate, 1,4-bis(3-mercaptobutyryloxy)butane, pentaerythritol tetrakis(3-mercaptobutylate), 1,3,5-tris(3-mercaptobutyloxyethyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, and the like.

[0182]

          The first interlayer forming composition (II-1) may contain only one type or two  
15       or more kinds of the other additives, and in a case in which the first interlayer forming composition contains two or more kinds of the other additives, the combination and ratio thereof can be arbitrarily selected.

[0183]

          In the first interlayer forming composition (II-1), the amount of the other  
20       additives is not particularly limited and may be appropriately selected depending on the type of the additives.

[0184]

[Solvent]

          The first interlayer forming composition (II-1) may also contain a solvent.

25       When the first interlayer forming composition (II-1) contains a solvent, the coating

aptitude to a coating target surface improves.

[0185]

<<Method for Manufacturing First Interlayer Forming Composition>>

5       The first interlayer forming composition such as the first interlayer forming composition (II-1) can be obtained by blending individual components for constituting the first interlayer forming composition.

      The addition order during the blending of the respective components is not particularly limited, and two or more kinds of components may be added at the same time.

10       In a case in which the solvent is used, the solvent may be used by mixing the solvent with all of the blending components other than the solvent so as to dilute these blending components in advance or may be used by mixing the solvent with the blending components without diluting all of the blending components other than the solvent in advance.

15       A method for mixing the respective components during blending is not particularly limited and may be appropriately selected from well-known methods such as a method in which the components are mixed together by rotating a stirring stick, a stirring blade, or the like; a method in which the components are mixed together using a mixer, and a method in which the components are mixed together by applying ultrasonic  
20       waves thereto.

      The temperature and the time during the addition and mixing of the respective components are not particularly limited as long as the respective blending components do not deteriorate and may be appropriately adjusted, but the temperature is preferably 15°C to 30°C.

25       [0186]

- Curable Resin layer

The curable resin layer (curable resin film) is a layer (film) for protecting the circuit surface of the semiconductor wafer and the semiconductor chip, and the bumps provided on the circuit surface.

5           The curable resin layer may be any one of a thermosetting resin layer (thermosetting resin film), and is an energy ray-curable resin layer (energy ray-curable resin film).

The curable resin layer forms the first protective film by curing.

[0187]

10           The visible light transmittance of the curable resin layer is 45% or less, which is sufficiently low. With the curable resin layer having such properties, it is possible to form the first protective film in which the visible light transmittance is suppressed in the same way. In the semiconductor wafer or the semiconductor chip having such a curable resin layer or a first protective film on the bump-formed surface, it is difficult or  
15 impossible to visually recognize the circuit surface due to the concealing action of the curable resin layer or the first protective film. Therefore, acquisition of information on a wiring pattern of the circuit surface by a third party can be suppressed. In addition, when attempting to bring the curable resin film into close contact with the circuit surface and the surface of the bump, an upper region including a top of the bump and the vicinity  
20 thereof does not penetrate the curable resin film, and even if the curable resin film remains on the upper region of the bump, the remaining curable resin film and the first protective film formed therefrom can be easily recognized.

[0188]

As an example of the curable resin layer capable of obtaining the  
25 above-mentioned effect, a curable resin layer having the transmittance of light having at

least one wavelength of 380 to 750 nm of 45% or less is exemplified, and a curable resin layer having the transmittance of light having all wavelength of 380 to 750 nm of 45% or less may be used.

Among them, as an example of the curable resin layer which is more remarkably  
5 capable of obtaining the above-mentioned effect, a curable resin layer having the transmittance of light having at least one wavelength of 450 to 570 nm of 45% or less is exemplified, and a curable resin layer having the transmittance of light having all wavelength of 450 to 570 nm of 45% or less may be used.

[0189]

10 In addition, the infrared transmittance of the curable resin layer is 33% or more and is sufficiently high. With the curable resin layer having such properties, it is possible to form the first protective film in which similarly, the infrared transmittance is sufficiently high. In the semiconductor wafer or the semiconductor chip provided with the curable resin layer or the first protective film on the bump-formed surface, by using  
15 an infrared camera, an infrared microscope or the like, the circuit surface of the semiconductor wafer or the semiconductor chip can be easily observed through the curable resin layer or the first protective film. With this, it is possible to confirm a state of the circuit surface through the curable resin layer or the first protective film. Also, for example, when performing dicing, a position of an alignment mark (a mark that  
20 positions a portion to be diced) present on the surface of a semiconductor wafer and a position of a dicing line (a line indicating a position where dicing is to be performed) can be recognized, and thus it is possible to specify a cutting position on the semiconductor wafer.

[0190]

25 As an example of the curable resin layer capable of obtaining the

above-mentioned effect, a curable resin layer having the transmittance of light having at least one wavelength of 800 to 2,000 nm of 33% or more is an exemplary example, and a curable resin layer having the transmittance of light having all wavelength of 800 to 2,000 nm of 33% or more may be used.

5           Among them, as an example of the curable resin layer which is more remarkably capable of obtaining the above-mentioned effect, a curable resin layer having the transmittance of light having at least one wavelength of 1,400 to 1,700 nm of 33% or more is an exemplary example, and a curable resin layer having the transmittance of light having all wavelength of 1,400 to 1,700 nm of 33% or more may be used.

10           [0191]

From the viewpoint that the effect of the present invention described above can be more remarkably obtained, the visible light transmittance of the curable resin layer is preferable as the value is small, and for example, is preferably 42.5% or less, is more preferably 40% or less, and is particularly preferably 37.5% or less.

15           The lower limit value of the visible light transmittance of the curable resin layer is not particularly limited, and may be 0%. For example, in consideration of a point that it is easy to form the first protective film having a low visible light transmittance, it is preferably 5%.

It is preferable that the curable resin layer has such a transmittance for light of at least one wavelength (for example, at least one wavelength of 380 to 750 nm) corresponding to the above-mentioned visible light.

[0192]

The visible light transmittance of the curable resin layer can be appropriately adjusted so as to be within a range set optionally combining the above-mentioned preferable lower limit value and upper limit value.

For example, in one embodiment, visible light transmittance of the curable resin layer is preferably 0% to 45%, is more preferably 0% to 42.5%, is still more preferably 0% to 40%, and is particularly preferably 0% to 37.5%.

5 In addition, in one embodiment, visible light transmittance of the curable resin layer is preferably 5% to 45%, is more preferably 5% to 42.5%, is still more preferably 5% to 40%, and is particularly preferably 5% to 37.5%.

Here, these are examples of the visible light transmittance of the curable resin layer.

As an example of the curable resin layer, those having such a transmittance for  
10 light of at least one wavelength corresponding to visible light are exemplary examples. For example, the curable resin layer may have such a transmittance for light of at least one wavelength of 380 to 750 nm and the transmittance for light of all wavelength of 380 to 750 nm. Further, for example, the curable resin layer may have such a transmittance for light of at least one wavelength of 450 to 570 nm and the transmittance for light of all  
15 wavelength of 450 to 570 nm.

[0193]

Further, from the viewpoint that the effect of the present invention described above can be more remarkably obtained, the infrared transmittance of the curable resin layer is preferable as the value is large, and for example, is preferably 35% or more, is  
20 more preferably 37.5% or more, and is particularly preferably 40% or more.

The upper limit value of the infrared transmittance of the curable resin layer is not particularly limited, and may be 100%. For example, in consideration of a point that it is easy to form the first protective film having a high infrared transmittance, it is preferably 97.5%.

25 It is preferable that the curable resin layer has such a transmittance for light of at

least one wavelength (for example, at least one wavelength of 800 to 2,000 nm) corresponding to the above-mentioned infrared.

[0194]

The infrared transmittance of the curable resin layer can be appropriately  
5 adjusted so as to be within a range set optionally combining the above-mentioned preferable lower limit value and upper limit value.

For example, in one embodiment, the infrared transmittance of the curable resin layer is preferably 33% to 100%, is more preferably 35% to 100%, is still more preferably 37.5% to 100%, and is particularly preferably 40% to 100%.

10 In addition, in one embodiment, the infrared transmittance of the curable resin layer is preferably 33% to 97.5%, is more preferably 35% to 97.5%, is still more preferably 37.5% to 97.5%, and is particularly preferably 40% to 97.5%.

Here, these are examples of the infrared transmittance of the curable resin layer.

As an exemplary example of the curable resin layer, those having such a  
15 transmittance for light of at least one wavelength corresponding to infrared can be provided. For example, the curable resin layer may have such a transmittance for light of at least one wavelength of 800 to 2,000 nm and the transmittance for light of all wavelength of 800 to 2,000 nm. Further, for example, the curable resin layer may have such a transmittance for light of at least one wavelength of 1,400 to 1,700 nm and the  
20 transmittance for light of all wavelength of 1,400 to 1,700 nm.

[0195]

Examples of the curable resin layer include those having both a visible light transmittance in any one of the numerical ranges described above and an infrared transmittance in any of the numerical ranges described above.

25 [0196]

From the viewpoint that the effect of the present invention described above can be more remarkably obtained,  $L^*$  in the  $L^* a^* b^*$  color system of the curable resin layer is preferably 1 to 40, is more preferably 2 to 37, and is particularly preferably 3 to 35.

5 [0197]

In addition, from the viewpoint that the effect of the present invention described above can be more remarkably obtained,  $a^*$  in the  $L^* a^* b^*$  color system of the curable resin layer is preferably 4 to 20, is more preferably 6 to 17, and is particularly preferably 8 to 14.

10 [0198]

From the viewpoint that the effect of the present invention described above can be more remarkably obtained,  $b^*$  in the  $L^* a^* b^*$  color system of the curable resin layer is preferably 8 to 35, is more preferably 12 to 30, and is particularly preferably 16 to 25.

15 [0199]

A color difference ( $\Delta E$ ) between the curable resin film and the silicon wafer obtained by calculating  $L^*$ ,  $a^*$ , and  $b^*$  calculated by measuring the light transmittance from the bump-formed surface side, of the semiconductor wafer which is a target to be attached of the curable resin film, and  $L^*$ ,  $a^*$ , and  $b^*$  of the curable resin layer is preferably 20 to 53, is more preferably 23 to 51, and is particularly preferably 26 to 49. When the color difference obtained by calculating  $L^*$ ,  $a^*$ , and  $b^*$  of the curable resin layer is within the above range, the same effect as in the case where the visible light transmittance of the curable resin layer is low as described above can be obtained. That is, when attempting to bring the curable resin film into close contact with the circuit surface and the surface of the bump, the upper region including the top of the bump and

20

25

the vicinity thereof does not penetrate the curable resin film, and even if the curable resin film remains on the upper region of the bump, the remaining curable resin film and the first protective film formed therefrom can be more easily recognized.

Here, the color difference ( $\Delta E$ ) can be calculated by Formula (f-1).

5            Formula (f-1):  $\Delta E = [(L11^* - L2^*)^2 + (a11^* - a2^*)^2 + (b11^* - b2^*)^2]^{1/2}$

(In Formula,  $L11^*$ ,  $a11^*$ , and  $b11^*$  are  $L^*$ ,  $a^*$ , and  $b^*$  of the curable resin layer, and  $L2^*$ ,  $a2^*$ , and  $b2^*$  are  $L^*$ ,  $a^*$ , and  $b^*$  calculated by measuring the light transmittance of the semiconductor wafer from the bump-formed surface side)

[0200]

10            Note that, in this specification,  $L^*$ ,  $a^*$ , and  $b^*$  mean those measured based on JIS Z8781-4:2013.

[0201]

The optical characteristics such as light transmittance and hue of the first protective film are the same as the optical characteristics such as the light transmittance  
15    and hue of the curable resin layer before curing.

[0202]

That is, from the viewpoint that the effect of the present invention described above can be more remarkably obtained, the visible light transmittance of the first protective film is preferable as the value is small, and for example, is preferably 45% or  
20    less, is more preferably 42.5% or less, is still more preferably 40% or less, and is particularly preferably 37.5% or less.

The lower limit value of the visible light transmittance of the first protective film is not particularly limited, and may be 0%. For example, in consideration of a point that it is easy to form the first protective film having a low visible light transmittance, it is  
25    preferably 5%.

It is preferable that the first protective film has such a transmittance for light of at least one wavelength (for example, at least one wavelength of 380 to 750 nm) corresponding to the above-mentioned infrared.

[0203]

5           The visible light transmittance of the first protective film can be appropriately adjusted so as to be within a range set optionally combining the above-mentioned preferable lower limit value and upper limit value.

For example, in one embodiment, visible light transmittance of the first protective film is preferably 0% to 45%, is more preferably 0% to 42.5%, is still more preferably 0% to 40%, and is particularly preferably 0% to 37.5%.

In addition, in one embodiment, visible light transmittance of the first protective film is preferably 5% to 45%, is more preferably 5% to 42.5%, is still more preferably 5% to 40%, and is particularly preferably 5% to 37.5%.

Here, these are examples of the visible light transmittance of the first protective film.

As an example of the first protective film, those having such a transmittance for light of at least one wavelength corresponding to visible light are exemplary examples. For example, the first protective film may have such a transmittance for light of at least one wavelength of 380 to 750 nm and the transmittance for light of all wavelength of 380 to 750 nm. For example, the first protective film may have such a transmittance for light of at least one wavelength of 450 to 570 nm and the transmittance for light of all wavelength of 450 to 570 nm.

[0204]

That is, from the viewpoint that the effect of the present invention described above can be more remarkably obtained, the infrared transmittance of the first protective

film is preferable as the value is large, and for example, is preferably 33% or more, is more preferably 35% or more, is still more preferably 37.5% or more, and is particularly preferably 40% or more.

The upper limit value of the infrared transmittance of the first protective film is not particularly limited, and may be 100%. For example, in consideration of a point that it is easy to form the first protective film having a high infrared transmittance, it is preferably 97.5%.

It is preferable that the first protective film has such a transmittance for light of at least one wavelength (for example, at least one wavelength of 800 to 2,000 nm) corresponding to the above-mentioned infrared.

[0205]

The infrared transmittance of the first protective film can be appropriately adjusted so as to be within a range set optionally combining the above-mentioned preferable lower limit value and upper limit value.

For example, in one embodiment, the infrared transmittance of the first protective film is preferably 33% to 100%, is more preferably 35% to 100%, is still more preferably 37.5% to 100%, and is particularly preferably 40% to 100%.

In addition, in one embodiment, the infrared transmittance of the first protective film is preferably 33% to 97.5%, is more preferably 35% to 97.5%, is still more preferably 37.5% to 97.5%, and is particularly preferably 40% to 97.5%.

Here, these are examples of the infrared transmittance of the first protective film.

As an exemplary example of the first protective film, those having such a transmittance for light of at least one wavelength corresponding to infrared can be provided. For example, the first protective film may have such a transmittance for light

of at least one wavelength of 800 to 2,000 nm and the transmittance for light of all wavelength of 800 to 2,000 nm. For example, the first protective film may have such a transmittance for light of at least one wavelength of 1,400 to 1,700 nm and the transmittance for light of all wavelength of 1,400 to 1,700 nm.

5 [0206]

Examples of the first protective film include those having both a visible light transmittance in at least any one of the numerical ranges described above and an infrared transmittance in at least any of the numerical ranges described above.

[0207]

10 From the viewpoint that the effect of the present invention described above can be more remarkably obtained,  $L^*$  in the  $L^* a^* b^*$  color system of the first protective film is preferably 1 to 40, is more preferably 2 to 37, and is particularly preferably 3 to 35.

From the viewpoint that the effect of the present invention described above can  
15 be more remarkably obtained,  $a^*$  in the  $L^* a^* b^*$  color system of the first protective film is preferably 4 to 20, is more preferably 6 to 17, and is particularly preferably 8 to 14.

From the viewpoint that the effect of the present invention described above can  
be more remarkably obtained,  $b^*$  in the  $L^* a^* b^*$  color system of the first protective  
20 film is preferably 8 to 35, is more preferably 12 to 30, and is particularly preferably 16 to 25.

[0208]

A color difference ( $\Delta E$ ) between the first protective film and the silicon wafer obtained by calculating  $L^*$ ,  $a^*$ , and  $b^*$  calculated by measuring the light transmittance  
25 from the bump-formed surface side, of the semiconductor wafer which is a target to be

formed of the first protective film, and  $L^*$ ,  $a^*$ , and  $b^*$  of the first protective film is preferably 20 to 53, is more preferably 23 to 51, and is particularly preferably 26 to 49.

When the color difference obtained by calculating  $L^*$ ,  $a^*$ , and  $b^*$  of the first protective film is within the above range, the same effect as in the case where the visible light

5 transmittance of the curable resin layer is low as described above can be obtained. That is, when attempting to bring the curable resin film into close contact with the circuit surface and the surface of the bump, the upper region including the top of the bump and the vicinity thereof does not penetrate the curable resin film, and even if the first protective film remains on the upper region of the bump, the remaining first protective  
10 film formed therefrom can be more easily recognized.

Here, the color difference ( $\Delta E$ ) can be calculated by Formula (f-2).

$$\text{Formula (f-2): } \Delta E = [(L12^* - L2^*)^2 + (a12^* - a2^*)^2 + (b12^* - b2^*)^2]^{1/2}$$

(In Formula,  $L12^*$ ,  $a12^*$ , and  $b12^*$  are  $L^*$ ,  $a^*$ , and  $b^*$  of the first protective film, and  $L2^*$ ,  $a2^*$ , and  $b2^*$  are  $L^*$ ,  $a^*$ , and  $b^*$  calculated by measuring the light transmittance of  
15 the semiconductor wafer from the bump-formed surface side)

[0209]

The curable resin layer may be a single layer (monolayer) or a plurality of two or more layers. The entire curable resin layer having two or more layers may satisfy the conditions of various optical characteristics such as visible light transmittance, infrared  
20 transmittance,  $L^*$ ,  $a^*$ , and  $b^*$  described above.

[0210]

The visible light transmittance, the infrared transmittance,  $L^*$ ,  $a^*$ , and  $b^*$  of the curable resin layer and the visible light transmittance, the infrared transmittance,  $L^*$ ,  $a^*$ , and  $b^*$  of the first protective film, can all be, for example, adjusted by adjusting the kinds  
25 of the curable resin layers.

The curable resin layer can be formed using a curable resin layer forming composition containing a constituent material thereof.

Accordingly, the visible light transmittance, the infrared transmittance,  $L^*$ ,  $a^*$ , and  $b^*$  can be adjusted by adjusting one or both of the kind and the amount of the contained components of the curable resin layer forming composition.

[0211]

Among the contained components of the curable resin layer forming composition, the kinds of the coloring agent (I) particularly described later and the amount of the coloring agent (I) of the curable resin layer forming composition greatly affect the optical characteristics of the curable resin layer and the first protective film.

In the present invention, by selecting an appropriate kind as the coloring agent (I) and adjusting the amount of the coloring agent (I) in the curable resin layer forming composition to an appropriate value, the visible light transmittance can be lowered easily, and the infrared transmittance can be increased easily.

[0212]

In addition, among the contained components of the curable resin layer forming composition, average particle diameter of a filler (D) particularly described later and the amount of the filler (D) of the curable resin layer forming composition may greatly affect the optical characteristics of the curable resin layer and the first protective film. In the present invention, by selecting one having an appropriate average particle diameter as the filler (D) and adjusting the amount of the filler (D) in the curable resin layer forming composition to an appropriate value, the visible light transmittance can be lowered easily, and the infrared transmittance can be increased easily.

The curable resin layer forming composition (thermosetting resin layer forming composition, the energy ray-curable resin layer forming composition), and the

manufacturing method thereof will be specifically described below.

[0213]

#### o Thermosetting Resin Layer

Examples of a preferable thermosetting resin layer include thermosetting resin  
5 layers containing the polymer component (A), the thermosetting component (B), and the  
coloring agent (I). The polymer component (A) is a component considered to be  
formed by a polymerization reaction of a polymerizable compound. In addition, the  
thermosetting component (B) is a component capable of a curing (polymerization)  
reaction using heat as a trigger of the reaction. Meanwhile, in the present invention, a  
10 polycondensation reaction is also considered as the polymerization reaction.

[0214]

The thermosetting resin layer may be a single layer (monolayer) or a plurality of  
layers of two or more layers, and, in a case in which the thermosetting resin layer is a  
plurality of layers, the respective layers in the plurality of layers may be identical to or  
15 different from one another, and the combination of the plurality of layers is not  
particularly limited.

[0215]

The thickness of the thermosetting resin layer is preferably 1 to 100  $\mu\text{m}$ , more  
preferably 5 to 75  $\mu\text{m}$ , and particularly preferably 5 to 50  $\mu\text{m}$ . When the thickness of  
20 the thermosetting resin layer is equal to or more than the lower limit value, it is possible  
to form a first protective film having a higher protection function. In addition, when the  
thickness of the thermosetting resin layer is equal to or less than the upper limit value,  
excessive thickness is suppressed.

Here, “the thickness of the thermosetting resin layer” refers to the thickness of  
25 the entire thermosetting resin layer, and, for example, the thickness of the thermosetting

resin layer made up of a plurality of layers refers to the total thickness of all of the layers constituting the thermosetting resin layer.

[0216]

The curing condition when the thermosetting resin layer is attached to the bump-formed surface of the semiconductor wafer, and is cured so as to form the first protective film is not particularly limited as long as the first protective film is cured so as to sufficiently exert its function, and may be appropriately selected according to the kinds of the thermosetting resin layers.

For example, the heating temperature at the time of the curing of the thermosetting resin layer is preferably 100°C to 200°C, more preferably 110°C to 180°C, and particularly preferably 120°C to 170°C. In addition, the heating time for the curing is preferably 0.5 to five hours, more preferably 0.5 to 3.5 hours, and particularly preferably one to 2.5 hours.

[0217]

<<Thermosetting Resin Layer Forming Composition>>

The thermosetting resin layer can be formed using a thermosetting resin layer forming composition containing a constituent material thereof. For example, the thermosetting resin layer can be formed at an intended portion by applying the thermosetting resin layer forming composition to a target surface on which the thermosetting resin layer is to be formed and drying the thermosetting resin layer forming composition as necessary.

[0218]

The thermosetting resin layer forming composition may be applied using a well-known method, and examples thereof include methods in which a variety of coaters such as an air knife coater, a blade coater, a bar coater, a gravure coater, a roll coater, a

roll knife coater, a curtain coater, a die coater, a knife coater, a screen coater, a Mayer bar coater, and a kiss coater are used.

[0219]

The drying conditions of the thermosetting resin layer forming composition are not particularly limited; however, in a case in which the thermosetting resin layer forming composition contains a solvent described below, the thermosetting resin layer forming composition is preferably heated and dried. The thermosetting resin layer forming composition containing a solvent is preferably dried at 70°C to 130°C for 10 seconds to 5 minutes.

10 [0220]

<Resin Layer Forming Composition (III-1)>

Examples of the thermosetting resin layer forming composition include a thermosetting resin layer forming composition (III-1) containing the polymer component (A), the thermosetting component (B), and the coloring agent (I) (in the present specification, in some cases, simply abbreviated as “the resin layer forming composition (III-1)”) and the like.

[0221]

[Polymer Component (A)]

The polymer component (A) is a polymer compound for imparting a film-forming property, flexibility, and the like to the thermosetting resin layer.

The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one kind or two or more kinds of the polymer components (A), and, in a case in which the resin layer forming composition and the thermosetting resin layer contain two or more kinds of the polymer components, the combination and ratio thereof can be optionally selected.

[0222]

Examples of the polymer component (A) include polyvinyl acetal, an acrylic resin, polyester, a urethane resin, an acrylic urethane resin, a silicone resin, a rubber resin, a phenoxy resin, and thermosetting polyimide, and polyvinyl acetal and an acrylic resin  
 5 are preferable.

[0223]

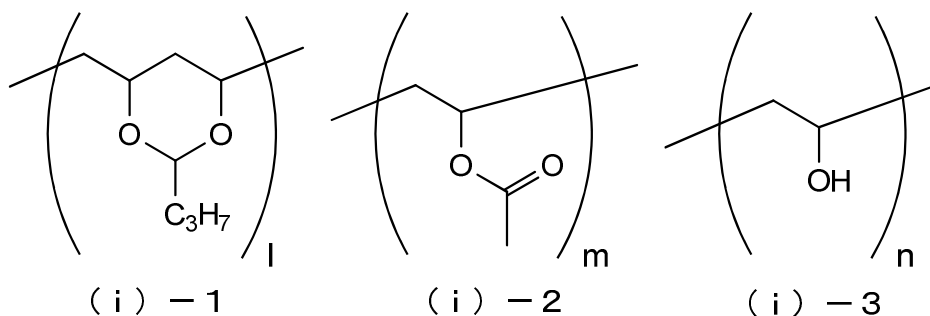
Examples of the polyvinyl acetal in the polymer component (A) include well-known substances.

Among them, preferable polyvinyl acetals include, for example, polyvinyl  
 10 formal and polyvinyl butyral, and polyvinyl butyral is more preferable.

Examples of the polyvinyl butyral include those having constituent units represented by Formulae (i)-1, (i)-2, and (i)-3.

[0224]

[Chem. 3]



15

(In Formula, l, m, and n are each independently an integer of 1 or more.)

[0225]

The weight-average molecular weight (M<sub>w</sub>) of the polyvinyl acetal is preferably 5,000 to 200,000, and is more preferably 8,000 to 100,000. When the weight-average  
 20 molecular weight of the polyvinyl acetal is within the above range, the effect of suppressing the residual of the thermosetting resin layer at the upper region (the upper

region including the top of the bump and the vicinity thereof) of the bump becomes higher when the thermosetting resin layer is attached to the bump-formed surface.

[0226]

The glass transition temperature (T<sub>g</sub>) of the polyvinyl acetal is preferably 40°C to 80°C and is more preferably 50°C to 70°C. When the T<sub>g</sub> of the polyvinyl acetal is within the above range, the effect of suppressing the residual of the thermosetting resin layer at the upper region of the bump becomes higher when the thermosetting resin layer is attached to the bump-formed surface.

[0227]

The ratio of three or more kinds of monomers constituting the polyvinyl acetal can be optionally selected.

[0228]

Examples of the acrylic resin in the polymer component (A) include well-known acrylic polymers.

The weight-average molecular weight (M<sub>w</sub>) of the acrylic resin is preferably 10,000 to 2,000,000, and is more preferably 100,000 to 1,500,000. When the weight-average molecular weight of the acrylic resin is equal to or more than the lower limit value, the shape stability (aging stability during storage) of the thermosetting resin layer improves. In addition, when the weight-average molecular weight of the acrylic resin is equal to or less than the upper limit value, it becomes easy for the thermosetting resin layer to follow the uneven surfaces of adherends, and the generation of voids and the like between an adherend and the thermosetting resin layer is further suppressed.

[0229]

The glass transition temperature (T<sub>g</sub>) of the acrylic resin is preferably -60°C to 70°C and more preferably -30°C to 50°C. When the T<sub>g</sub> of the acrylic resin is equal to

or higher than the lower limit value, the adhesive force between the first protective film and the first supporting sheet is suppressed, and thus the peeling property of the first supporting sheet improves. In addition, when the Tg of the acrylic resin is equal to or lower than the upper limit value, the adhesive force of the thermosetting resin layer and the first protective film to adherends are improved.

[0230]

Examples of the acrylic resin include a polymer of one or more type of (meth)acrylic acid esters; and a copolymer obtained by copolymerization of one kind or two or more kinds of monomer selected from (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene, and N-methylol acrylamide other than (meth) acrylic acid ester.

[0231]

Examples of the (meth)acrylic acid esters constituting the acrylic resin include alkyl (meth)acrylic acid esters in which an alkyl group constituting the alkyl ester has 1 to 18 carbon atoms and has a chain-like shape such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (stearyl (meth)acrylate), and the like; cycloalkyl (meth)acrylic acid esters such as isobornyl (meth)acrylate and dicyclopentanyl (meth)acrylate; aralkyl (meth)acrylic acid esters such

as benzyl (meth)acrylate; cycloalkenyl (meth)acrylic acid esters such as dicyclopentenyl (meth)acrylate; cycloalkenyloxy alkyl (meth)acrylic acid esters such as dicyclopentenylloxyethyl (meth)acrylate; imide (meth)acrylate; glycidyl group-containing (meth)acrylic acid esters such as glycidyl (meth)acrylate; hydroxyl group-containing (meth)acrylic acid esters such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, and 4-hydroxybutyl (meth)acrylate; and substituted amino group-containing (meth)acrylic acid esters such as N-methylaminoethyl (meth)acrylate; and the like. Here, “the substituted amino group” refers to a group formed by substituting one or two hydrogen atoms in an amino group with a group other than a hydrogen atom.

[0232]

The acrylic resin may be constituted of only one kind or two or more kinds of monomers, and in a case in which the acrylic resin is constituted of two or more kinds of monomers, the combination and ratio thereof can be optionally selected.

[0233]

The acrylic resin may also have a functional group capable of bonding to other compounds such as a vinyl group, a (meth)acryloyl group, an amino group, a hydroxyl group, a carboxy group, or an isocyanate group. The functional group in the acrylic resin may be bonded to other compounds through a crosslinking agent (F) described below or may be directly bonded to other compounds without the crosslinking agent (F). When the acrylic resin is bonded to other compounds through the functional group, there is a tendency that the reliability of packages obtained using the sheet for forming a first protective film improves.

[0234]

In the present invention, as the polymer component (A), a thermoplastic resin other than the polyvinyl acetal and the acrylic resin (hereinafter, in some cases, simply abbreviated as “the thermoplastic resin”) may be used singly without using the polyvinyl acetal and the acrylic resin or may be jointly used with the polyvinyl acetal and the acrylic resin. When the thermoplastic resin is used, there are cases in which the peeling property of the first protective film from the first supporting sheet improves, it becomes easy for the thermosetting resin layer to follow the uneven surfaces of adherends, and the generation of voids and the like between an adherend and the thermosetting resin layer is further suppressed.

10 [0235]

The weight-average molecular weight of the thermoplastic resin is preferably 1,000 to 100,000 and more preferably 3,000 to 80,000.

[0236]

The glass transition temperature ( $T_g$ ) of the thermoplastic resin is preferably  
15  $-30^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  and more preferably  $-20^{\circ}\text{C}$  to  $120^{\circ}\text{C}$ .

[0237]

Examples of the thermoplastic resin include polyesters, polyurethanes, phenoxy resins, polybutene, polybutadienes, polystyrenes, and the like.

[0238]

20 The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one kind or two or more kinds of the thermoplastic resins, and in a case in which the resin layer forming composition and the thermosetting resin layer contains two or more kinds of the thermoplastic resins, the combination and ratio thereof can be optionally selected.

25 [0239]

In the resin layer forming composition (III-1), the ratio of the amount of the polymer component (A) (that is, the amount of the polymer component (A) in the thermosetting resin layer) to the total amount of all of the components other than the solvent is preferably 5% to 85% by mass and more preferably 5% to 80% by mass

5 regardless of the type of the polymer component (A), and for example, may be one of 5% to 70% by mass, 5% to 60% by mass, 5% to 50% by mass, 5% to 40% by mass, and 5% to 30% by mass. However, these amounts in the resin layer forming composition (III-1) are mere examples.

[0240]

10 There are cases in which the polymer component (A) corresponds to the thermosetting component (B). In the present invention, in a case in which the resin layer forming composition (III-1) contains components corresponding both the polymer component (A) and the thermosetting component (B) as described above, the resin layer forming composition (III-1) is considered to contain the polymer component (A) and the  
15 thermosetting component (B).

[0241]

[Thermosetting component (B)]

The thermosetting component (B) is a component for curing the thermosetting resin layer so as to form a rigid first protective film.

20 The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one kind or two or more kinds of the thermosetting components (B), and, in a case in which the resin layer forming composition and the thermosetting resin layer contains two or more kinds of the thermosetting components, the combination and ratio thereof can be optionally selected.

25 [0242]

Examples of the thermosetting component (B) include epoxy-based thermosetting resins, thermosetting polyimides, polyurethanes, unsaturated polyesters, silicone resins, and the like, and epoxy-based thermosetting resins are preferable.

[0243]

#### 5 (Epoxy-Based Thermosetting Resin)

The epoxy-based thermosetting resin is made up of an epoxy resin (B1) and a thermal curing agent (B2).

The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one kind or two or more kinds of the epoxy-based thermosetting resins, and, in a case in which the resin layer forming composition and the thermosetting resin layer contains two or more kinds of the epoxy-based thermosetting resins, the combination and ratio thereof can be optionally selected.

[0244]

· Epoxy resin (B1)

As the epoxy resin (B1), well-known epoxy resins can be exemplified. Examples thereof include polyfunctional epoxy resins, biphenyl compounds, bisphenol A diglycidyl ethers and hydrogenated substances thereof, orthocresol novolac epoxy resins, dicyclopentadiene-type epoxy resins, biphenyl-type epoxy resins, bisphenol A-type epoxy resins, bisphenol F-type epoxy resins, phenylene skeleton-type epoxy resins, and the like, and di- or higher-functional epoxy compounds.

[0245]

As the epoxy resin (B1), an epoxy resin having an unsaturated hydrocarbon group may also be used. The epoxy resin having an unsaturated hydrocarbon group has more compatibility with acrylic resins than epoxy resins not having an unsaturated hydrocarbon group. Therefore, when the epoxy resin having an unsaturated

hydrocarbon group is used, the reliability of packages obtained using the sheet for forming a first protective film improves.

[0246]

Examples of the epoxy resin having an unsaturated hydrocarbon group include  
5 compounds formed by converting a part of epoxy groups in a polyfunctional epoxy resin to groups having an unsaturated hydrocarbon group. The above-described compound can be obtained by, for example, an addition reaction of (meth)acrylic acid or a derivative thereof to an epoxy group.

In addition, examples of the epoxy resin having an unsaturated hydrocarbon  
10 group include compounds in which a group having an unsaturated hydrocarbon group is directly bonded to an aromatic ring or the like constituting an epoxy resin and the like.

The unsaturated hydrocarbon group is a polymerizable unsaturated group, and specific examples thereof include ethenyl groups (vinyl groups), 2-propenyl group (allyl group), (meth)acryloyl groups, (meth)acrylamide groups, and the like, and acryloyl  
15 groups are preferable.

[0247]

The number-average molecular weight of the epoxy resin (B1) is not particularly limited, but is preferably 300 to 30,000, more preferably 400 to 10,000, and particularly preferably 500 to 3,000 from the viewpoint of the curing property of the thermosetting  
20 resin layer and the strength and thermal resistance of the first protective film after curing.

The epoxy equivalent of the epoxy resin (B1) is preferably 100 to 1,000 g/eq and more preferably 130 to 800 g/eq.

[0248]

The epoxy resin (B1) may be used singly or two or more kinds thereof may be  
25 jointly used, and in a case in which two or more kinds thereof are jointly used, the

combination and ratio thereof can be optionally selected.

[0249]

· Thermal Curing Agent (B2)

5 The thermal curing agent (B2) functions as a curing agent of the epoxy resin (B1).

Examples of the thermal curing agent (B2) include compounds having two or more functional groups capable of reacting with an epoxy group in one molecule.

Examples of the functional group include phenolic hydroxyl groups, alcoholic hydroxyl groups, an amino group, a carboxy group, groups in which an acid group is turned into an anhydride, and the like, phenolic hydroxyl groups, amino groups, or groups in which an acid group is turned into an anhydride are preferable, and phenolic hydroxyl groups or amino groups are more preferable.

10

[0250]

As the thermal curing agent (B2), examples of phenolic curing agents having a phenolic hydroxyl group include polyfunctional phenolic resins, biphenol, novolac-type phenol resins, dicyclopentadiene-based phenolic resins, aralkylphenol resins, and the like.

15

As the thermal curing agent (B2), examples of amine-based curing agents having an amino group include dicyandiamide (in the specification, in some cases, abbreviated as “DICY”), and the like.

20

[0251]

The thermal curing agent (B2) may also have an unsaturated hydrocarbon group.

Examples of the thermal curing agent (B2) having an unsaturated hydrocarbon group include compounds formed by substituting a part of hydroxyl groups in a phenolic resin with groups having an unsaturated hydrocarbon group, compounds formed by

25

directly bonding a group having an unsaturated hydrocarbon group to an aromatic ring of a phenolic resin, and the like.

The unsaturated hydrocarbon group in the thermal curing agent (B2) is identical to the unsaturated hydrocarbon group in the above-described epoxy resin having an  
5 unsaturated hydrocarbon group.

[0252]

In a case in which a phenolic curing agent is used as the thermal curing agent (B2), the thermal curing agent (B2) preferably has a high softening point or glass transition temperature since the peeling property from the first supporting sheet of the  
10 first protective film improves.

[0253]

The number-average molecular weight of the resin component such as a polyfunctional phenolic resin, a novolac-type phenolic resin, a dicyclopentadiene-based phenolic resin, or an aralkylphenolic resin as the thermal curing agent (B2) is preferably  
15 300 to 30,000, more preferably 400 to 10,000, and particularly preferably 500 to 3,000.

The molecular weight of a non-resin component, for example, biphenol or dicyandiamide as the thermal curing agent (B2) is not particularly limited, and is preferably, for example, 60 to 500.

[0254]

20 The thermal curing agent (B2) may be used singly or two or more kinds thereof may be jointly used, and in a case in which two or more kinds thereof are jointly used, the combination and ratio thereof can be optionally selected.

[0255]

In the resin layer forming composition (III-1) and the thermosetting resin layer,  
25 the amount of the thermal curing agent (B2) is preferably 0.1 to 500 parts by mass, and is

more preferably 1 to 200 parts by mass, and may be 5 to 100 parts by mass, 10 to 80 parts by mass, 15 to 60 parts by mass, 25 to 55 parts by mass, and 35 to 55 parts by mass with respect to 100 parts by mass of the epoxy resin (B1). When the amount of the thermal curing agent (B2) is equal to or more than the lower limit value, it becomes easier for the curing of the thermosetting resin layer to proceed. In addition, when the amount of the thermal curing agent (B2) is equal to or less than the upper limit value, the moisture absorptivity of the thermosetting resin layer is decreased, and thus the reliability of packages obtained by using the sheet for forming a first protective film further improves.

10 [0256]

In the resin layer forming composition (III-1) and the thermosetting resin layer, the amount of the thermosetting component (B) (for example, the total amount of the epoxy resin (B1) and the thermal curing agent (B2) is preferably 50 to 1,000 parts by mass, more preferably 100 to 900 parts by mass, and particularly preferably 150 to 800 parts by mass, and may be, for example, any one of 200 to 700 parts by mass, 300 to 700 parts by mass, 300 to 600 parts by mass, and 300 to 500 parts by mass of the amount (100 parts by mass) of the polymer component (A). When the amount of the thermosetting component (B) is in the above-described range, the adhesive force between the first protective film and the first supporting sheet is suppressed, and thus the peeling property of the first supporting sheet improves.

[0257]

[Coloring Agent (I)]

The coloring agent (I) is a component for giving appropriate light transmittance to the thermosetting resin layer and the first protective film.

25 The coloring agent (I) may be a known one, and may be, for example, a dye or a

pigment.

For example, the dye may be any of an acidic dye, a reactive dye, a direct dye, a disperse dye, and a cationic dye.

[0258]

- 5           Examples of the coloring agent (I) include a black coloring agent, a cyan coloring agent, a magenta coloring agent, and a yellow coloring agent.

[0259]

Examples of the black coloring agent include an inorganic black pigment, an organic black pigment, and a black dye.

- 10           In addition, examples of the black coloring agent include a coloring agent mixture obtained by mixing a cyan coloring agent (bluish green coloring agent), a magenta coloring agent (reddish purple coloring agent) and a yellow coloring agent (yellow coloring agent).

[0260]

- 15           Among the black coloring agents, examples of the black coloring pigments include carbon black such as furnace black, channel black, acetylene black, thermal black, and lamp black; graphite; copper oxide; manganese dioxide; an azo pigment such as azomethine azo black; aniline black; perylene black; titanium black; cyanine black; activated carbon; ferrite such as nonmagnetic ferrite and magnetic ferrite; magnetite;
- 20           chromium oxide; iron oxide; molybdenum disulfide; chromium complex; composite oxide black colorant; anthraquinone organic black colorant; C. I. Pigment Black 1; and the same black 7(C. I. Pigment Black 7).

[0261]

Among the black coloring agents, examples of the black dyes include C.I.

- 25           Solvent Black 3, C.I. Solvent Black 7, C.I. Solvent Black 22, C.I. Solvent Black 27, C.I.

Solvent Black 29, C.I. Solvent Black 34, C.I. Solvent Black 43, and C.I. Solvent Black 70; C.I. Direct Black 17, C.I. Direct Black 19, C.I. Direct Black 22, C.I. Direct Black 32, C.I. Direct Black 38, C.I. Direct Black 51, and C.I. Direct Black 71; C.I. Acid Black 1, C.I. Acid Black 2, C.I. Acid Black 24, C.I. Acid Black 26, C.I. Acid Black 31, C.I. Acid Black 48, C.I. Acid Black 52, C.I. Acid Black 107, C.I. Acid Black 109, C.I. Acid Black 110, C.I. Acid Black 119, and C.I. Acid Black 154; and C.I. Disperse Black 1, C.I. Disperse Black 3, C.I. Disperse Black 10, and C.I. Disperse Black 24.

[0262]

Examples of the commercially available black coloring agent include Oil Black BY (product name), Oil Black BS (product name), Oil Black HBB (product name), Oil Black 803 (product name), Oil Black 860 (product name), Oil Black 5970 (product name), Oil Black 5906 (product name), and Oil Black 5905 (product name) (which are manufactured by ORIENT CHEMICAL INDUSTRIES CO., LTD.).

[0263]

Among the cyan coloring agents, examples of the cyan dyes include C.I. Solvent Blue 25, C.I. Solvent Blue 36, C.I. Solvent Blue 60, C.I. Solvent Blue 70, C.I. Solvent Blue 93, and C.I. Solvent Blue 95; and C.I. Acid Blue 6 and Acid Blue 45.

[0264]

Among the cyan coloring agents, examples of the cyan pigment include C.I. Pigment Blue 1, C.I. Pigment Blue 2, C.I. Pigment Blue 3, C.I. Pigment Blue 15, C.I. Pigment Blue 15:1, C.I. Pigment Blue 15:2, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Blue 15:5, C.I. Pigment Blue 15:6, C.I. Pigment Blue 16, C.I. Pigment Blue 17, C.I. Pigment Blue 17:1, C.I. Pigment Blue 18, C.I. Pigment Blue 22, C.I. Pigment Blue 25, C.I. Pigment Blue 56, C.I. Pigment Blue 60, C.I. Pigment Blue 63, C.I. Pigment Blue 65, and C.I. Pigment Blue 66; C.I. Purple Bleu 4 and C.I. Purple Bleu 60;

and C.I. Pink Green 7.

[0265]

Among the magenta coloring agents, examples of the magenta dyes include C.I. Solvent Red 1, C.I. Solvent Red 3, C.I. Solvent Red 8, C.I. Solvent Red 23, C.I. Solvent Red 24, C.I. Solvent Red 25, C.I. Solvent Red 27, C.I. Solvent Red 30, C.I. Solvent Red 49, C.I. Solvent Red 52, C.I. Solvent Red 58, C.I. Solvent Red 63, C.I. Solvent Red 81, C.I. Solvent Red 82, C.I. Solvent Red 83, C.I. Solvent Red 84, C.I. Solvent Red 100, C.I. Solvent Red 109, C.I. Solvent Red 111, C.I. Solvent Red 121, and C.I. Solvent Red 122; C.I. Spider Thread 9; C.I. Solvent Violet 8, C.I. Solvent Violet 13, C.I. Solvent Violet 14, C.I. Solvent Violet 21, and C.I. Solvent Violet 27; C.I. Disperse Violet 1; C.I. Basic Red 1, C.I. Basic Red 2, C.I. Basic Red 9, C.I. Basic Red 12, C.I. Basic Red 13, C.I. Basic Red 14, C.I. Basic Red 15, C.I. Basic Red 17, C.I. Basic Red 18, C.I. Basic Red 22, C.I. Basic Red 23, C.I. Basic Red 24, C.I. Basic Red 27, C.I. Basic Red 29, C.I. Basic Red 32, C.I. Basic Red 34, C.I. Basic Red 35, C.I. Basic Red 36, C.I. Basic Red 37, C.I. Basic Red 38, C.I. Basic Red 39, and C.I. Basic Red 40; and C.I. Basic Violet 1, C.I. Basic Violet 3, C.I. Basic Violet 7, C.I. Basic Violet 10, C.I. Basic Violet 14, C.I. Basic Violet 15, C.I. Basic Violet 21, C.I. Basic Violet 25, C.I. Basic Violet 26, C.I. Basic Violet 27, and C.I. Basic Violet 28.

[0266]

Among the magenta coloring agents, examples of the magenta pigment include C.I. Pigment Red 1, C.I. Pigment Red 2, C.I. Pigment Red 3, C.I. Pigment Red 4, C.I. Pigment Red 5, C.I. Pigment Red 6, C.I. Pigment Red 7, C.I. Pigment Red 8, C.I. Pigment Red 9, C.I. Pigment Red 10, C.I. Pigment Red 11, C.I. Pigment Red 12, C.I. Pigment Red 13, C.I. Pigment Red 14, C.I. Pigment Red 15, C.I. Pigment Red 16, C.I. Pigment Red 17, C.I. Pigment Red 18, C.I. Pigment Red 19, C.I. Pigment Red 21, C.I.

Pigment Red 22, C.I. Pigment Red 23, C.I. Pigment Red 30, C.I. Pigment Red 31, C.I.  
 Pigment Red 32, C.I. Pigment Red 37, C.I. Pigment Red 38, C.I. Pigment Red 39, C.I.  
 Pigment Red 40, C.I. Pigment Red 41, C.I. Pigment Red 42, C.I. Pigment Red 48:1, C.I.  
 Pigment Red 48:2, C.I. Pigment Red 48:3, C.I. Pigment Red 48:4, C.I. Pigment Red 49,  
 5 C.I. Pigment Red 49:1, C.I. Pigment Red 50, C.I. Pigment Red 51, C.I. Pigment Red 52,  
 C.I. Pigment Red 52:2, C.I. Pigment Red 53:1, C.I. Pigment Red 54, C.I. Pigment Red 55,  
 C.I. Pigment Red 56, C.I. Pigment Red 57:1, C.I. Pigment Red 58, C.I. Pigment Red 60,  
 C.I. Pigment Red 60:1, C.I. Pigment Red 63, C.I. Pigment Red 63:1, C.I. Pigment Red  
 63:2, C.I. Pigment Red 64, C.I. Pigment Red 64:1, C.I. Pigment Red 67, C.I. Pigment  
 10 Red 68, C.I. Pigment Red 81, C.I. Pigment Red 83, C.I. Pigment Red 87, C.I. Pigment  
 Red 88, C.I. Pigment Red 89, C.I. Pigment Red 90, C.I. Pigment Red 92, C.I. Pigment  
 Red 101, C.I. Pigment Red 104, C.I. Pigment Red 105, C.I. Pigment Red 106, C.I.  
 Pigment Red 108, C.I. Pigment Red 112, C.I. Pigment Red 114, C.I. Pigment Red 122,  
 C.I. Pigment Red 123, C.I. Pigment Red 139, C.I. Pigment Red 144, C.I. Pigment Red  
 15 146, C.I. Pigment Red 147, C.I. Pigment Red 149, C.I. Pigment Red 150, C.I. Pigment  
 Red 151, C.I. Pigment Red 163, C.I. Pigment Red 166, C.I. Pigment Red 168, C.I.  
 Pigment Red 170, C.I. Pigment Red 171, C.I. Pigment Red 172, C.I. Pigment Red 175,  
 C.I. Pigment Red 176, C.I. Pigment Red 177, C.I. Pigment Red 178, C.I. Pigment Red  
 179, C.I. Pigment Red 184, C.I. Pigment Red 185, C.I. Pigment Red 187, C.I. Pigment  
 20 Red 190, C.I. Pigment Red 193, C.I. Pigment Red 202, C.I. Pigment Red 206, C.I.  
 Pigment Red 207, C.I. Pigment Red 209, C.I. Pigment Red 219, C.I. Pigment Red 222,  
 C.I. Pigment Red 224, C.I. Pigment Red 238, and C.I. Pigment Red 245; C.I. Pigment  
 Violet 3, C.I. Pigment Violet 9, C.I. Pigment Violet 19, C.I. Pigment Violet 23, C.I.  
 Pigment Violet 31, C.I. Pigment Violet 32, C.I. Pigment Violet 33, C.I. Pigment Violet 36,  
 25 C.I. Pigment Violet 38, C.I. Pigment Violet 43, and C.I. Pigment Violet 50; and C.I. Vat

Red 1, C.I. Vat Red 2, C.I. Vat Red 10, C.I. Vat Red 13, C.I. Vat Red 15, C.I. Vat Red 23, C.I. Vat Red 29, and C.I. Vat Red 35.

[0267]

Among the yellow coloring agents, examples of the yellow dyes include C.I. Solvent Yellow 19, C.I. Solvent Yellow 44, C.I. Solvent Yellow 77, C.I. Solvent Yellow 79, C.I. Solvent Yellow 81, C.I. Solvent Yellow 82, C.I. Solvent Yellow 93, C.I. Solvent Yellow 98, C.I. Solvent Yellow 103, C.I. Solvent Yellow 104, C.I. Solvent Yellow 112, and C.I. Solvent Yellow 162.

[0268]

Among the yellow coloring agents, examples of the yellow pigment include C.I. Pigment Orange 31 and C.I. Pigment Orange 43; C.I. Pigment Yellow 1, C.I. Pigment Yellow 2, C.I. Pigment Yellow 3, C.I. Pigment Yellow 4, C.I. Pigment Yellow 5, C.I. Pigment Yellow 6, C.I. Pigment Yellow 7, C.I. Pigment Yellow 10, C.I. Pigment Yellow 11, C.I. Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14, C.I. Pigment Yellow 15, C.I. Pigment Yellow 16, C.I. Pigment Yellow 17, C.I. Pigment Yellow 23, C.I. Pigment Yellow 24, C.I. Pigment Yellow 34, C.I. Pigment Yellow 35, C.I. Pigment Yellow 37, C.I. Pigment Yellow 42, C.I. Pigment Yellow 53, C.I. Pigment Yellow 55, C.I. Pigment Yellow 65, C.I. Pigment Yellow 73, C.I. Pigment Yellow 74, C.I. Pigment Yellow 75, C.I. Pigment Yellow 81, C.I. Pigment Yellow 83, C.I. Pigment Yellow 93, C.I. Pigment Yellow 94, C.I. Pigment Yellow 95, C.I. Pigment Yellow 97, C.I. Pigment Yellow 98, C.I. Pigment Yellow 100, C.I. Pigment Yellow 101, C.I. Pigment Yellow 104, C.I. Pigment Yellow 108, C.I. Pigment Yellow 109, C.I. Pigment Yellow 110, C.I. Pigment Yellow 113, C.I. Pigment Yellow 114, C.I. Pigment Yellow 116, C.I. Pigment Yellow 117, C.I. Pigment Yellow 120, C.I. Pigment Yellow 128, C.I. Pigment Yellow 129, C.I. Pigment Yellow 133, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139,

C.I. Pigment Yellow 147, C.I. Pigment Yellow 150, C.I. Pigment Yellow 151, C.I. Pigment Yellow 153, C.I. Pigment Yellow 154, C.I. Pigment Yellow 155, C.I. Pigment Yellow 156, C.I. Pigment Yellow 167, C.I. Pigment Yellow 172, C.I. Pigment Yellow 173, C.I. Pigment Yellow 180, C.I. Pigment Yellow 185, and C.I. Pigment Yellow 195; and C.I. Violet Yellow 1, C.I. Violet Yellow 3, and C.I. Violet Yellow 20.

[0269]

The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one kind or two or more kinds of the coloring agent (I), and, in a case in which the resin layer forming composition and the thermosetting resin layer contain two or more kinds of the polymer components, the combination and ratio thereof can be optionally selected.

For example, in the present invention, one kind of each of the black coloring agent, the cyan coloring agent, the magenta coloring agent and the yellow coloring agent may be used alone (as one example, the black coloring agent may be used alone), and two or more thereof may be used in combination (as one example, two or more kinds of the black coloring agents may be used).

In addition, for example, in the present invention, two or more kinds of coloring agents selected from the group consisting of a black coloring agent, a cyan coloring agent, a magenta coloring agent, and a yellow coloring agent may be used in combination (as one example, the black coloring agent and the cyan coloring agent may be used in combination).

[0270]

The amount of the coloring agent (I) of the resin layer forming composition (III-1) is not particularly limited and may be appropriately adjusted such that the visible light transmittance of the thermosetting resin layer and the infrared transmittance become

a desired value. For example, the amount of the coloring agent (I) may be appropriately adjusted in accordance with the kinds of the coloring agents (I) or the combination of these coloring agents (I) in a case of using two or more kinds of the coloring agents (I) in combination.

5 [0271]

Generally, in the resin layer forming composition (III-1), the ratio of the amount of the coloring agent (I) with respect to the total amount of all of the components other than the solvent (that is, the amount of the coloring agent (I) of the thermosetting resin layer) is preferably 0.01% to 10% by mass.

10 For example, in a case in which the black coloring agent is used as the coloring agent (I), in the resin layer forming composition (III-1), the ratio of the amount of the black coloring agent (that is, the amount of the black coloring agent in the thermosetting resin layer) to the total amount of all of the components other than the solvent is preferably 0.01% to 2% by mass and more preferably 0.03% to 1% by mass.

15 [0272]

[Curing Accelerator (C)]

The resin layer forming composition (III-1) and the thermosetting resin layer may also contain a curing accelerator (C). The curing accelerator (C) is a component for adjusting the resin layer forming composition (III-1).

20 Examples of preferable curing accelerators (C) include tertiary amines such as triethylene diamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol, and tris(dimethylaminomethyl)phenol; imidazoles (imidazoles in which one or more hydrogen atoms are substituted with groups other than a hydrogen atom) such as 2-methylimidazole, 2-phenyl imidazole, 2-phenyl-4-methylimidazole,  
25 2-phenyl-4,5-dihydroxymethylimidazole, and

2,-phenyl-4-methyl-5-hydroxymethylimidazole; organic phosphines (phosphines in which one or more hydrogen atoms are substituted with organic groups) such as tributyl phosphine, diphenyl phosphine, and triphenyl phosphine; and tetraphenyl boron salts such as tetraphenyl phosphonium tetraphenyl borate and triphenyl phosphine tetraphenyl borate.

[0273]

The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one kind or two or more kinds of the curing accelerators (C), and in a case in which the resin layer forming composition and the thermosetting resin layer contain two or more kinds of the curing accelerators, the combination and the ratio thereof can be optionally selected.

[0274]

In a case in which the curing accelerator (C) is used, in the resin layer forming composition (III-1) and the thermosetting resin layer, the amount of the curing accelerator (C) is preferably 0.01 to 10 parts by mass and is more preferably 0.1 to 5 parts by mass with respect to the amount (100 parts by mass) of the thermosetting component (B). When the amount of the curing accelerator (C) is equal to or more than the lower limit value, the effects of the use of the curing accelerator (C) can be more significantly obtained. When the amount of the curing accelerator (C) is equal to or less than the upper limit value, for example, an effect of suppressing a highly polar curing accelerator (C) migrating toward the adhesion interface with adherends in the thermosetting resin layer under high temperature and high humidity conditions and segregating becomes significant, and the reliability of packages obtained using the sheet for forming a first protective film further improves.

[0275]

[Filler (D)]

The resin layer forming composition (III-1) and the thermosetting resin layer may also contain a filler (D). When the thermosetting resin layer contains the filler (D), the coefficient of thermal expansion of the first protective film obtained by curing the thermosetting resin layer can be easily adjusted. Further, when this coefficient of thermal expansion is optimized for a subject on which the first protective film is to be formed, the reliability of packages obtained using the sheet for forming a first protective film further improves. In addition, when the thermosetting resin layer contains the filler (D), it is also possible to decrease the moisture absorptivity of the first protective film or improving the heat dissipation property.

[0276]

The filler (D) may be any one of an organic filler and an inorganic filler, but is preferably an inorganic filler.

Examples of preferable inorganic fillers include powder of silica, alumina, talc, calcium carbonate, titanium white, colcothar, silicon carbide, boron nitride, and the like; beads obtained by spherodizing this inorganic filler; surface-modified products of these inorganic fillers; and single crystal fibers of these inorganic fillers; glass fibers.

Among these, the inorganic filler is preferably silica or alumina.

[0277]

The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one kind or two or more kinds of the fillers (D), and in a case in which the resin layer forming composition and the thermosetting resin layer contain two or more kinds of the fillers, a combination and a ratio thereof can be optionally selected.

[0278]

As such, the average particle diameter of the filler (D) particularly described

later and the amount of the filler (D) of the curable resin layer forming composition may greatly affect the optical characteristics of the curable resin layer and the first protective film.

The average particle diameter of the filler (D) is preferably 2  $\mu\text{m}$  or less, is more preferably 1.4  $\mu\text{m}$  or less, and is particularly preferably 0.8  $\mu\text{m}$  or less. When the average particle diameter of the filler (D) is the upper limit value or less, the curable resin layer and the infrared transmittance of the first protective film are further improved.

The lower limit value of the average particle diameter of the filler (D) is not particularly limited, and from the viewpoint of more remarkably obtaining an effect by using the filler (D), for example, it is preferably 0.3  $\mu\text{m}$ .

Note that, in this specification, “average particle diameter” means a value of particle diameter ( $D_{50}$ ) at an integrated value of 50% in a particle size distribution curve obtained by a laser diffraction scattering method, unless otherwise specified.

[0279]

The average particle diameter of the filler (D) can be appropriately adjusted so as to be within a range set optionally combining the above-mentioned preferable lower limit value and upper limit value.

For example, in one embodiment, the average particle diameter of the filler (D) is preferably 0.3 to 2  $\mu\text{m}$ , is more preferably 0.3 to 1.4  $\mu\text{m}$ , and is particularly preferably 0.3 to 0.8  $\mu\text{m}$ . Here, these are examples of the average particle diameter of the filler (D).

[0280]

In a case in which the filler (D) is used, in the resin layer forming composition (III-1), the ratio of the amount of the filler (D) (that is, the amount of the filler (D) in the

thermosetting resin layer) to the total amount of all of the components other than the solvent is preferably 3% to 45% by mass and more preferably 3% to 30% by mass.

When the amount of the filler (D) is in the above-described range, the adjustment of the coefficient of thermal expansion becomes easier. Further, when the amount of the filler (D) is the upper limit value or less, the curable resin layer and the infrared transmittance of the first protective film are further improved.

[0281]

In a case of using the filler (D), in the resin layer forming composition (III-1), both of the average particle diameter of the filler (D) and the ratio of the amount of the filler (D) to the total amount of all of the components other than the solvent are preferably within the above preferable numerical range.

For example, in the present invention, the average particle diameter of the filler (D) is preferably 2  $\mu\text{m}$  or less, is more preferably is 1.4  $\mu\text{m}$  or less, and is particularly preferably 0.8  $\mu\text{m}$  or less, and in the resin layer forming composition (III-1), the ratio of the amount of the filler (D) to the total amount of all of the components other than the solvent is preferably 3% to 45% by mass, and is more preferably 3% to 30% by mass.

In addition, in the present invention, the average particle diameter of the filler (D) is preferably 0.3 to 2  $\mu\text{m}$ , is more preferably is 0.3 to 1.4  $\mu\text{m}$ , and is particularly preferably 0.3 to 0.8  $\mu\text{m}$ , and in the resin layer forming composition (III-1), the ratio of the amount of the filler (D) to the total amount of all of the components other than the solvent is preferably 3% to 45% by mass, and is more preferably 3% to 30% by mass.

[0282]

[Coupling Agent (E)]

The resin layer forming composition (III-1) and the thermosetting resin layer

may also contain a coupling agent (E). When a coupling agent having a functional group capable of reacting with an inorganic compound or an organic compound is used as the coupling agent (E), it is possible to improve the adhesiveness and adhesion of the thermosetting resin layer to adherends. In addition, when the coupling agent (E) is used,

5 the first protective film obtained by curing the thermosetting resin layer is not impaired in the thermal resistance and is improved in terms of the water resistance.

[0283]

The coupling agent (E) is preferably a compound having a functional group capable of reacting with the functional group in the polymer component (A), the thermosetting component (B), or the like and more preferably a silane coupling agent.

10

Examples of preferable silane coupling agents include

3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropylmethyldiethoxysilane, 3-glycidyloxypropyltriethoxysilane, 3-glycidyloxymethyldiethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,

15 3-methacryloyloxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-(2-aminoethylamino)propyltrimethoxysilane, 3-(2-aminoethylamino)propylmethyldiethoxysilane, 3-(phenylamino)propyltrimethoxysilane, 3-anilinopropyltrimethoxysilane, 3-ureidopropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane,

20 3-mercaptopropylmethyldimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfane, methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, vinyltriacetoxysilane, imidazolesilane, and the like.

[0284]

The resin layer forming composition (III-1) and the thermosetting resin layer

25 may contain only one kind or two or more kinds of the coupling agents (E), and in a case

in which the resin layer forming composition and the thermosetting resin layer contain two or more kinds of the coupling agents, a combination and a ratio thereof can be optionally selected.

[0285]

5           In a case where the coupling agent (E) is used, in the resin layer forming composition (III-1) and the thermosetting resin layer, the amount of the coupling agent (E) is preferably 0.03 to 20 parts by mass, more preferably 0.05 to 10 parts by mass, and particularly preferably 0.1 to 5 parts by mass of the total amount (100 parts by mass of the polymer component (A) and the thermosetting component (B)). When the amount  
10   of the coupling agent (E) is equal to or more than the lower limit value, the effects of the use of the coupling agent (E) such as the improvement of the dispersibility of the filler (D) in resins and the improvement of the adhesiveness of the thermosetting resin layer to adherends can be significantly obtained. In addition, when the amount of the coupling agent (E) is equal to or less than the upper limit value, the generation of outgas is further  
15   suppressed.

[0286]

[Crosslinking Agent (F)]

          In a case in which a polymer component having a functional group such as a vinyl group, a (meth)acryloyl group, an amino group, a hydroxyl group, a carboxy group,  
20   or an isocyanate group which is capable of bonding with other compounds such as the above-described acrylic resin is used as the polymer component (A), the resin layer forming composition (III-1) and the thermosetting resin layer may also contain a crosslinking agent (F). The crosslinking agent (F) is a component for crosslinking the functional group in the polymer component (A) by bonding with the other compound,  
25   and the initial adhesive force and the agglomerative force of the thermosetting resin layer

can be adjusted by crosslinking in this way.

[0287]

Examples of the crosslinking agent (F) include organic polyhydric isocyanate compounds, organic polyhydric imine compounds, metal chelate-based crosslinking agents (crosslinking agents having a metal chelate structure), aziridine-based crosslinking agents (crosslinking agents having an aziridiny group), and the like.

[0288]

Examples of the organic polyhydric isocyanate compounds include aromatic polyhydric isocyanate compounds, aliphatic polyhydric isocyanate compounds, and alicyclic polyhydric isocyanate compounds (hereinafter, in some cases, these compounds will be collectively abbreviated as “aromatic polyhydric isocyanate compounds and the like”); isocyanurate bodies, and adduct bodies of the aromatic polyhydric isocyanate compounds and the like; terminal isocyanate urethane prepolymers obtained by reacting the aromatic polyhydric isocyanate compounds and the like and a polyol compound. The “adduct body” refers to a reactant of the aromatic polyhydric isocyanate compound, the aliphatic polyhydric isocyanate compound, or the alicyclic polyhydric isocyanate compound and a low-molecular-weight active hydrogen-containing compound such as ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane, or castor oil. Examples of the adduct body include xylylene diisocyanate adduct bodies of trimethylolpropane as described below. In addition, “the terminal isocyanate urethane prepolymer” is as described above.

[0289]

More specific examples of the organic polyhydric isocyanate compound include 2,4-tolylene diisocyanate; 2,6-tolylene diisocyanate; 1,3-xylylene diisocyanate; 1,4-xylylene diisocyanate; diphenylmethane-4,4'-diisocyanate;

diphenylmethane-2,4'-diisocyanate; 3-methyldiphenylmethane diisocyanate;  
 hexamethylene diisocyanate; isophorone diisocyanate;  
 dicyclohexylmethane-4,4'-diisocyanate; dicyclohexylmethane-2,4'-diisocyanate;  
 compounds obtained by adding any one or more kinds of tolylene diisocyanate,

- 5 hexamethylene diisocyanate, and xylylene diisocyanate to all or some of hydroxyl groups  
 in a polyol such as trimethylolpropane; lysine diisocyanate; and the like.

[0290]

Examples of the organic polyhydric imine compounds include

- N,N'-diphenylmethane-4,4'-bis(1-aziridinecarboxamide), trimethylolpropane  
 10 tri- $\beta$ -aziridinypropionate, tetramethylolmethane-tri- $\beta$ -aziridinypropionate,  
 N,N'-toluene-2,4-bis(1-aziridinecarboxamide) triethylene melamine, and the like.

[0291]

- In a case in which the organic polyhydric isocyanate compound is used as the  
 crosslinking agent (F), a hydroxyl group-containing polymer is preferably used as the  
 15 polymer component (A). In a case in which the crosslinking agent (F) has an isocyanate  
 group and the polymer component (A) has a hydroxyl group, it is possible to simply  
 introduce a crosslinking structure into the thermosetting resin layer by a reaction between  
 the crosslinking agent (F) and the polymer component (A).

[0292]

- 20 The resin layer forming composition (III-1) and the thermosetting resin layer  
 may contain only one kind or two or more kinds of the crosslinking agents (F), and in a  
 case in which the resin layer forming composition and the thermosetting resin layer  
 contain two or more kinds of the crosslinking agents, the combination and the ratio  
 thereof can be optionally selected.

- 25 [0293]

In a case in which the crosslinking agent (F) is used, the amount of the crosslinking agent (F) in the resin layer forming composition (III-1) and the thermosetting resin layer is preferably 0.01 to 20 parts by mass, more preferably 0.1 to 10 parts by mass, and particularly preferably 0.5 to 5 parts by mass of the amount (100 parts by mass) of the polymer component (A). When the amount of the crosslinking agent (F) is equal to or more than the lower limit value, the effects of the use of the crosslinking agent (F) can be significantly obtained. In addition, when the amount of the crosslinking agent (F) is equal to or less than the upper limit value, the excess use of the crosslinking agent (F) is suppressed.

10 [0294]

[Energy Ray-Curable Resin (G)]

The resin layer forming composition (III-1) and the thermosetting resin layer may also contain an energy ray-curable resin (G). When the thermosetting resin layer contains the energy ray-curable resin (G), it is possible to change the characteristics by irradiation with energy rays.

[0295]

The energy ray-curable resin (G) is obtained by polymerizing (curing) an energy ray-curable compound.

Examples of the energy ray-curable compound include compounds having at least one polymerizable double bond in the molecule, and acrylate-based compounds having a (meth)acryloyl group are preferable.

[0296]

Examples of the acrylate-based compounds include chain-like aliphatic skeleton-containing (meth)acrylates such as trimethylolpropane tri(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, pentaerythritol tri(meth)acrylate,

pentaerythritol tetra(meth)acrylate, dipentaerythritol monohydroxy penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, 1,4-butylene glycol di(meth)acrylate, and 1,6-hexanediol di(meth)acrylate; cyclic aliphatic skeleton-containing (meth)acrylates such as dicyclopentanyl di(meth)acrylate; polyalkylene glycol (meth)acrylates such as polyethylene glycol di(meth)acrylate; oligo ester (meth)acrylates; urethane (meth)acrylate oligomers; epoxy-modified (meth)acrylates; polyether (meth)acrylates other than the above-described polyalkylene glycol (meth)acrylates; itaconic acid oligomers; and the like.

[0297]

10 The weight-average molecular weight of the energy ray-curable compound is preferably 100 to 30,000 and more preferably 300 to 10,000.

[0298]

Only one kind or two or more kinds of the energy ray-curable compounds may be used for polymerization, and, in a case in which two or more kinds of the energy ray-curable compounds are used, the combination and ratio thereof can be optionally selected.

[0299]

The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one kind or two or more kinds of the energy ray-curable resins (G), and in a case in which the resin layer forming composition and the thermosetting resin layer contains two or more kinds of the energy ray-curable resins, the combination and ratio thereof can be optionally selected.

[0300]

In a case of using the energy ray-curable resin (G), the amount of the energy ray-curable resin (G) in the resin layer forming composition (III-1) is preferably 1% to

95% by mass, more preferably 5% to 90% by mass, and particularly preferably 10% to 85% by mass.

[0301]

[Photopolymerization Initiator (H)]

5           In the case of containing the energy ray-curable resin (G), the resin layer forming composition (III-1) and the thermosetting resin layer may also contain a photopolymerization initiator (H) in order to cause the polymerization reaction of the energy ray curable resin (G) to more efficiently proceed.

[0302]

10           Examples of the photopolymerization initiator (H) in the resin layer forming composition (III-1) include the same photopolymerization initiators as those in the first pressure-sensitive adhesive composition (I-1).

[0303]

15           The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one kind or two or more kinds of the photopolymerization initiator (H), and in a case in which the resin layer forming composition and the thermosetting resin layer contain two or more kinds of the photopolymerization initiators, a combination and a ratio thereof can be optionally selected.

[0304]

20           In a case in which the photopolymerization initiator (H) is used, in the resin layer forming composition (III-1) and the thermosetting resin layer, the amount of the photopolymerization initiators (H) is preferably 0.1 to 20 parts by mass, more preferably 1 to 10 parts by mass, and particularly preferably 2 to 5 parts by mass of the amount (100 parts by mass) of the energy ray-curable resin (G).

25           [0305]

[Versatile Additive (J)]

The resin layer forming composition (III-1) and the thermosetting resin layer may also contain a versatile additive (J) as long as the effects of the present invention are not impaired.

5           The versatile additive (J) may be a well-known versatile additive, can be optionally selected depending on the purpose, and is not particularly limited, and examples of preferable versatile additives include a plasticizer, an antistatic agent, an antioxidant, a gettering agent, and the like.

[0306]

10           The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one kind or two or more kinds of the versatile additives (J), and, in a case in which the resin layer forming composition and the thermosetting resin layer contains two or more kinds of the versatile additives, the combination and ratio thereof can be optionally selected.

15           The amount of the versatile additive (J) in the resin layer forming composition (III-1) and the thermosetting resin layer is not particularly limited and may be appropriately selected depending on the purpose.

[0307]

[Solvent]

20           The resin layer forming composition (III-1) preferably further contains a solvent. The resin layer forming composition (III-1) containing a solvent improves in terms of the handling property.

          The solvent is not particularly limited, but preferable examples thereof include hydrocarbons such as toluene and xylene; alcohols such as methanol, ethanol, 2-propanol,  
25   isobutyl alcohol (2-methyl propane-1-ol), and 1-butanol; esters such as ethyl acetate;

ketones such as acetone and methyl ethyl ketone; ethers such as tetrahydrofuran; amides (compounds having an amide bond) such as dimethyl formamide and N-methyl pyrrolidone, and the like.

The resin layer forming composition (III-1) may contain only one kind or two or  
5 more kinds of the solvents, and in a case in which the resin layer forming composition contains two or more kinds of the solvents, the combination and ratio thereof can be optionally selected.

[0308]

The solvent contained in the resin layer forming composition (III-1) is  
10 preferably methyl ethyl ketone or the like since it is possible to more uniformly mix the components contained in the resin layer forming composition (III-1).

[0309]

The amount of the solvent of the resin layer forming composition (III-1) is not particularly limited, and for example, it may be appropriately selected depending on the  
15 kinds of components other than the solvent.

[0310]

Examples of preferable resin layer forming composition (III-1) include those which contain the polymer component (A), the thermosetting component (B), the coloring agent (I), and the filler (D) and of which the amounts of these components are  
20 within the above preferable numerical range, and those in which the average particle diameter of the filler (D) is within the above preferable numerical range.

As one embodiment of the preferable resin layer forming composition (III-1), for example, those in which the ratio of the amount of the coloring agent (I) (that is, the amount of the coloring agent (I) in the thermosetting resin layer) to the total amount of  
25 all of the components other than the solvent is 0.01% to 10% by mass and the ratio of the

amount of the filler (D) (that is, the amount of the filler (D) in the thermosetting resin layer) to the total amount of all of the components other than the solvent is 3% to 45% by mass, and the average particle diameter of the filler (D) is 2  $\mu\text{m}$  or less are exemplary examples.

5           As one embodiment of the preferable resin layer forming composition (III-1), for example, those in which the ratio of the amount of the coloring agent (I) (that is, the amount of the coloring agent (I) in the thermosetting resin layer) to the total amount of all of the components other than the solvent is preferably 0.01% to 2% by mass, and is more preferably 0.03% to 1% by mass and the ratio of the amount of the filler (D) (that is,  
10   the amount of the filler (D) in the thermosetting resin layer) to the total amount of all of the components other than the solvent is 3% to 30% by mass, and the average particle diameter of the filler (D) is 2  $\mu\text{m}$  or less are exemplary examples.

However, these are examples of the resin layer forming composition (III-1).

[0311]

15   <<Method for Manufacturing Thermosetting Resin Layer Forming Composition>>

The thermosetting resin layer forming composition such as the resin layer forming composition (III-1) can be obtained by blending individual components for constituting the thermosetting resin layer forming composition.

The addition order during the blending of the respective components is not  
20   particularly limited, and two or more kinds of components may be added at the same time.

In a case in which the solvent is used, the solvent may be used by mixing the solvent with all of the blending components other than the solvent so as to dilute these blending components in advance or may be used by mixing the solvent with the blending  
25   components without diluting all of the blending components other than the solvent in

advance.

A method for mixing the respective components during blending is not particularly limited and may be appropriately selected from well-known methods such as a method in which the components are mixed together by rotating a stirring stick, a stirring blade, or the like; a method in which the components are mixed together using a mixer, and a method in which the components are mixed together by applying ultrasonic waves thereto.

The temperature and the time during the addition and mixing of the respective components are not particularly limited as long as the respective blending components do not deteriorate and may be appropriately adjusted, but the temperature is preferably 15°C to 30°C.

[0312]

#### o Energy Ray-Curable Resin Layer

Examples of the preferable energy ray-curable resin layer include those containing the energy ray-curable component (a) and the coloring agent.

In the energy ray-curable resin layer, the energy ray-curable component (a) is preferably uncured and is preferably pressure-sensitive adhesive and more preferably uncured and pressure-sensitive adhesive. Here, “energy ray” and “energy ray-curable” are as described above.

[0313]

The energy ray-curable resin layer may be a single layer (monolayer) or a plurality of layers of two or more layers, and, in a case in which the energy ray-curable resin layer is a plurality of layers, the respective layers in the plurality of layers may be identical to or different from one another, and the combination of the plurality of layers is not particularly limited.

[0314]

The thickness of the energy ray-curable resin layer is preferably 1 to 100  $\mu\text{m}$ , more preferably 5 to 75  $\mu\text{m}$ , and particularly preferably 5 to 50  $\mu\text{m}$ . When the thickness of the energy ray-curable resin layer is equal to or more than the lower limit value, it is possible to form a first protective film having a higher protection function. In addition, when the thickness of the energy ray-curable resin layer is equal to or less than the upper limit value, excessive thickness is suppressed.

Here, “the thickness of the energy ray-curable resin layer” refers to the thickness of the entire energy ray-curable resin layers, and, for example, the thickness of the energy ray-curable resin layer made up of a plurality of layers refers to the total thickness of all of the layers constituting the energy ray-curable resin layer.

[0315]

The curing condition when the energy ray-curable resin layer is attached to the bump-formed surface of the semiconductor wafer, and is cured so as to form the first protective film is not particularly limited as long as the first protective film is cured so as to sufficiently exert its function, and may be appropriately selected according to the kinds of the energy ray-curable resin layers.

For example, it is preferable that the illuminance of the energy ray during the curing of the energy ray-curable resin layer is 180 to 280  $\text{mW}/\text{cm}^2$ . In addition, it is preferable that the light intensity of the energy ray during the curing is 450 to 1,000  $\text{mJ}/\text{cm}^2$ .

[0316]

#### <<Energy Ray-Curable Resin Layer Forming Composition>>

The energy ray-curable resin layer can be formed using an energy ray-curable resin layer forming composition containing a constituent material thereof. For example,

the energy ray-curable resin layer can be formed at an intended portion by applying an energy ray-curable resin layer forming composition to a target surface on which the energy ray-curable resin layer is to be formed and drying the energy ray-curable resin layer forming composition as necessary.

5 [0317]

The energy ray-curable resin layer forming composition may be applied using a well-known method, and examples thereof include methods in which a variety of coaters such as an air knife coater, a blade coater, a bar coater, a gravure coater, a roll coater, a roll knife coater, a curtain coater, a die coater, a knife coater, a screen coater, a Mayer bar  
10 coater, and a kiss coater are used.

[0318]

The drying conditions of the energy ray-curable resin layer forming composition are not particularly limited; however, in a case in which the energy ray-curable resin layer forming composition contains a solvent described below, the energy ray-curable  
15 resin layer forming composition is preferably heated and dried. The energy ray-curable resin layer forming composition containing a solvent is preferably dried at 70°C to 130°C for 10 seconds to 5 minutes.

[0319]

<Resin Layer Forming Composition (IV-1)>

20 Examples of the energy ray-curable resin layer forming composition include an energy ray-curable resin layer forming composition (IV-1) containing the energy ray-curable component (a) and the coloring agent (in the present specification, in some cases, abbreviated as “the resin layer forming composition (IV-1)”) and the like.

[0320]

25 [Energy Ray-Curable Component (a)]

The energy ray-curable component (a) is a component that is cured by irradiation with energy rays and is a component for imparting a film-forming property, flexibility, and the like to the energy ray-curable resin layer.

Examples of the energy ray-curable component (a) include a polymer (a1) which  
 5 has an energy ray-curable group and a weight-average molecular weight of 80,000 to 2,000,000 and a compound (a2) which has an energy ray-curable group and a molecular weight of 100 to 80,000. The polymer (a1) may be a polymer at least a part of which is crosslinked using a crosslinking agent or a polymer which is not crosslinked.

[0321]

10 (Polymer Having Energy Ray-Curable Group and weight-average molecular weight of 80,000 to 2,000,000 (a1))

Examples of the polymer (a1) which has an energy ray-curable group and a weight-average molecular weight of 80,000 to 2,000,000 include an acrylic resin (a1-1) formed by polymerizing an acrylic polymer (a11) having a functional group capable of  
 15 reacting with groups in other compounds and an energy ray-curable compound (a12) having a group that reacts with the functional group and an energy ray-curable group such as an energy ray-curable double bond.

[0322]

Examples of the functional group capable of reacting with groups in other  
 20 compounds include a hydroxyl group, a carboxy group, an amino group, a substituted amino group (a group formed by substituting one or two hydrogen atoms in an amino group with a group other than a hydrogen atom), an epoxy group, and the like. Here, the functional group is preferably a group other than a carboxy group from the viewpoint of preventing the corrosion of circuits such as semiconductor wafers or semiconductor  
 25 chips.

Among these, the functional group is preferably a hydroxyl group.

[0323]

· Acrylic Polymer Having Functional Group (a11)

Examples of the acrylic polymer (a11) having the functional group include

5 acrylic polymers formed by copolymerizing an acrylic monomer having the above-described functional group and an acrylic monomer not having the above-described functional group, and the acrylic polymer may be an acrylic polymer formed by copolymerizing the above-described monomers and, furthermore, a monomer other than acrylic monomers (non-acrylic monomer).

10 In addition, the acrylic polymer (a11) may be a random copolymer or a block copolymer.

[0324]

Examples of the acrylic monomer having the functional group include hydroxyl group-containing monomers, carboxy group-containing monomers, amino

15 group-containing monomers, substituted amino group-containing monomers, epoxy group-containing monomers, and the like.

[0325]

Examples of the hydroxyl group-containing monomers include hydroxyalkyl (meth)acrylates such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 20 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, and 4-hydroxybutyl (meth)acrylate; non-(meth)acrylic unsaturated alcohols such as vinyl alcohol and allyl alcohol (unsaturated alcohols not having a (meth)acryloyl skeleton); and the like.

[0326]

25 Examples of the carboxy group-containing monomers include ethylenic

unsaturated monocarboxylic acids (monocarboxylic acids having an ethylenic unsaturated bond) such as (meth)acrylic acid and crotonic acid; ethylenic unsaturated dicarboxylic acids (dicarboxylic acids having an ethylenic unsaturated bond) such as fumaric acid, itaconic acid, maleic acid, and citraconic acid; anhydrides of the ethylenic unsaturated dicarboxylic acid; carboxyalkyl (meth)acrylates such as 2-carboxyethyl methacrylate; and the like.

[0327]

The functional group-containing acrylic monomer is preferably the hydroxyl group-containing monomer or the carboxy group-containing monomer and more preferably the hydroxyl group-containing monomer.

[0328]

The acrylic polymer (a11) may be constituted of only one kind or two or more kinds of the acrylic monomers having the functional group. In a case in which the acrylic polymer (a11) is constituted of two or more kinds of the acrylic monomers having the functional group, the combination and ratio thereof can be optionally selected.

[0329]

Examples of the acrylic monomer not having the functional group include alkyl (meth)acrylates in which an alkyl group constituting the alkyl ester has 1 to 18 carbon atoms and has a chain-like shape such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl

(meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (stearyl (meth)acrylate) and the like.

[0330]

5           In addition, examples of the acrylic monomer not having the functional group also include alkoxyalkyl group-containing (meth)acrylic acid esters such as methoxymethyl (meth)acrylate, methoxyethyl (meth)acrylate, ethoxymethyl (meth)acrylate, and ethoxyethyl (meth)acrylate; (meth)acrylic acid esters having an aromatic group which includes (meth)acrylic acid aryl ester such as phenyl (meth)acrylate or the like; non-crosslinkable (meth)acrylamides and derivatives thereof; (meth)acrylic acid esters having a non-crosslinkable tertiary amino group such as N,N-dimethyl aminoethyl (meth)acrylate and N,N-dimethyl aminopropyl (meth)acrylate; and the like.

[0331]

15           The acrylic polymer (a11) may be constituted of only one kind or two or more kinds of the acrylic monomers not having the functional group, and in a case in which the acrylic polymer is constituted of two or more kinds of the acrylic monomers not having the functional group, the combination and ratio thereof can be optionally selected.

[0332]

20           Examples of the non-acrylic monomer include olefins such as ethylene and norbornene; vinyl acetate; styrene; and the like.

          The acrylic polymer (a11) may be constituted of only one kind or two or more kinds of the non-acrylic monomers, and in a case in which the acrylic polymer is constituted of two or more kinds of the non-acrylic monomers, the combination and ratio thereof can be optionally selected.

25

[0333]

The ratio (amount/content) of the amount of a constituent unit derived from the acrylic monomer having the functional group to the entire mass of constituent units constituting the acrylic polymer (a11) is preferably 0.1% to 50% by mass, more preferably 1% to 40% by mass, and particularly preferably 3% to 30% by mass. When the ratio is in the above-described range, in the acrylic resin (a1-1) obtained by polymerization between the acrylic polymer (a11) and the energy ray-curable compound (a12), it becomes possible to easily adjust the degree of curing of the first protective film to a preferable range with the amount of the energy ray-curable group.

[0334]

The acrylic polymer (a11) may be constituted of only one kind or two or more kinds of the acrylic resins (a1-1), and in a case in which the acrylic polymer is constituted of two or more kinds of the acrylic resins, the combination and ratio thereof can be optionally selected.

[0335]

In the resin layer forming composition (IV-1), the amount of the acrylic resin (a1-1) is preferably 1 to 40, is more preferably 2 to 30, and is particularly preferably 3 to 20.

[0336]

· Energy Ray-Curable Compound (a12)

The energy ray-curable compound (a12) is preferably an energy ray-curable compound having one or more kinds of groups selected from the group consisting of an isocyanate group, an epoxy group, and a carboxy group as the group capable of reacting with the functional group in the acrylic polymer (a11) and more preferably an energy ray-curable compound having an isocyanate group as the above-described group. For

example, in a case in which the energy ray-curable compound (a12) has an isocyanate group as the above-described group, this isocyanate group easily reacts with a hydroxyl group in the acrylic polymer (a11) having the hydroxyl group as the functional group.

[0337]

5           The number of the energy ray-curable groups in one molecule of the energy ray-curable compound (a12) is preferably 1 to 5 and more preferably 1 or 2.

[0338]

Examples of the energy ray-curable compound (a12) include

2-methacryloyloxyethyl isocyanate, methaisopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate,  
10   methacryloyl isocyanate, allyl isocyanate, 1,1-(bisacryloyloxymethyl)ethyl isocyanate;  
acryloyl monoisocyanate compounds obtained by a reaction between a diisocyanate compound or a polyisocyanate compound and hydroxyethyl (meth)acrylate; and acryloyl monoisocyanate compounds obtained from a reaction among a diisocyanate compound or a polyisocyanate compound, a polyol compound, and hydroxyethyl (meth)acrylate; and  
15   the like.

Among these, the energy ray-curable compound (a12) is preferably 2-methacryloyloxyethyl isocyanate.

[0339]

The energy ray-curable compound (a12) may be constituted of only one kind or  
20   two or more kinds of the acrylic resins (a1-1), and in a case in which the energy ray-curable compound is constituted of two or more kinds of the acrylic resins, the combination and ratio thereof can be optionally selected.

[0340]

The ratio of the amount of an energy ray-curable group derived from the energy  
25   ray-curable compound (a12) to the amount of the functional group derived from the

acrylic polymer (a11) in the acrylic resin (a1-1) is preferably 20 to 120 mol%, more preferably 35 to 100 mol%, and particularly preferably 50 to 100 mol%. When the amount is in the above-described range, the adhesive force of the first protective film after curing becomes stronger. Meanwhile, in a case in which the energy ray-curable compound (a12) is a monofunctional compound (having one group in one molecule), the upper limit value of the amount becomes 100 mol%; however, in a case in which the energy ray-curable compound (a12) is a polyfunctional compound (having two or more groups in one molecule), the upper limit value of the amount exceeds 100 mol% in some cases.

10 [0341]

The weight-average molecular weight (Mw) of the polymer (a1) is preferably 100,000 to 2,000,000 and more preferably 300,000 to 1,500,000.

Here, “the weight-average molecular weight” is as described above.

[0342]

15 In a case in which at least a part of the polymer (a1) is crosslinked with a crosslinking agent, the polymer (a1) may be a polymer that is formed by polymerizing monomers which do not correspond to any of the monomers described above as the monomers constituting the acrylic polymer (a11) and have a group that reacts with the crosslinking agent and is crosslinked in the group that reacts with the crosslinking agent  
20 or may be a polymer crosslinked in a group which is derived from the energy ray-curable compound (a12) and reacts with the functional group.

[0343]

The resin layer forming composition (IV-1) and the energy ray-curable resin layer may contain only one kind or two or more kinds of the polymers (a1), and, in a case  
25 in which the resin layer forming composition and the energy ray-curable resin layer

contain two or more kinds of the polymers, the combination and ratio thereof can be optionally selected.

[0344]

(Compound (a2) Having Energy Ray-Curable Group and Molecular Weight of 100 to  
5 80,000)

Examples of the energy ray-curable group in the compound (a2) which has an energy ray-curable group and a molecular weight of 100 to 80,000 include groups having an energy ray-curable double bond, and preferable examples thereof include a (meth)acryloyl group, a vinyl group, and the like.

10 [0345]

The compound (a2) is not particularly limited as long as the compound satisfies the above-described conditions, and examples thereof include low-molecular-weight compounds having an energy ray-curable group, epoxy resins having an energy ray-curable group, phenolic resins having an energy ray-curable group, and the like.

15 [0346]

Among the compound (a2), examples of the low-molecular-weight compounds having an energy ray-curable group include polyfunctional monomers, oligomers, and the like, and acrylate compounds having a (meth)acryloyl group are preferable.

Examples of the acrylate compounds include difunctional (meth)acrylates such  
20 as 2-hydroxy-3-(meth)acryloyloxypropyl methacrylate, polyethylene glycol di(meth)acrylate, propoxylated ethoxylated bisphenol A di(meth)acrylate, 2,2-bis[4-((meth)acryloxypolyethoxy)phenyl]propane, ethoxylated bisphenol A di(meth)acrylate, 2,2-bis[4-((meth)acryloxydiethoxy)phenyl]propane, 9,9-bis[4-(2-(meth)acryloyloxyethoxy)phenyl]fluorene,  
25 2,2-bis[4-((meth)acryloxypolypropoxy)phenyl]propane, tricyclodecanedimethanol

di(meth)acrylate, 1,10-decanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, polytetramethylene glycol di(meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 2,2-bis[4-((meth)acryloylethoxy)phenyl]propane, neopentyl glycol di(meth)acrylate, ethoxylated polypropylene glycol di(meth)acrylate, and 2-hydroxy-1,3-di(meth)acryloxypropane; polyfunctional (meth)acrylates such as tris(2-(meth)acryloxyethyl) isocyanurate,  $\epsilon$ -caprolacton-modified tris-(2-(meth)acryloxyethyl) isocyanurate, ethoxylated glycerin tri(meth)acrylate, pentaerythritol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol poly(meth)acrylate, and dipentaerythritol hexa(meth)acrylate; polyfunctional (meth)acrylate oligomers such as urethane (meth)acrylate oligomers; and the like.

15 [0347]

Among the compound (a2), as the epoxy resins having an energy ray-curable group, the phenolic resins having an energy ray-curable group, for example, the epoxy resins described in Paragraph 0043 and the like of “Japanese Unexamined Patent Application, First Publication No. 2013-194102” can be used. These resins also correspond to resins constituting a thermosetting component described below; however, in the present invention, the resins will be handled as the compound (a2).

[0348]

The weight-average molecular weight of the compound (a2) is preferably 100 to 30,000 and more preferably 300 to 10,000.

25 [0349]

The resin layer forming composition (IV-1) and the energy ray-curable resin layer may contain only one kind or two or more kinds of the compounds (a2), and, in a case in which the resin layer forming composition and the energy ray-curable resin layer contain two or more kinds of the compounds, the combination and ratio thereof can be  
5 optionally selected.

[0350]

[Polymer (b) Not Having Energy Ray-Curable Group]

In the case of containing the compound (a2) as the energy ray-curable component (a), the resin layer forming composition (IV-1) and the energy ray-curable  
10 resin layer preferably further contain a polymer (b) not having any energy ray-curable groups.

The polymer (b) may be a polymer at least a part of which is crosslinked with a crosslinking agent or a polymer which is not crosslinked.

[0351]

15 Examples of the polymer (b) not having any energy ray-curable group include acrylic polymers, phenoxy resins, urethane resins, polyesters, rubber-based resins, acrylic urethane resins, and the like.

Among these, the polymer (b) is preferably an acrylic polymer (hereinafter, in some cases, abbreviated as “the acrylic polymer (b-1)”).

20 [0352]

The acrylic polymer (b-1) may be a well-known acrylic polymer, and, for example, the acrylic polymer may be a homopolymer of one kind of acrylic monomer, a copolymer of two or more kinds of acrylic monomers, or a copolymer of one or more kinds of acrylic monomers and one or more kinds of monomers other than acrylic  
25 monomers (non-acrylic monomers).

[0353]

Examples of the acrylic monomer constituting the acrylic polymer (b-1) include alkyl (meth)acrylates, (meth)acrylic acid ester having a cyclic skeleton, glycidyl group-containing (meth)acrylic acid ester, hydroxyl group-containing (meth)acrylic acid esters, and substituted amino group-containing (meth)acrylic acid esters. Here, “substituted amino group” is as described above.

[0354]

Examples of the alkyl (meth)acrylates include alkyl (meth)acrylates in which an alkyl group constituting the alkyl ester has 1 to 18 carbon atoms and has a chain-like shape such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (stearyl (meth)acrylate) and the like.

[0355]

Examples of the (meth)acrylic acid esters having a cyclic skeleton include cycloalkyl (meth)acrylates such as isobornyl (meth)acrylate and dicyclopentanyl (meth)acrylate; aralkyl (meth)acrylic acid esters such as benzyl (meth)acrylate; cycloalkenyl (meth)acrylic acid esters such as dicyclopentenyl (meth)acrylate; and cycloalkenyloxy alkyl (meth)acrylate such as dicyclopentenylloxyethyl (meth)acrylate; and the like.

[0356]

Examples of the glycidyl group-containing (meth)acrylic acid esters include glycidyl (meth)acrylate and the like.

Examples of the hydroxyl group-containing (meth)acrylic acid esters include

5 hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, and the like.

Examples of the substituted amino group-containing (meth)acrylic acid esters include N-methylaminoethyl (meth)acrylate and the like.

10 [0357]

Examples of the non-acrylic monomer constituting the acrylic polymer (b-1) include olefins such as ethylene and norbornene; vinyl acetate; styrene; and the like.

[0358]

Examples of the polymer (b) at least a part of which is crosslinked with a  
15 crosslinking agent and which does not have the energy ray-curable group include polymers in which a reactive functional group in the polymer (b) reacts with a crosslinking agent.

The reactive functional group may be appropriately selected depending on the type and the like of the crosslinking agent and is not particularly limited. For example,  
20 in a case in which the crosslinking agent is a polyisocyanate compound, examples of the reactive functional group include a hydroxyl group, a carboxy group, an amino group, and the like, and, among these, the hydroxyl group that is highly reactive with isocyanate groups is preferable. In addition, in a case in which the crosslinking agent is an epoxy-based compound, examples of the reactive functional group include a carboxy  
25 group, an amino group, an amide group, and the like, and, among these, the carboxy

group that is highly reactive with epoxy groups is preferable. Here, the reactive functional group is preferably a group other than a carboxy group from the viewpoint of preventing the corrosion of circuits such as semiconductor wafers or semiconductor chips.

5 [0359]

Examples of the polymer (b), which has the reactive functional group but does not have any energy ray-curable groups, include polymers obtained by polymerizing monomers having at least the reactive functional group. In the case of the acrylic polymer (b-1), as any one or both of the acrylic monomer and the non-acrylic monomer  
10 that have been exemplified as the monomers constituting the acrylic polymer, monomers having the reactive functional group may be used. For example, examples of the polymer (b) having a hydroxyl group as the reactive functional group include polymers obtained by polymerizing hydroxyl group-containing (meth)acrylic acid ester and also include polymers obtained by polymerizing monomers formed by substituting one or  
15 more hydrogen atoms in the previously exemplified acrylic monomer or non-acrylic monomer with the reactive functional group.

[0360]

In the polymer (b) having the reactive functional group, the ratio (amount) of the amount of a constituent unit derived from a monomer having the reactive functional  
20 group is preferably 1 to 20% by mass and more preferably 2 to 10% by mass of the entire mass of constituent units constituting the polymer. When the ratio is in the above-described range, in the polymer (b), the degree of crosslinking is in a more preferable range.

[0361]

25 The weight-average molecular weight ( $M_w$ ) of the polymer (b) not having any

energy ray-curable groups is preferably 10,000 to 2,000,000 and more preferably 100,000 to 1,500,000 since the film-forming property of the resin layer forming composition (IV-1) becomes more favorable. Here, “the weight-average molecular weight” is as described above.

5 [0362]

The resin layer forming composition (IV-1) and the energy ray-curable resin layer may contain only one kind or two or more kinds of the polymers (b) not having any energy ray-curable groups, and, in a case in which the resin layer forming composition and the energy ray-curable resin layer contain two or more kinds of the polymers not  
10 having any energy ray-curable groups, the combination and ratio thereof can be optionally selected.

[0363]

Examples of the resin layer forming composition (IV-1) include compositions containing any one or both of the polymer (a1) and the compound (a2). In the case of  
15 containing the compound (a2), the resin layer forming composition (IV-1) preferably further contains a polymer (b) not having an energy ray-curable group, and in this case, the polymer (a1) is further preferably contained. In addition, the resin layer forming composition (IV-1) may contain the polymer (a1) and the polymer (b) not having any energy ray-curable groups without containing the compound (a2).

20 [0364]

In a case where the resin layer forming composition (IV-1) contains the polymer (a1), the compound (a2), and the polymer (b) not having any energy ray-curable groups, in the resin layer forming composition (IV-1), the amount of the compound (a2) is preferably 10 to 400 parts by mass, and more preferably 30 to 350 parts by mass of the  
25 total amount (100 parts by mass) of the polymer (a1) and the polymer (b) not having any

energy ray-curable groups.

[0365]

In the resin layer forming composition (IV-1), the ratio of the total amount of the energy ray-curable component (a) and the polymer (b) not having any energy ray-curable groups (that is, the total amount of the energy ray-curable component (a) and the polymer (b) not having any energy ray-curable groups in the energy ray-curable resin layer) to the total amount of the components other than the solvent is preferably 5% to 90% by mass, more preferably 10% to 80% by mass, and particularly preferably 20% to 70% by mass. When the amount of the energy ray-curable component is in the above-described range, the energy ray-curing property of the energy ray-curable resin layer becomes more favorable.

[0366]

[Coloring Agent]

The coloring agent in the resin layer forming composition (IV-1) is a component for giving appropriate light transmittance to the energy ray-curable resin layer and the first protective film.

Examples of the coloring agent in the resin layer forming composition (IV-1) include the same one as that of the coloring agent (I) in the resin layer forming composition (III-1).

[0367]

The resin layer forming composition (IV-1) and the energy ray-curable resin layer may contain only one kind or two or more kinds of the coloring agents, and in a case in which the resin layer forming composition and the energy ray-curable resin layer contain two or more kinds of the coloring agents, the combination and ratio thereof can be optionally selected.

[0368]

The amount of the coloring agent of the resin layer forming composition (IV-1) is not particularly limited and may be appropriately adjusted such that the visible light transmittance of the energy ray-curable resin layer and the infrared transmittance become  
5 a desired value. For example, the amount of the coloring agent may be appropriately adjusted in accordance with the kinds of the coloring agents or the combination of these coloring agents in a case of using two or more kinds of the coloring agents in combination.

Generally, in the resin layer forming composition (IV-1), the ratio of the amount  
10 of the coloring agent with respect to the total amount of all of the components other than the solvent (that is, the amount of the coloring agent of the energy ray-curable resin layer) is preferably 0.01% to 10% by mass.

[0369]

The resin layer forming composition (IV-1) may also contain, in addition to the  
15 energy ray-curable component (a) and the coloring agent, one or more kinds of elements selected from the group consisting of a thermosetting component, a photopolymerization initiator, a filler, a coupling agent, a crosslinking agent, and a versatile additive depending on the purpose. For example, when the resin layer forming composition (IV-1) containing the energy ray-curable component and a thermosetting component is  
20 used, the adhesive force of an energy ray-curable resin layer to be formed to adherends improves by heating, and the strength of the first protective film formed of this energy ray-curable resin layer also improves.

[0370]

As the thermosetting component, the photopolymerization initiator, the filler, the  
25 coupling agent, the crosslinking agent, and the versatile additive in the resin layer

forming composition (IV-1), it is possible to exemplify those which are the same as the thermosetting component (B), the photopolymerization initiator (H), the filler (D), the coupling agent (E), the crosslinking agent (F), and the versatile additive (J) in the resin layer forming composition (III-1).

5 [0371]

In the resin layer forming composition (IV-1), one kind of each of the thermosetting component, the photopolymerization initiator, the filler, the coupling agent, the crosslinking agent, and the versatile additive may be used singly or two or more kinds thereof may be jointly used, and in a case in which two or more kinds thereof are used,  
10 the combination and ratio thereof can be optionally selected.

The amounts of the thermosetting component, the photopolymerization initiator, the filler, the coupling agent, the crosslinking agent, and the versatile additive in the resin layer forming composition (IV-1) may be appropriately adjusted depending on the purpose and are not particularly limited.

15 [0372]

From the view point that the handling property of the resin layer forming composition (IV-1) improves by dilution, it is preferable that the resin layer forming composition further contains a solvent.

Examples of the solvent contained in the resin layer forming composition (IV-1)  
20 include the same solvent as that in the resin layer forming composition (III-1).

The resin layer forming composition (IV-1) may contain only one kind or two or more kinds of the solvents.

[0373]

<<Method of Manufacturing of Energy Ray-Curable Resin Layer Forming  
25 Composition>>

The energy ray-curable resin layer forming composition such as the resin layer forming composition (IV-1) can be obtained by blending individual components for constituting the energy ray-curable resin layer forming composition.

The addition order during the blending of the respective components is not particularly limited, and two or more kinds of components may be added at the same time.

In a case in which the solvent is used, the solvent may be used by mixing the solvent with all of the blending components other than the solvent so as to dilute these blending components in advance or may be used by mixing the solvent with the blending components without diluting all of the blending components other than the solvent in advance.

A method for mixing the respective components during blending is not particularly limited and may be appropriately selected from well-known methods such as a method in which the components are mixed together by rotating a stirring stick, a stirring blade, or the like; a method in which the components are mixed together using a mixer, and a method in which the components are mixed together by applying ultrasonic waves thereto.

The temperature and the time during the addition and mixing of the respective components are not particularly limited as long as the respective blending components do not deteriorate and may be appropriately adjusted, but the temperature is preferably 15°C to 30°C.

[0374]

#### ◇ Method for Manufacturing Sheet for forming a first protective film

The sheet for forming a first protective film can be manufactured by sequentially stacking the respective layers described above so as to obtain the corresponding

positional relationship. The methods for forming the respective layers are as described above.

For example, in the manufacturing of the first supporting sheet, in a case in which the first pressure-sensitive adhesive layer or the first interlayer is stacked on the first base material, the first pressure-sensitive adhesive layer or the first interlayer can be stacked by applying the first pressure-sensitive adhesive composition or the first interlayer forming composition described above onto the first base material and drying the composition or irradiating the composition with energy rays as necessary.

[0375]

Meanwhile, for example, in a case in which the curable resin layer is further stacked on the first pressure-sensitive adhesive layer that has been stacked on the first base material, the thermosetting resin film can be directly formed by applying the thermosetting resin layer forming composition or the energy ray-curable resin layer forming composition to the first pressure-sensitive adhesive layer. Similarly, in a case in which the first pressure-sensitive adhesive layer is further stacked on the first interlayer that has been stacked on the first base material, the first pressure-sensitive adhesive layer can be directly formed by applying the first pressure-sensitive adhesive composition onto the first interlayer. As described above, in a case in which a stacking structure of two continuous layers is formed using any compositions, it is possible to newly form a layer by further applying the composition onto a layer formed of the above-described composition. Here, the stacking structure of two continuous layers is preferably formed by forming, between these two layers, the layer which is stacked from the back on a separate peeling film in advance using the above-described composition and attaching the exposed surface opposite to the surface of the already-formed layer in contact with the peeling film to the exposed surface of the other layer that has been

formed. At this time, the above-described composition is preferably applied onto a peeling-treated surface of the peeling film. The peeling film may be removed as necessary after the formation of the stacking structure.

[0376]

5           For example, in a case in which a sheet for forming a first protective film (the sheet for forming a first protective film in which the first supporting sheet is a stacked substance of the first base material and the first pressure-sensitive adhesive layer) formed by stacking the first pressure-sensitive adhesive layer on the first base material and stacking the curable resin layer on the first pressure-sensitive adhesive layer is  
10   manufactured, the sheet for forming a first protective film can be obtained by applying the first pressure-sensitive adhesive composition onto the first base material and drying the first pressure-sensitive adhesive composition as necessary so as to stack the first pressure-sensitive adhesive layer on the first base material, separately, applying the thermosetting resin layer forming composition or the energy ray-curable resin layer  
15   forming composition onto the peeling film and drying the energy ray-curable resin layer forming composition as necessary so as to form the curable resin layer on the peeling film, and attaching the exposed surface of the curable resin layer to the exposed surface of the first pressure-sensitive adhesive layer that has been stacked on the first base material so as to stack the curable resin layer on the first pressure-sensitive adhesive  
20   layer.

          In addition, for example, in a case in which a first supporting sheet formed by stacking the first interlayer on the first base material and stacking the pressure-sensitive adhesive layer on the first interlayer is manufactured, the first supporting sheet can be obtained by applying the first interlayer forming composition onto the first base material  
25   and drying the first interlayer forming composition or irradiating the first interlayer

forming composition with energy rays as necessary so as to stack the first interlayer on the first base material, separately, applying the first pressure-sensitive adhesive composition onto the peeling film and drying the first pressure-sensitive adhesive composition as necessary so as to form the first pressure-sensitive adhesive layer on the peeling film, and attaching the exposed surface of the first pressure-sensitive adhesive layer to the exposed surface of the first interlayer that has been stacked on the first base material so as to stack the first pressure-sensitive adhesive layer on the first interlayer.

In this case, the sheet for forming a first protective film can be obtained by, for example, separately, further applying the thermosetting resin layer forming composition or the

energy ray-curable resin layer forming composition onto the peeling film and drying the curable resin layer forming composition as necessary so as to form the curable resin layer on the peeling film and attaching the exposed surface of the curable resin layer to the exposed surface of the first pressure-sensitive adhesive layer that has been stacked on the first interlayer so as to stack the curable resin layer on the first pressure-sensitive adhesive layer.

[0377]

Meanwhile, in a case in which the first pressure-sensitive adhesive layer or the first interlayer is stacked on the first base material, as described above, the first pressure-sensitive adhesive layer or the first interlayer may be stacked on the first base material by, instead of applying the first pressure-sensitive adhesive composition or the first interlayer forming composition onto the first base material, applying the first pressure-sensitive adhesive composition or the first interlayer forming composition onto the peeling film and drying the composition or irradiating the composition with energy rays as necessary so as to form the first pressure-sensitive adhesive layer or the first interlayer on the peeling film and attaching the exposed surface of this layer to one

surface of the first base material so as to stack the first pressure-sensitive adhesive layer or the first interlayer on the first base material.

In any of the methods, the peeling film may be removed at an arbitrary timing after the formation of the intended stacking structure.

5 [0378]

As described above, all of the layers other than the first base material which constitute the sheet for forming a first protective film can be stacked using a method in which the layers are formed on the peeling film in advance and attached on a surface of an intended layer, and thus the sheet for forming a first protective film may be  
10 manufactured by appropriately selecting layers for which the above-described steps are employed as necessary.

[0379]

Meanwhile, the sheet for forming a first protective film is, generally, stored in a state in which the peeling film is attached to the surface of the outermost layer on the  
15 opposite side to the first supporting sheet (for example, the curable resin layer).

Therefore, the sheet for forming a first protective film can also be obtained by applying a composition for forming a layer constituting the outermost layer such as thermosetting resin layer forming composition or the energy ray-curable resin layer forming composition onto the peeling film (preferably the peeling-treated surface thereof) and  
20 drying the energy ray-curable resin layer forming composition as necessary so as to form the layer constituting the outermost layer on the peeling film, stacking the remaining layers on the exposed surface on the opposite side to the surface of the layer in contact with the peeling film using any of the above-described methods, and leaving the layers in the attached state without removing the peeling film.

25 [Examples]

[0380]

Hereinafter, the present invention will be more specifically described using specific examples. However, the present invention is not limited to examples described below.

5 [0381]

The components used for manufacturing the thermosetting resin layer forming composition are indicated below.

· Polymer Component

Polymer component (A) -1: A polyvinyl butyral resin (“BL-1” manufactured by  
10 Sekisui Chemical Company, Limited, and glass transition temperature of 66°C)

· Epoxy resin

Epoxy resin (B1)-1: A bisphenol A type epoxy resin (“jER828” manufactured by  
Mitsubishi Chemical Corporation, and epoxy equivalent of 184 to 194 g/eq)

Epoxy resin (B1)-2: A polyfunctional aromatic type epoxy resin (“EPPN-502H”  
15 manufactured by Nippon Kayaku Co., Ltd., and epoxy equivalent of 158 to 178 g/eq)

Epoxy resin (B1)-3: A dicyclopentadiene type epoxy resin (“EPICLON  
HP-7200” manufactured by DIC Corporation, and epoxy equivalent of 254 to 264 g/eq)

· Thermal Curing Agent

Thermal curing agent (B2)-1: A straight novolac type phenolic resin  
20 (“BRG-556” manufactured by Showa Denko KK)

· Curing Accelerator

Curing accelerator (C)-1: 2-phenyl-4,5-dihydroxymethylimidazole (“Curezol  
2PHZ” manufactured by Shikoku Chemicals Corporation)

· Filler

Filler (D)-1: Silica filler ("SC 2050 MA" manufactured by Admatechs., a filler surface-modified with an epoxy-based compound, average particle diameter of 0.5  $\mu\text{m}$ )

Filler (D)-2: Silica filler ("UF310" manufactured by Tokuyama Corporation, average particle diameter of 3 $\mu\text{m}$ )

5 Filler (D)-3: Silica filler ("SV-10" manufactured by TATSUMORI LTD., average particle diameter of 8  $\mu\text{m}$ )

· Coloring Agent

Coloring Agent (I)-1: Carbon black ("MA650" manufactured by Mitsubishi Chemical Corporation, average particle diameter of 28 nm)

10 [0382]

[Example 1]

<Manufacturing of thermosetting resin film and Sheet for forming a first protective film>  
(Manufacturing of Thermosetting Resin Layer Forming Composition)

A polymer component (A)-1, an epoxy resin (B1)-1, an epoxy resin (B1)-2, an  
15 epoxy resin (B1)-3, a thermal curing agent (B2)-1, a curing accelerator (C)-1, a filler (D)-1 and a coloring agent (I)-1 were dissolved and dispersed in methyl ethyl ketone such that the amount of these components is the value indicated in the following Table 1, and stirred at 23°C so as to obtain a resin layer forming composition (III-1) having the solid content concentration of 55% by mass as a thermosetting resin layer forming  
20 composition.

Note that, the description "-" in the column of contained components in the following Table 1 means that the thermosetting resin layer forming composition does not contain that component. What has been described above is also true for Table 2.

[0383]

(Manufacturing of thermosetting resin film and Sheet for forming a first protective film)

A first peeling film ("SP-PET382150" manufactured by Lintec Corporation., thickness of 38  $\mu\text{m}$ ), and a second peeling film ("SP-PET381031" manufactured by Lintec Corporation., thickness of 38  $\mu\text{m}$ ) which were obtained by peeling one surface of polyethylene terephthalate film by silicone treatment were prepared.

[0384]

The thermosetting resin layer forming composition obtained above was applied onto the peeled surface of the first peeling film, and dried at 100°C for two minutes so as to form a thermosetting resin film (thermosetting resin layer) having a thickness of 23  $\mu\text{m}$ . Then, the peeled surface of the second peeling film was attached to an exposed surface (a surface on the side opposite to the side on which the first peeling film is provided) of the thermosetting resin film so as to obtain a sheet for forming a first protective film by stacking the first peeling film, the thermosetting resin film, and the second peeling film in this order in the thickness direction. A plurality of such sheets for forming first protective film were prepared and the following evaluations were made.

[0385]

#### <Manufacturing of Silicon Wafer with Thermosetting Resin Film>

As a semiconductor wafer, a silicon wafer (# 200 polished, a diameter of 200 mm, a thickness of 350  $\mu\text{m}$ ) having bumps having a shape similar to that shown in FIG. 1 and a height of 250  $\mu\text{m}$  at a pitch of 500  $\mu\text{m}$  was prepared on a circuit surface of an 8-inch silicon wafer.

Then, the second peeling film was removed from the sheet for forming a first protective film obtained above, while heating the thermosetting resin film at 70°C, a newly generated exposed surface (a surface on the side opposite to the side on which the

first peeling film is provided) of the thermosetting resin film was attached to the bump-formed surface of the silicon wafer, and then the curable resin film was brought into close contact with the circuit surface and the surface of the bump.

Then, the first peeling film was removed from the thermosetting resin film so as to obtain a silicon wafer with thermosetting resin film.

[0386]

#### <Evaluation of Thermosetting Resin Film>

##### (Visible Light Transmittance and Infrared Transmittance)

The first peeling film and the second peeling film were removed from the sheet for forming a first protective film obtained from above so as to obtain a thermosetting resin film.

Then, regarding this thermosetting resin film, the light transmittance was measured using a spectrophotometer ("UV-VIS-NIR SPECTROPHOTOMETER UV-3600" manufactured by SHIMADZU) and the transmittance (%) of light (visible light) at a wavelength of 550 nm and the transmittance (%) of light (infrared) at a wavelength of 1600 nm were extracted. At this time, the transmittance (%) of the light was measured without using the built-in integrating sphere by using a large sample chamber MPC-3100 attached to the spectrophotometer. The results are indicated in Table 1.

[0387]

##### (Calculation of Color Difference ( $\Delta E$ ) Between Thermosetting Resin Film and Silicon Wafer)

By using the spectrophotometer ("UV-VIS-NIR SPECTROPHOTOMETER UV-3600" manufactured by SHIMADZU), the light transmittance was measured for the thermosetting resin film obtained above and the silicon wafer. Note that, the light

transmittance was measured from the bump-formed surface side in the silicon wafer. At this time, the light transmittance was measured without using the built-in integrating sphere by using a large sample chamber MPC-3100 attached to the spectrophotometer. In addition, from the measurement results, based on JIS Z8781-4:2013,  $L^*$ ,  $a^*$ , and  $b^*$  were calculated for each of the thermosetting resin film and the silicon wafer. The calculation results for the thermosetting resin film are indicated in Table 1. Note that,  $L^*$  of the silicon wafer was 46,  $a^*$  was 1.6, and  $b^*$  was -2.9.

Further, from these calculated values, a color difference ( $\Delta E$ ) was calculated according to Formula (f-1). The results are indicated in Table 1.

10 [0388]

(Concealing Property of Circuit Surface)

The silicon wafer with the thermosetting resin film obtained above was visually observed from the side of the thermosetting resin film and the concealing property of the circuit surface of the silicon wafer by the thermosetting resin film was evaluated

15 according to the following criteria. The results are indicated in Table 1.

A: Circuit surface cannot be visually recognized, and concealing property is extremely high.

B: Although circuit surface can be visually recognized very slightly, wiring pattern cannot be recognized and concealing property is extremely high.

20 C: Circuit surface relatively easily recognized, wiring pattern can be almost recognized, and concealing property is low.

D: Circuit surface can be clearly recognized, wiring pattern can be perfectly recognized, and concealing property is not recognized.

[0389]

25 (Observability of Circuit Surface)

By using an infrared microscope (“BX-IR” manufactured by Olympus Corporation), the silicon wafer with the thermosetting resin film obtained above was observed from the side of the thermosetting resin film and the observability of the circuit surface of the silicon wafer by the thermosetting resin film was evaluated according to the following criteria. The results are indicated in Table 1.

A: Circuit surface can be clearly observed and observability is excellent.

B: Circuit surface can be easily observed and observability is high.

C: Circuit surface can be very slightly observed and observability is low.

D: Circuit surface cannot be observed and observability is not recognized.

[0390]

#### <Evaluation of Cured Material of Thermosetting Resin Film>

(Visible Light Transmittance and Infrared Transmittance)

The second peeling film was removed from the sheet for forming a first protective film obtained above, and the remaining laminate obtained by stacking the first peeling film and the thermosetting resin film was placed in an oven, and heated at 130°C for two hours under an atmosphere to thermally cure the thermosetting resin film so as to form a cured material (that is, a first protective film).

Subsequently, the first peeling film was removed from the cured laminate so as to obtain the cured material.

Then, regarding the cured material, the light transmittance was measured in the same method as that used in a case of the thermosetting resin film, and the transmittance (%) of light (visible light) at a wavelength of 550 nm and the transmittance (%) of light (infrared) at a wavelength of 1600 nm were extracted. The results are indicated in Table 1.

[0391]

(Calculation of Color Difference ( $\Delta E$ ) Between Cured material of Thermosetting Resin Film and Silicon Wafer)

Regarding the cured material, in the same method as that used in a case of the above-described thermosetting resin film,  $L^*$ ,  $a^*$ , and  $b^*$  were calculated. The results are indicated in Table 1.

Further, the color difference ( $\Delta E$ ) was calculated from the calculated value and the calculated values of  $L^*$ ,  $a^*$ , and  $b^*$  of the silicon wafer according to Formula (f-2). The results are indicated in Table 1.

[0392]

#### 10 (Concealing Property of Circuit Surface)

The silicon wafer with thermosetting resin film obtained above was placed in an oven, and heated at 130°C for two hours under an atmosphere to thermally cure the thermosetting resin film so as to form a first protective film.

Then, the obtained silicon wafer with first protective film was visually observed from the first protective film side, and then the concealing property of the circuit surface of the silicon wafer by the first protective film was evaluated in the same method as that used in a case of the silicon wafer with thermosetting resin film. The results are indicated in Table 1.

[0393]

#### 20 (Observability of Circuit Surface)

By using an infrared microscope (“BX-IR” manufactured by Olympus Corporation), the silicon wafer with first protective film obtained above was observed from the first protective film side, and then the observability of the circuit surface of the silicon wafer of the first protective film was evaluated in the same method as that in the case of the silicon wafer with thermosetting resin film. The results are indicated in

Table 1.

[0394]

<Manufacturing Thermosetting Resin Film, Manufacturing Sheet for forming a first  
protective film, Manufacturing Silicon Wafer with Thermosetting Resin Film, Evaluation  
5 of Thermosetting Resin Film, and Evaluation of Cured material of Thermosetting Resin  
Film>

[Examples 2 to 6 and Comparative Examples 1 and 5]

(Manufacturing of Thermosetting Resin Layer Forming Composition)

The thermosetting resin film, the sheet for forming a first protective film, and  
10 the silicon wafer with thermosetting resin film were manufactured and the thermosetting  
resin film and the cured material thereof were evaluated in the same manner as in  
Example 1 except that at the time of manufacturing the thermosetting resin layer forming  
composition, one or both of the kind and the amount of each component were set as  
indicated in Table 1 or 2. The results are indicated in Table 1 or 2.

[0395]

[Table 1]

|                                                                                             |                                             |               | Example 1     | Example 2 | Example 3 | Example 4 | Example 5 | Example 6 |    |
|---------------------------------------------------------------------------------------------|---------------------------------------------|---------------|---------------|-----------|-----------|-----------|-----------|-----------|----|
| Contained component (amount(part by mass)) of thermosetting resin layer forming composition | Polymer component                           | (A)-1         | 830           | 830       | 830       | 830       | 830       | 830       |    |
|                                                                                             | Epoxy resin                                 | (B1)-1        | 690           | 690       | 690       | 690       | 690       | 690       |    |
|                                                                                             |                                             | (B1)-2        | 490           | 490       | 490       | 490       | 490       | 490       |    |
|                                                                                             |                                             | (B1)-3        | 770           | 770       | 770       | 770       | 770       | 770       |    |
|                                                                                             | Thermal curing agent                        | (B2)-1        | 970           | 970       | 970       | 970       | 970       | 970       |    |
|                                                                                             | Curing accelerator                          | (C)-1         | 10            | 10        | 10        | 10        | 10        | 10        |    |
|                                                                                             | Filler                                      | (D)-1         | 900           | 900       | 900       | 900       | 450       | 200       |    |
|                                                                                             |                                             | (D)-2         | -             | -         | -         | -         | -         | -         |    |
| (D)-3                                                                                       |                                             | -             | -             | -         | -         | -         | -         |           |    |
| Coloring agent                                                                              | (I)-1                                       | 5             | 10            | 15        | 20        | 8         | 8         |           |    |
| Amount (% by mass) of filler of thermosetting resin layer                                   |                                             |               | 19.3          | 19.3      | 19.3      | 19.2      | 10.7      | 5.0       |    |
| Amount (% by mass) of coloring agent of thermosetting resin layer                           |                                             |               | 0.1           | 0.2       | 0.3       | 0.4       | 0.2       | 0.2       |    |
| Evaluation of thermosetting resin layer and cured material thereof                          | Transmittance (%) of visible light (550 nm) | Before curing | 15            | 11        | 8         | 7         | 20        | 35        |    |
|                                                                                             |                                             | After curing  | 15            | 11        | 8         | 7         | 20        | 35        |    |
|                                                                                             | Concealing property of circuit surface      | Before curing | A             | A         | A         | A         | A         | B         |    |
|                                                                                             |                                             | After curing  | A             | A         | A         | A         | A         | B         |    |
|                                                                                             | Transmittance (%) of infrared (1600 nm)     | Before curing | 65            | 53        | 46        | 41        | 80        | 95        |    |
|                                                                                             |                                             | After curing  | 65            | 53        | 46        | 41        | 80        | 95        |    |
|                                                                                             | Observability of circuit surface            | Before curing | A             | A         | B         | B         | A         | A         |    |
|                                                                                             |                                             | After curing  | A             | A         | B         | B         | A         | A         |    |
|                                                                                             | L*, a*, and b* color system                 | L*            | Before curing | 25        | 16        | 9         | 5         | 30        | 34 |
|                                                                                             |                                             |               | After curing  | 25        | 16        | 9         | 5         | 30        | 34 |
|                                                                                             |                                             | a*            | Before curing | 12        | 12        | 12        | 12        | 12        | 12 |
|                                                                                             |                                             |               | After curing  | 12        | 12        | 12        | 12        | 12        | 12 |
|                                                                                             |                                             | b*            | Before curing | 20        | 20        | 20        | 20        | 20        | 20 |
|                                                                                             |                                             |               | After curing  | 20        | 20        | 20        | 20        | 20        | 20 |
|                                                                                             | Color difference (ΔE)                       | Before curing | 32.77         | 39.15     | 44.74     | 48.10     | 29.81     | 27.87     |    |
|                                                                                             |                                             | After curing  | 32.77         | 39.15     | 44.74     | 48.10     | 29.81     | 27.87     |    |

[0396]

[Table 2]

|                                                                                             |                                             |               | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 | Comparative Example 4 | Comparative Example 5 |       |
|---------------------------------------------------------------------------------------------|---------------------------------------------|---------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-------|
| Contained component (amount(part by mass)) of thermosetting resin layer forming composition | Polymer component                           | (A)-1         | 830                   | 830                   | 830                   | 830                   | 830                   |       |
|                                                                                             | Epoxy resin                                 | (B1)-1        | 690                   | 690                   | 690                   | 690                   | 690                   |       |
|                                                                                             |                                             | (B1)-2        | 490                   | 490                   | 490                   | 490                   | 490                   |       |
|                                                                                             |                                             | (B1)-3        | 770                   | 770                   | 770                   | 770                   | 770                   |       |
|                                                                                             | Thermal curing agent                        | (B2)-1        | 970                   | 970                   | 970                   | 970                   | 970                   |       |
|                                                                                             | Curing accelerator                          | (C)-1         | 10                    | 10                    | 10                    | 10                    | 10                    |       |
|                                                                                             | Filler                                      | (D)-1         | 900                   | 900                   | -                     | -                     | 100                   |       |
|                                                                                             |                                             | (D)-2         | -                     | -                     | 900                   | -                     | -                     |       |
|                                                                                             |                                             | (D)-3         | -                     | -                     | -                     | 900                   | -                     |       |
| Coloring agent                                                                              | (I)-1                                       | 50            | 0                     | 10                    | 10                    | 8                     |                       |       |
| Amount (% by mass) of filler of thermosetting resin layer                                   |                                             |               | 19.1                  | 19.3                  | 19.3                  | 19.3                  | 2.6                   |       |
| Amount (% by mass) of coloring agent of thermosetting resin layer                           |                                             |               | 1.1                   | 0                     | 0.2                   | 0.2                   | 0.2                   |       |
| Evaluation of thermosetting resin layer and cured material thereof                          | Transmittance (%) of visible light (550 nm) | Before curing | 1                     | 50                    | 15                    | 10                    | 48                    |       |
|                                                                                             |                                             | After curing  | 1                     | 50                    | 15                    | 10                    | 48                    |       |
|                                                                                             | Concealing property of circuit surface      | Before curing | A                     | D                     | A                     | A                     | C                     |       |
|                                                                                             |                                             | After curing  | A                     | D                     | A                     | A                     | C                     |       |
|                                                                                             | Transmittance (%) of infrared (1600 nm)     | Before curing | 13                    | 74                    | 30                    | 26                    | 96                    |       |
|                                                                                             |                                             | After curing  | 13                    | 74                    | 30                    | 26                    | 96                    |       |
|                                                                                             | Observability of circuit surface            | Before curing | D                     | A                     | C                     | C                     | A                     |       |
|                                                                                             |                                             | After curing  | D                     | A                     | C                     | C                     | A                     |       |
|                                                                                             | L*, a*, and b* color system                 | L*            | Before curing         | 1                     | 43                    | 5                     | 4                     | 44    |
|                                                                                             |                                             |               | After curing          | 1                     | 43                    | 5                     | 4                     | 44    |
|                                                                                             |                                             | a*            | Before curing         | 12                    | 12                    | -12                   | -15                   | 12    |
|                                                                                             |                                             |               | After curing          | 12                    | 12                    | -12                   | -15                   | 12    |
|                                                                                             |                                             | b*            | Before curing         | 20                    | 20                    | 24                    | 26                    | 20    |
|                                                                                             |                                             |               | After curing          | 20                    | 20                    | 24                    | 26                    | 20    |
|                                                                                             | Color difference (ΔE)                       |               | Before curing         | 51.55                 | 25.33                 | 50.89                 | 53.62                 | 25.23 |
|                                                                                             |                                             |               | After curing          | 51.55                 | 25.33                 | 50.89                 | 53.62                 | 25.23 |

[0397]

As is apparent from the above results, the curable resin film of Examples 1 to 6 and the first protective film which is a cured material thereof had a visible light transmittance of 7% to 35%, which was sufficiently low. As a result, in the silicon wafer with thermosetting resin film and the silicon wafer with first protective film, the concealing property of the circuit surface was high. Further, it was possible to easily recognize that neither the curable resin film nor the first protective film remained in the upper region of the bump after the curable resin film was brought into close contact with the circuit surface and the surface of the bump. Since the color difference between the thermosetting resin film and the silicon wafer, and the color difference between the first protective film and the silicon wafer are both 27.87 to 48.10, if the curable resin film or the first protective film remains, it is surly easy to recognize these.

In addition, the curable resin film and the first protective film in Examples 1 to 6 had the infrared transmittance of 41% to 95%, which was sufficiently high. As a result, in the silicon wafer with thermosetting resin film and the silicon wafer with first protective film, the observability of the circuit surface was high.

[0398]

In the thermosetting resin layer forming composition of Examples 1 to 6, the ratio of the amount of the filler (D) (that is, the amount of the filler (D) in the thermosetting resin layer) to the total amount of all of the components other than the solvent is 5.0% to 19.2% by mass, the ratio of the amount of the coloring agent (I) (that is, the amount of the coloring agent (I) in the thermosetting resin layer) to the total amount of all of the components other than the solvent is 0.11% to 0.43% by mass, and the average particle diameter of the filler (D) is 2  $\mu\text{m}$ .

[0399]

Among them, the curable resin film and the first protective film in Examples 1, 2, and 5 were particularly excellent in both of the concealing property and the observability of the circuit surface. In these curable resin film and first protective film, the visible light transmittance was 11% to 20%, and the infrared transmittance was 53% to 80%. The reason why the curable resin film and the first protective film are particularly excellent in both the concealing property and the observability of the circuit surface is presumed that in the thermosetting resin layer forming composition, the ratio of the amount of the filler (D) (that is, the amount of the filler (D) in the thermosetting resin layer) to the total amount of all of the components other than the solvent is 10.7% to 19.3% by mass, the ratio of the amount of the coloring agent (I) (that is, the amount of the coloring agent (I) in the thermosetting resin layer) to the total amount of all of the components other than the solvent is 0.11% to 0.21% by mass, and the average particle diameter of the filler (D) is 2  $\mu\text{m}$ .

[0400]

In contrast, the curable resin film and the first protective film which is a cured material thereof in Comparative Example 1 had low infrared transmittance. The reason for this is that the amount of the coloring agent of the thermosetting resin layer forming composition was excessively large. As a result, in the silicon wafer with thermosetting resin film and the silicon wafer with first protective film, the observability of the circuit surface was not recognized.

[0401]

In addition, the curable resin film and the first protective film which is a cured material thereof in Comparative Example 2 had high visible light transmittance. The reason for this is that the thermosetting resin layer forming composition did not contain the coloring agent. As a result, in the silicon wafer with thermosetting resin film and

the silicon wafer with first protective film, the concealing property of the circuit surface was not recognized.

[0402]

In addition, the curable resin film and the first protective film which is a cured material thereof in Comparative Examples 3 and 4 had low infrared transmittance. The reason for this is that the average particle diameter of the filler in the thermosetting resin layer forming composition was excessively large and the infrared was diffusely reflected. As a result, in the silicon wafer with thermosetting resin film and the silicon wafer with first protective film, the observability of the circuit surface was low.

10 [0403]

In addition, the curable resin film and the first protective film which is a cured material thereof in Comparative Example 5 had high visible light transmittance. The reason for this is that both of the amount of filler and the amount of the coloring agent of the thermosetting resin layer forming composition were excessively small. As a result, in the silicon wafer with thermosetting resin film and the silicon wafer with first protective film, the concealing property of the circuit surface was low.

#### Industrial Applicability

[0404]

20 The present invention can be used for manufacturing a semiconductor chip or the like having a bump at a connection pad portion used in a flip chip mounting method.

#### Reference Signs List

[0405]

25 1, 2, 3... SHEET FOR FORMING FIRST PROTECTIVE FILM

11... FIRST BASE MATERIAL

11a... ONE SURFACE OF FIRST BASE MATERIAL

12... CURABLE RESIN LAYER (CURABLE RESIN FILM)

12'... FIRST PROTECTIVE FILM

5 13... FIRST PRESSURE-SENSITIVE ADHESIVE LAYER

13a... ONE SURFACE OF FIRST PRESSURE-SENSITIVE ADHESIVE  
LAYER

14... FIRST INTERLAYER

101, 102, 103... FIRST SUPPORTING SHEET

10 101a, 102a, 103a... ONE SURFACE OF FIRST SUPPORTING SHEET

90... SEMICONDUCTOR WAFER

90a... CIRCUIT SURFACE OF SEMICONDUCTOR WAFER

91... BUMP

91a... SURFACE OF BUMP

15

## CLAIMS

What is claimed is:

1. A curable resin film for forming a first protective film on a surface having a bump of a semiconductor wafer by being attached to the surface, and being cured,  
5 wherein a visible light transmittance of the curable resin film before curing is 45% or less, and  
wherein an infrared transmittance of the curable resin film before curing is 33% or more.
- 10 2. A sheet for forming a first protective film, comprising:  
a first supporting sheet; and  
the curable resin film according to Claim 1 on one surface of the first supporting sheet.