

DESCRIPTION

Title of Invention

PROTECTIVE FILM FORMING SHEET

5

Technical Field

[0001]

The present invention relates to a protective film forming sheet.

Priority is claimed on Japanese Patent Application No. 2015-217115, filed on
10 November 4, 2015, the content of which is incorporated herein by reference.

Background Art

[0002]

In the related art, in a case in which a multi-pin LSI package, which is used in
15 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
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
20 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
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
25 the above-described semiconductor chip, generally, for the purpose of protecting the

circuit surface and the bumps of the semiconductor wafer, a curable resin film stacked on a supporting sheet is attached to the bump-formed surface, and this film is cured so as to form a protective film on the bump-formed surface.

[0004]

5 As the above-described curable resin film, a curable resin film containing a thermosetting component that is cured by heating is broadly used, and, as a protective film forming sheet including the above-described thermosetting resin layer, a protective film forming sheet formed by stacking a thermoplastic resin layer having a predetermined thermal elastic modulus on the film and further stacking a thermoplastic
10 resin layer which is not plastic at 25°C on the uppermost layer of the thermoplastic resin layer has been disclosed (refer to Patent Document 1). In addition, according to Patent Document 1, this protective film forming sheet is excellent in terms of the bump filling property of the protective film, the wafer workability, the electric connection reliability after resin sealing, and the like.

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Citation List

Patent Literature

[0005]

[Patent Document 1] Japanese Unexamined Patent Application, First

20 Publication No. 2005-028734

Summary of Invention

Technical Problem

[0006]

25 However, in attempts of the related art to form a protective film on the

bump-formed surface using a protective film forming sheet formed by stacking a thermosetting resin layer on a supporting sheet, there are cases in which, during the peeling of the supporting sheet, the supporting sheet and the thermosetting resin layer are not favorably peeled off from each other in the interface, an attempt to forcibly peel the supporting sheet leads to peeling in an interface in the supporting sheet such as the interface between a base material and a pressure-sensitive adhesive layer, and poor peeling such as the attachment of the pressure-sensitive adhesive to the protective film is frequently observed.

[0007]

The present invention has been made in consideration of the above-described circumstances, and an object of the present invention is to provide a protective film forming sheet which is excellent in terms of the easy peeling property in the interface between the supporting sheet and the thermosetting resin layer.

Solution to Problem

[0008]

The present invention is a protective film forming sheet formed by stacking a thermosetting resin layer on a first supporting sheet, in which the thermosetting resin layer is adhered to a surface having bumps of a semiconductor wafer and is cured by heat, whereby the first protective film is formed on the semiconductor wafer surface, and a difference between a surface free energy of a first supporting sheet-side surface of the thermosetting resin layer before thermal curing and a surface free energy of a thermosetting resin layer-side surface of the first supporting sheet is 10 mJ/m^2 or more.

In the protective film forming sheet, a difference between a contact angle of the first supporting sheet-side surface of the thermosetting resin layer before thermal curing

with respect to water and a contact angle of the thermosetting resin layer-side surface of the first supporting sheet with respect to water is preferably 30° or more.

Advantageous Effects of Invention

5 [0009]

The protective film forming sheet of the present invention is excellent in terms of the easy peeling property in the interface between the first supporting sheet and the thermosetting resin layer.

10 Brief Description of Drawings

[0010]

FIG. 1 is a cross-sectional view schematically showing an embodiment of a protective film forming sheet of the present invention.

FIG. 2 is a cross-sectional view schematically showing another embodiment of
15 the protective film forming sheet of the present invention.

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

FIG. 4 is a cross-sectional view schematically showing an example of a semiconductor wafer having bumps.

20 FIG. 5 is a cross-sectional view schematically showing a state in which the protective film forming sheet of the present invention is attached to a bump-provided surface of the semiconductor wafer.

FIG. 6 is a cross-sectional view schematically showing an example of the semiconductor wafer including the protective film formed using the protective film
25 forming sheet of the present invention.

Description of Embodiments

[0011]

The present invention is a protective film forming sheet formed by stacking a
 5 thermosetting resin layer on a first supporting sheet, in which the thermosetting resin
 layer is adhered to a surface having bumps of a semiconductor wafer and is cured by heat,
 whereby the first protective film is formed on the semiconductor wafer surface, and a
 difference between a surface free energy of a first supporting sheet-side surface of the
 thermosetting resin layer before thermal curing and a surface free energy of a
 10 thermosetting resin layer-side surface of the first supporting sheet is 10 mJ/m² or more.

[0012]

The surface free energy γ_s^{total} of each solid can be obtained by solving a
 simultaneous equation regarding the surface free energy γ_s^d of a dispersion force
 component, the surface free energy γ_s^p of a polar component, and the surface free energy
 15 γ_s^h of a hydrogen bond component in Expression (2) by measuring the respective contact
 angles on the solid surface of liquids having known surface free energies such as the
 surface free energy γ_L^d of the dispersion force component, the surface free energy γ_L^p of
 the polar component, and the surface free energy γ_L^h of the hydrogen bond component,
 for example, pure water, diiodomethane, and 1-bromonaphthalene and substituting the
 20 results into Expression (1).

$$\gamma_s^{\text{total}} = \gamma_s^d + \gamma_s^p + \gamma_s^h \quad \dots \quad (1)$$

$$\gamma_L(1 + \cos\theta) = 2 \cdot (\gamma_s^d \cdot \gamma_L^d)^{1/2} + 2 \cdot (\gamma_s^p \cdot \gamma_L^p)^{1/2} + 2 \cdot (\gamma_s^h \cdot \gamma_L^h)^{1/2} \quad \dots \quad (2)$$

[0013]

The protective film forming sheet of the present invention is used in a state of

being attached to a bump-provided surface of a semiconductor wafer through the thermosetting resin layer. In addition, the attached thermosetting resin layer becomes more fluid when heated, spreads among bumps so as to cover the bumps, adheres to the circuit surface, and cover the surfaces of the bumps, particularly, the surfaces of portions
5 close to the circuit surface, thereby burying the bumps. The thermosetting resin layer in this state is further thermally cured by heating and forms a first protective film in the end, thereby protecting the bumps in a state of adhering to the surfaces of the bumps on the circuit surface.

For example, in the semiconductor wafer to which the protective film forming
10 sheet has been attached, a surface opposite to the circuit surface is ground, then, a first supporting sheet is removed, subsequently, the thermosetting resin layer buries the bumps and forms the first protective film by being heated, and, finally, the semiconductor wafer is combined into a semiconductor device in a state of including this first protective film.

[0014]

15 In the protective film forming sheet of the present invention, when the difference between the surface free energy of the first supporting sheet-side surface of the thermosetting resin layer before thermal curing and the surface free energy of the thermosetting resin layer-side surface of the first supporting sheet is 10 mJ/m^2 or more, there is no migration of the components in the interface between both elements, and the
20 easy peeling property in the interface between the first supporting sheet and the thermosetting resin layer is excellent during the removal of the first supporting sheet.

The difference between the surface free energy of the first supporting sheet-side surface of the thermosetting resin layer before thermal curing and the surface free energy of the thermosetting resin layer-side surface of the first supporting sheet is preferably 12 to 100

25 mJ/m^2 , more preferably 15 to 90 mJ/m^2 , more preferably 18 to 85 mJ/m^2 , and particularly

preferably 20 to 80 mJ/m².

[0015]

In addition, when the difference between a contact angle of the first supporting sheet-side surface of the thermosetting resin layer before thermal curing with respect to water and a contact angle of the thermosetting resin layer-side surface of the first supporting sheet with respect to water is 30° or more, during the removal of the first supporting sheet, the easy peeling property in the interface between the first supporting sheet and the thermosetting resin layer becomes superior.

[0016]

Meanwhile, in the protective film forming sheet of the present invention, there are cases in which the thermosetting resin layer-side surface of the first supporting sheet is made of an energy ray-curable pressure-sensitive adhesive or a non-energy ray-curable pressure-sensitive adhesive, and, in the case of being made of an energy ray-curable pressure-sensitive adhesive, the value of the difference in the surface free energy before energy ray curing falls in the above-described range, and thus there is no migration of the components in the interface between both elements before energy ray curing, and the easy peeling property in the interface between the first supporting sheet and the thermosetting resin layer becomes excellent even when the first supporting sheet is removed after energy ray curing. Even when the value of the difference in the surface free energy after energy ray curing is outside the above-described range, there is only a small influence on the migration of the components in the interface between both elements before energy ray curing, and the easy peeling property in the interface between the first supporting sheet and the thermosetting resin layer during the removal of the first supporting sheet is not significantly affected.

[0017]

Hereinafter, the protective film forming sheet according to the present invention will be described in detail with reference to the accompanying drawings.

Meanwhile, in the drawings which will be used in the following description, there are cases in which the protective film forming sheet is varied from the actual protective film forming sheet for convenience. In addition, materials, conditions, and the like in the following description are simply exemplary examples, and the present invention is not limited thereto and can be carried out in appropriately modified manners within the scope of the gist of the present invention.

[0018]

10 ⊗ 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 “a 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”, and 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”, which will be true not only for the first supporting sheet but also for other elements.

[0019]

25 Examples of a preferred first supporting sheet include a first supporting sheet in

which the first pressure-sensitive adhesive layer is stacked on the first base material, a first supporting sheet in which a first interlayer is stacked on the first base material and the first pressure-sensitive adhesive layer is stacked on the first interlayer, a first supporting sheet made of only the first base material, and the like.

5 [0020]

Hereinafter, exemplary examples of the protective film forming sheet of the present invention including each of the types of first supporting sheets above will be described with reference to the drawings.

[0021]

10 FIG. 1 is a cross-sectional view schematically showing an embodiment of the protective film forming sheet of the present invention. A protective film forming sheet 1 shown in this drawing is a protective film forming sheet in which, as a first supporting sheet 101, a first supporting sheet formed by stacking a first pressure-sensitive adhesive layer 13 on a first base material 11 is used. That is, the protective film forming sheet 1
15 is constituted by including the first pressure-sensitive adhesive layer 13 on the first base material 11 and including a thermosetting resin layer 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, and the thermosetting resin layer 12 is provided on one surface 101a of the first supporting sheet 101, that is, on one
20 surface 13a of the first pressure-sensitive adhesive layer 13. In the protective film forming sheet 1, when the difference between the surface free energy of the first supporting sheet 101-side surface of the thermosetting resin layer 12 before thermal curing and the surface free energy of the thermosetting resin layer 12-side surface of the first pressure-sensitive adhesive layer 13 is 10 mJ/m^2 or more, there is no migration of
25 the components in the interface between both elements, the adhesive force is stabilized,

and thus the interface between the first supporting sheet 101 and the thermosetting resin layer 12 becomes excellent in terms of the easy peeling property. The difference between the surface free energy of the first supporting sheet 101-side surface of the thermosetting resin layer 12 before thermal curing and the surface free energy of the thermosetting resin layer 12-side surface of the first pressure-sensitive adhesive layer 13 is preferably 12 to 100 mJ/m², more preferably 15 to 90 mJ/m², preferably 18 to 85 mJ/m², and particularly preferably 20 to 80 mJ/m².

[0022]

FIG. 2 is a cross-sectional view schematically showing another embodiment of the protective film forming sheet of the present invention. Meanwhile, in FIG. 2, the same constituent element as in FIG. 1 is given the same reference sign as in FIG. 1 and will not be described in detail. What has been described above is also true for FIG. 3 and the subsequent drawings.

In a protective film forming sheet 2 shown in this drawing, as a first supporting sheet 102, a first supporting sheet formed by stacking a first interlayer 14 on the first base material 11 and stacking the first pressure-sensitive adhesive layer 13 on the first interlayer 14 is used. That is, the protective film forming sheet 2 is constituted by including the first interlayer 14 on the first base material 11, including the first pressure-sensitive adhesive layer 13 on the first interlayer 14, and including the curable resin layer 12 on the first pressure-sensitive adhesive layer 13. The first supporting sheet 102 is a stacked body formed by stacking the first base material 11, the first interlayer 14, and the first pressure-sensitive adhesive layer 13 in this order, and the thermosetting 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 protective film forming sheet 2 is the protective film forming

sheet 1 shown in FIG. 1 which further includes the first interlayer 14 in the interface between the first base material 11 and the first pressure-sensitive adhesive layer 13. In the protective film forming sheet 2, when the difference between the surface free energy of the first supporting sheet 102-side surface of the thermosetting resin layer 12 before thermal curing and the surface free energy of the thermosetting resin layer 12-side surface of the first pressure-sensitive adhesive layer 13 is 10 mJ/m^2 or more, there is no migration of the components in the interface between both elements, the adhesive force is stabilized, and thus the interface between the first supporting sheet 102 and the thermosetting resin layer 12 becomes excellent in terms of the easy peeling property.

The difference between the surface free energy of the first supporting sheet 102-side surface of the thermosetting resin layer 12 before thermal curing and the surface free energy of the thermosetting resin layer 12-side surface of the first pressure-sensitive adhesive layer 13 is preferably 12 to 100 mJ/m^2 , more preferably 15 to 90 mJ/m^2 , preferably 18 to 85 mJ/m^2 , and particularly preferably 20 to 80 mJ/m^2 .

[0023]

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

In a protective film forming sheet 3 shown in this drawing, as a first supporting sheet 103, a first supporting sheet made of the first base material 11 alone is used. That is, the protective film forming sheet 3 is constituted by including the curable resin layer 12 on the first base material 11. The first supporting sheet 103 is constituted of the first base material 11 alone, and the curable resin layer 12 is provided in direct contact on one surface 103a of the first supporting sheet 103, that is, on one surface 11a of the first base material 11.

In other words, the protective film forming sheet 3 is the protective film forming

sheet 1 shown in FIG. 1 from which the first pressure-sensitive adhesive layer 13 is removed. In the protective film forming sheet 3, when the difference between the surface free energy of the first supporting sheet 103-side surface of the thermosetting resin layer 12 before thermal curing and the surface free energy of the thermosetting resin layer 12-side surface of the first supporting sheet 103 is 10 mJ/m² or more, there is no migration of the components in the interface between both elements, the adhesive force is stabilized, and thus the interface between the first supporting sheet 103 and the thermosetting resin layer 12 becomes excellent in terms of the easy peeling property. The difference between the surface free energy of the first supporting sheet 103-side surface of the thermosetting resin layer 12 before thermal curing and the surface free energy of the thermosetting resin layer 12-side surface of the first supporting sheet 103 is preferably 12 to 100 mJ/m², more preferably 15 to 90 mJ/m², preferably 18 to 85 mJ/m², and particularly preferably 20 to 80 mJ/m².

[0024]

FIG. 4 is a cross-sectional view schematically showing an example of a semiconductor wafer 90 having bumps 91. 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 shape of the bump is not limited to the shape as shown in the drawing, but an effect (an easy peeling property in the interface between the first supporting sheet and the thermosetting resin layer) of the present invention is particularly exhibited with spherical bumps having a plane of projection including an elliptical shape.

[0025]

FIG. 5 is a cross-sectional view schematically showing a state in which the protective film forming sheet of the present invention is attached to the bump 91-provided surface of the semiconductor wafer 90. The attached thermosetting resin layer 12 becomes more fluid when heated, spreads among the bumps so as to cover the bumps, adheres to the circuit surface, and cover the surfaces of the bumps, particularly, the surfaces of the portions close to the circuit surface, thereby burying the bumps.

When the thickness of the curable resin layer 12 is set to be thinner than the height of the bump 91, and the total thickness of the curable resin layer 12 and the first pressure-sensitive adhesive layer 13 is set to be thicker than the height of the bump 91, all of the bumps 91 are covered with the curable resin layer 12 and the first pressure-sensitive adhesive layer 13.

[0026]

In the semiconductor wafer to which the protective film forming sheet has been attached, for example, the surface opposite to the circuit surface is ground, then, the first supporting sheet 101 is removed, subsequently, a first protective film 12' is formed by heating the thermosetting resin layer 12, and, finally, the semiconductor wafer is chip-cut to a predetermined size in a state of including the first protective film 12' and is combined into a semiconductor device.

[0027]

FIG. 6 is a cross-sectional view schematically showing an example of the semiconductor wafer 90 including the first protective film 12' formed using the protective film forming sheet 1 of the present invention. The first protective film 12' is a protective film formed using the thermosetting resin film of the present invention, covers the circuit surface 90a of the semiconductor wafer 90, and further covers, among surfaces 91a of the bumps 91, tops 911 of the bumps 91 and regions other than portions

close to the tops.

[0028]

In the protective film forming sheet 1 of the present invention, the easy peeling property in the interface between the first supporting sheet 101 and the thermosetting resin layer 12, that is, the easy peeling property in the interface between the first pressure-sensitive adhesive layer 13 and the thermosetting resin layer 12 is excellent, and thus there are no cases in which poor peeling occurs during the removal of the first supporting sheet 101 by peeling, and, as shown in FIG. 6, it is possible to protect the circuit surface and the bumps by leaving the thermosetting resin layer 12 which will turn into the first protective film 12' after curing.

[0029]

○ First Base Material

The first base material may be a first base material made of a single layer (monolayer) or a first base material made up of a plurality of layers of two or more layers. In a case in which the base material is made up 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 “a 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”, and 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”, which will be true not only for the base material but also for other elements.

[0030]

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)acrylate 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 polymers; 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 described above; poly(meth)acrylic acid esters; polyurethane; polyurethane acrylate; polyimide; polyamide; polycarbonate; fluororesin; polyacetal; modified polyphenylene oxides; polyphenylene sulfides; polysulfone; polyether ketones; and the like.

In addition, exemplary 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 preferably polymer alloys in which the amount of the resin other than the polyester is relatively small.

In addition, examples of the resins also include crosslinked resins in which one or more of the exemplary examples of resins above are crosslinked with each other; modified resins such as ionomers for which one or more of the exemplary examples of

resins above are used; and the like.

[0031]

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 “acrylate” and “methacrylate”, and “a (meth)acryloyl group” refers to both “an acryloyl group” and “a methacryloyl group”.

[0032]

Only one type or two or more types of resins may constitute the first base material, and, in a case in which two or more types of resins constitute the first base material, the combination and ratio thereof can be arbitrarily selected.

[0033]

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.

[0034]

The thickness of the first base material is preferably 5 to 1,000 μm , more preferably 10 to 500 μm , still more preferably 15 to 300 μm , and particularly preferably 20 to 150 μm .

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.

[0035]

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 that can be used to constitute the above-described first base material having a high accuracy in thickness include polyethylene, polyolefin other than polyethylene, polyethylene terephthalate, ethylene-vinyl acetate copolymers, and the like.

[0036]

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).

[0037]

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.

[0038]

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.

[0039]

○ 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 pressure-sensitive adhesive resins such as acrylic resins (pressure-sensitive adhesives made of a resin having a (meth)acryloyl group), urethane-based resins (pressure-sensitive adhesives made of a resin having a urethane bond), rubber-based resins (pressure-sensitive adhesives made of a resin having a rubber structure), silicone-based resins (pressure-sensitive adhesives made of a resin having a siloxane bond), epoxy-based resins (pressure-sensitive adhesives made of a resin having an epoxy group), polyvinyl ethers, and polycarbonate, and acrylic resins are preferred.

[0040]

Meanwhile, in the present invention, “pressure-sensitive adhesive resins” refer to both resins having a pressure-sensitive adhesive property and resins having an adhesive property, and examples thereof include not only resins having an adhesive property for themselves but also resins exhibiting a pressure-sensitive adhesive property 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.

[0041]

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.

[0042]

The thickness of the first pressure-sensitive adhesive layer is preferably 1 to

1,000 μm , more preferably 5 to 500 μm , and particularly preferably 10 to 100 μm .

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
5 refers to the total thickness of all of the layers constituting the first pressure-sensitive adhesive layer.

[0043]

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
10 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
15 electromagnetic waves or charged particle radiation, and examples thereof include ultraviolet rays, electron beams, and the like.

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

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

[0044]

25 <<First Pressure-Sensitive Adhesive Composition>>

The first pressure-sensitive adhesive layer can be formed using a first 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 forming the first pressure-sensitive adhesive layer will be described below in detail together with methods for forming other layers. The ratio between the amounts of components, which do not gasify at normal temperature, in the first pressure-sensitive adhesive composition is, generally, identical to the ratio between the amounts of the above-described components in the first pressure-sensitive adhesive layer. Meanwhile, in the present specification, “normal temperature” refers to a temperature that is not particularly cooled or heated, that is, a temperature in an ordinary state, and examples thereof include a temperature of 15°C to 25°C and the like.

[0045]

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 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.

[0046]

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, and, in this case, the first pressure-sensitive

adhesive composition is preferably dried under conditions of, for example, 70°C to 130°C and 10 seconds to five minutes.

[0047]

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.

[0048]

<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.

[0049]

[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 types of constituent units, and, in a case in which the acrylic resin has two or more types of constituent units, the combination and ratio thereof can be arbitrarily selected.

5 [0050]

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 alkyl group is preferably a linear alkyl group or a branched alkyl group.

More specific examples of the alkyl (meth)acrylate include methyl
 10 (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,
 15 dodecyl (meth)acrylate (also referred to as lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (also referred to as myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (also referred to as palmityl (meth)acrylate), heptadecyl (meth)acrylate, octadecyl (meth)acrylate (also referred to as stearyl (meth)acrylate), nonadecyl (meth)acrylate, icosyl (meth)acrylate, and the like.

20 [0051]

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
 25 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.

[0052]

5 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
10 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.

[0053]

Examples of the functional group in the functional group-containing monomer
15 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.

20 [0054]

Examples of the hydroxyl group-containing monomers include hydroxyalkyl (meth)acrylates 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;
25 non-(meth)acrylic unsaturated alcohols such as vinyl alcohol and allyl alcohol

(unsaturated alcohols not having a (meth)acryloyl skeleton); and the like.

[0055]

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 unsaturated dicarboxylic acid; carboxyalkyl (meth)acrylates such as 2-carboxyethyl methacrylate; and the like.

10 [0056]

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

[0057]

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

[0058]

20 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.

[0059]

25 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.

5 Examples of the different monomer include styrene, α -methylstyrene, vinyl toluene, vinyl formate, vinyl acetate, acrylonitrile, acrylamide, and the like.

[0060]

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

[0061]

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

15 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
20 a property of being polymerized by irradiation with energy rays.

[0062]

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

selected.

[0063]

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

5 preferably 10% to 95% by mass, and particularly preferably 15% to 90% by mass of the total mass of the first pressure-sensitive adhesive composition (I-1).

[0064]

[Energy Ray-Curable Compound]

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

Among the energy ray-curable compounds, examples of monomers include polyhydric (meth)acrylates such as trimethylol propane tri(meth)acrylate, pentaerythritol
15 (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; polyether (meth)acrylate; polyether (meth)acrylate; epoxy (meth)acrylate; and the like.

Among the energy ray-curable compounds, examples of oligomers include
20 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 decreased.

25 [0065]

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

[0066]

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 90% by mass, and particularly preferably 10% to 85% by mass of the total mass of the
10 first pressure-sensitive adhesive composition (I-1).

[0067]

[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 the functional group-containing monomer as the pressure-sensitive adhesive resin (I-1a),
15 the first pressure-sensitive adhesive composition (I-1) preferably further contains a crosslinking agent.

[0068]

The crosslinking agent is, for example, a substance that reacts with the
20 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 adducts of the above-described diisocyanate; epoxy-based crosslinking agents (crosslinking agents having a glycidyl
25 group) such as ethylene glycol glycidyl ether; aziridine-based crosslinking agents

(crosslinking agents having an aziridine 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.

10 [0069]

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

15 [0070]

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 total amount (100 parts by mass) of the pressure-sensitive adhesive resin (I-1a).

20 [0071]

[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

25

rays.

[0072]

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; α -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 diacetylene; 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.

[0073]

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

selected.

[0074]

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 total amount (100 parts by mass) of the energy ray-curable compound.

[0075]

[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 a variety of 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 ($-C(=O)-$) in one molecule.

[0076]

The first pressure-sensitive adhesive composition (I-1) may contain only one type or two or more types of the other additives, and, in a case in which the first

pressure-sensitive adhesive composition contains two or more types of the other additives, the combination and ratio thereof can be arbitrarily selected.

[0077]

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

[0078]

[Solvent]

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

[0079]

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
15 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.

[0080]

As the solvent, a solvent used during the manufacturing of the pressure-sensitive
20 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).

25 [0081]

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

5 [0082]

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

[0083]

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

10 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).

[0084]

15 [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).

20 [0085]

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).

25 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
5 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.

[0086]

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

[0087]

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

[0088]

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
20 preferably 10% to 95% by mass, and particularly preferably 10% to 90% by mass of the total mass of the first pressure-sensitive adhesive composition (I-2).

[0089]

[Crosslinking Agent]

In a case in which, as the pressure-sensitive adhesive resin (I-2a), for example,
25 the acrylic polymer having the constituent unit derived from the functional

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) preferably further contains a crosslinking agent.

[0090]

5 Examples of the crosslinking agent in the first pressure-sensitive adhesive 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 types of the crosslinking agents, and, in a case in which the first
10 pressure-sensitive adhesive composition contains two or more types of the crosslinking agents, the combination and ratio thereof can be arbitrarily selected.

[0091]

 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
15 by mass, and particularly preferably 1 to 10 parts by mass of the total amount (100 parts by mass) of the pressure-sensitive adhesive resin (I-2a).

[0092]

[Photopolymerization Initiator]

 The first pressure-sensitive adhesive composition (I-2) may also further contain
20 a photopolymerization initiator. The first pressure-sensitive adhesive composition (I-2) 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.

[0093]

25 Examples of the photopolymerization initiator in the first pressure-sensitive

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 types of the photopolymerization initiators, and, in a case in which
5 the first pressure-sensitive adhesive composition contains two or more types of the photopolymerization initiators, the combination and ratio thereof can be arbitrarily selected.

[0094]

In the first pressure-sensitive adhesive composition (I-2), the amount of the
10 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).

[0095]

[Other Additives]

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

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

25 [0096]

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.

[0097]

5 [Solvent]

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).

10 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 composition (I-1).

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

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

[0098]

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

20 As described above, the first pressure-sensitive adhesive composition (I-3) contains the pressure-sensitive adhesive resin (I-2a) and an energy ray-curable low-molecular-weight compound.

[0099]

In the first pressure-sensitive adhesive composition (I-3), the amount of the
25 pressure-sensitive adhesive resin (I-2a) 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 mass of the first pressure-sensitive adhesive composition (I-3).

[0100]

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

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

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

15 [0101]

 In the first pressure-sensitive adhesive composition (I-3), the amount of the 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 total amount (100 parts by mass) of the pressure-sensitive adhesive
20 resin (I-2a).

[0102]

[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)
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.

[0103]

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 types of the photopolymerization initiators, and, in a case in which the first pressure-sensitive adhesive composition contains two or more types of the photopolymerization initiators, the combination and ratio thereof can be arbitrarily selected.

[0104]

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.

[0105]

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

[0106]

5 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 the type of the additives.

[0107]

[Solvent]

10 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 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

15 composition (I-1).

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

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

[0108]

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

25 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 types 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)).

[0109]

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 non-energy ray-curable pressure-sensitive adhesive compositions include non-energy ray-curable pressure-sensitive adhesive compositions containing a pressure-sensitive adhesive resin such as an acrylic resin (a resin having a (meth)acryloyl group), an urethane-based resin (a resin having a urethane bond), a rubber-based resin (a resin having a rubber structure), a silicone-based resin (a resin having a siloxane bond), an epoxy-based resin (a resin having an epoxy group), a polyvinyl ether, or a polycarbonate, and non-energy ray-curable pressure-sensitive adhesive compositions containing an acrylic resin are preferred.

[0110]

The first pressure-sensitive adhesive compositions other than the first pressure-sensitive adhesive compositions (I-1) to (I-3) preferably contain one or more types 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.

[0111]

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

The first pressure-sensitive adhesive compositions such as the first
5 pressure-sensitive adhesive compositions (I-1) to (I-3) 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
10 particularly limited, and two or more types 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
15 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
20 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
25 not deteriorate and may be appropriately adjusted, but the temperature is preferably 15°C

to 30°C.

[0112]

○ First Interlayer

The first interlayer has a sheet form or a film form, and a constituent material
5 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 protective film by reflecting the shape of bumps present on a semiconductor surface in the protective film that covers the semiconductor surface, examples of a preferred
10 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.

[0113]

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
15 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.

[0114]

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
20 preferably 50 to 600 μm , more preferably 70 to 500 μm , and particularly preferably 80 to 400 μm 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
25 plurality of layers refers to the total thickness of all of the layers constituting the first

interlayer.

[0115]

<<First Interlayer Forming Composition>>

The first interlayer can be formed using a first interlayer forming composition
5 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 irradiation with energy rays as necessary. A
10 more specific method for forming the first interlayer will be described below in detail
together with methods for forming other layers. The ratio between the amounts of
components, which do not gasify at normal temperature, in the first interlayer forming
composition is, generally, identical to the ratio between the amounts of the
above-described components in the first interlayer. Here, “normal temperature” is as
15 described above.

[0116]

The first interlayer 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
20 curtain coater, a die coater, a knife coater, a screen coater, a Mayer bar coater, and a kiss
coater are used.

[0117]

The drying conditions of the first interlayer forming composition are not
particularly limited; however, in a case in which the first interlayer forming composition
25 contains a solvent described below, the first interlayer forming composition is preferably

heated and dried, and, in this case, the first interlayer forming composition is preferably dried under conditions of, for example, 70°C to 130°C and 10 seconds to five minutes.

In a case in which the first interlayer forming composition is energy ray-curable, the first interlayer forming composition is preferably further cured by irradiation with

5 energy rays after drying.

[0118]

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

[0119]

10 <First Interlayer Forming Composition (II-1)>

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

[0120]

[Urethane (Meth)acrylate]

15 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 be a di- or higher-functional urethane (meth)acrylate (urethane (meth)acrylate having two
20 or more (meth)acryloyl groups in one molecule), that is, a multifunctional urethane (meth)acrylate, but urethane (meth)acrylate having at least one (meth)acryloyl group is preferably used.

[0121]

Examples of the urethane (meth)acrylate contained in the first interlayer forming
25 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” refers to a prepolymer having a urethane bond and having an isocyanate group at a terminal portion of the molecule.

[0122]

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

[0123]

(Polyol Compound)

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

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

[0124]

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

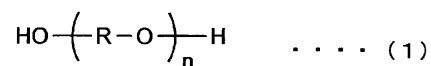
The polyol compound may be any one of a difunctional diol, a trifunctional triol, and tetra- or higher-functional polyols, but a diol is preferred since the diol can be easily procured and is excellent in terms of versatility, reactivity, and the like.

[0125]

· Polyether-Type Polyol

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

5 [0126]



(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.)

10 [0127]

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.

15 [0128]

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

20 tetramethylene group.

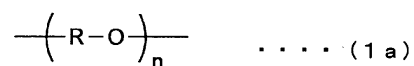
[0129]

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

[0130]

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.

[0131]



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

[0132]

· 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.

[0133]

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.

[0134]

Examples of the saturated aliphatic polybasic acids include saturated aliphatic dibasic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, 5 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; 10 aromatic tribasic acids such as trimellitic acid; aromatic tetrabasic acids such as pyromellitic acid; and the like.

[0135]

Examples of the derivatives of the polybasic acids include acid anhydrides of the saturated aliphatic polybasic acids, the unsaturated aliphatic polybasic acids, and the 15 aromatic polybasic acids described above, hydrogenated dimer acids, and the like.

[0136]

One type of any of the polybasic acids or the derivatives thereof may be used singly or two or more types of any of the polybasic acids or the derivatives thereof may be jointly used, and, in a case in which two or more types of any of the polybasic acids or 20 the derivatives thereof are jointly used, the combination and ratio thereof can be arbitrarily selected.

[0137]

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 25 hardness.

[0138]

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
5 stannous octanoate; alkoxy titanium such as tetrapropyl titanate; and the like.

[0139]

· 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
10 represented by Formula (1) and alkylene carbonate, and the like.

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

[0140]

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
20 1,000 or more, the excess generation of urethane bonds is suppressed, and it becomes easier to suppress the viscoelastic characteristic of the first interlayer. In addition, when 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
25 polyol compound refers to a value computed from the following expression.

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

[0141]

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

[0142]

(Polyhydric Isocyanate Compound)

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

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

[0143]

- Examples of the polyhydric isocyanate compound include chain-like diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate, and trimethylhexamethylene diisocyanate; cyclic aliphatic diisocyanates such as isophorone
20 diisocyanate, norbornane diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, dicyclohexylmethane-2,4'-diisocyanate, and ω,ω' -diisocyanate dimethylcyclohexane; 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
25 diisocyanate, hexamethylene diisocyanate, or xylylene diisocyanate from the viewpoint

of the handling property.

[0144]

((Meth)acrylic Compound)

The (meth)acrylic compound that is reacted with the terminal isocyanate
 5 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.

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

[0145]

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,
 15 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 4-hydroxycyclohexyl
 (meth)acrylate, 5-hydroxycyclooctyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl
 (meth)acrylate, penterithritol 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
 20 (meth)acrylic acid with vinyl alcohol, vinyl phenol, or bisphenol A glycidyl ether; and the
 like.

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.

25 [0146]

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.

[0147]

5 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.

[0148]

10 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.

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
15 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 polymers of the urethane (meth)acrylate and a polymerizable monomer described below.

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

[0149]

[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
25 improving the film-forming property.

The polymerizable monomer refers to polymerizable monomers except for 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.

5 [0150]

Examples of the polymerizable monomer include alkyl (meth)acrylates in which 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;

10 (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.

[0151]

Examples of the alkyl (meth)acrylates having a chain-like alkyl group having 1
 15 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
 20 (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, octadecyl (meth)acrylate (stearyl (meth)acrylate), isooctadecyl (meth)acrylate (isostearyl (meth)acrylate), nonadecyl (meth)acrylate, icosyl
 25 (meth)acrylate, and the like.

[0152]

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, 5 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 10 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 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”); 15 (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 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, 20 referred to as “the epoxy group-containing (meth)acrylic acid esters”); and the like.

[0153]

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 ($-NH_2$). Similarly, “the monosubstituted amino 25 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 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.

- 5 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 disubstituted amino group” include alkyl groups and the like.

[0154]

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

[0155]

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

[0156]

 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.

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

[0157]

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

- 25 N-vinylcaprolactam, and the like.

[0158]

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

[0159]

5 The polymerizable monomer preferably has a group having a relatively large volume since the compatibility with the urethane (meth)acrylate is favorable, examples thereof 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
10 more preferred.

[0160]

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

[0161]

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
20 80% by mass of the total mass of the first interlayer forming composition (II-1).

[0162]

[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
25 initiator. The first interlayer forming composition (II-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.

[0163]

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).

[0164]

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

[0165]

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 of the total amount (100 parts by mass) of the urethane (meth)acrylate and the polymerizable monomer.

[0166]

[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 invention are not impaired.

The types 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.

[0167]

[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
5 of the present invention are not impaired.

Examples of the other additives include a variety of additives such as a 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
10 group (mercapto group) in one molecule.

[0168]

Examples of the thiol compounds include nonyl mercaptan, 1-dodecanethiol, 1,2-ethanedithiol, 1,3-propanedithiol, triazinethiol, triazinedithiol, triazinetrithiol, 1,2,3-propanetrithiol, tetraethylene glycol bis(3-mercaptopropionate), trimethylolpropane
15 tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), dipentaerythritol hexakis(3-mercaptopropionate), tris[(3-mercaptopropionyloxy)-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.

20 [0169]

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

25 [0170]

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

[0171]

5 [Solvent]

The first interlayer forming composition (II-1) may also contain a solvent. When the first interlayer forming composition (II-1) contains a solvent, the coating aptitude to a coating target surface improves.

[0172]

10 <<Method for Manufacturing First Interlayer Forming Composition>>

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.

15 The addition order during the blending of the respective components is not particularly limited, and two or more types 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.

20 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

25

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.

[0173]

⊗ Thermosetting Resin Layer

The thermosetting resin layer is a layer intended to protect the circuit surface of the semiconductor wafer and the bumps provided on the circuit surface and forms the first protective film by curing.

[0174]

Examples of a preferred thermosetting resin layer include thermosetting resin layers containing a polymer component (A) and a thermosetting component (B). 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 polycondensation reaction is also considered as the polymerization reaction.

[0175]

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, these respective layers may be identical to or different from one another, and the combination of the plurality of layers is not particularly limited.

[0176]

The thickness of the thermosetting resin layer is preferably 1 to 100 μm , more preferably 5 to 75 μm , and particularly preferably 5 to 50 μm . When the thickness of 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 protective function. In addition, when the
5 thickness of the thermosetting resin layer is equal to or less than the upper limit value, an effect of suppressing the inclusion of air bubbles in the first protective film becomes stronger.

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

[0177]

<<Thermosetting Resin Layer Forming Composition>>

The thermosetting resin layer can be formed using a thermosetting resin layer
15 forming composition containing a constituent material thereof. For example, the thermosetting resin layer can be formed at an intended portion by applying a 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. The ratio between the amounts of components, which do not
20 gasify at normal temperature, in the thermosetting resin layer forming composition is, generally, identical to the ratio between the amounts of the above-described components in the thermosetting resin layer. Here, “normal temperature” is as described above.

[0178]

The thermosetting resin layer forming composition may be applied using a
25 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.

[0179]

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

10 [0180]

<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) and the thermosetting component (B) (in the present specification, in some cases, simply abbreviated as “the resin layer forming composition (III-1)”) and the like.

[0181]

[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.

20 The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one type or two or more types 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 types of the polymer components, the combination and ratio thereof can be arbitrarily selected.

25 [0182]

Examples of the polymer component (A) include acrylic resins (resins having a (meth)acryloyl group), polyesters, urethane-based resins (resins having a urethane bond), acrylic urethane resins, silicone-based resins (resin having a siloxane bond), rubber-based resins (resins having a rubber structure), phenoxy resins, thermosetting polyimides, and the like, and acrylic resins are preferred.

[0183]

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

The weight-average molecular weight (M_w) of the acrylic resin is preferably 10,000 to 2,000,000 and 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.

[0184]

The glass transition temperature (T_g) of the acrylic resin is preferably -60°C to 70°C and more preferably -30°C to 50°C . When the T_g 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 T_g 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 improves.

[0185]

Examples of the acrylic resin include polymers of one or more type of

(meth)acrylic acid esters; copolymers of two or more types of monomers selected from (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene, N-methylol acrylamide, and the like; and the like.

[0186]

- 5 Examples of the (meth)acrylic acid esters constituting the acrylic resin 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
- 10 (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
- 15 (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (stearyl (meth)acrylate) and the like;
- cycloalkyl (meth)acrylates such as isobornyl (meth)acrylate and dicyclopentanyll (meth)acrylate;
- aralkyl (meth)acrylates such as benzyl (meth)acrylate;
- 20 cycloalkenyl (meth)acrylates such as dicyclopentenyl (meth)acrylate;
- cycloalkenyloxy alkyl (meth)acrylate such as dicyclopentenylloxyethyl (meth)acrylate;
- imide (meth)acrylate;
- glycidyl group-containing (meth)acrylic acid esters such as glycidyl
- 25 (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

5 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.

[0187]

10 The acrylic resin may be, for example, in addition to the (meth)acrylic acid ester, a resin formed by the copolymerization of one or more types of monomers selected from (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene, N-methylol acrylamide, and the like.

[0188]

15 The acrylic resin may be constituted of only one type or two or more types of monomers, and, in a case in which the acrylic resin is constituted of two or more types of monomers, the combination and ratio thereof can be arbitrarily selected.

[0189]

The acrylic resin may also have a functional group capable of reacting with
20 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
25 group, there is a tendency that the reliability of packages obtained using the protective

film forming sheet improves.

[0190]

In the present invention, as the polymer component (A), a thermoplastic resin other than the acrylic resin (hereinafter, in some cases, simply abbreviated as “the thermoplastic resin”) may be used singly without using the acrylic resin or may be jointly
5 used with 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.

10 [0191]

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

[0192]

The glass transition temperature (T_g) of the thermoplastic resin is preferably
15 -30°C to 150°C and more preferably -20°C to 120°C.

[0193]

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

[0194]

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

25 [0195]

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).

[0196]

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
10 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 thermosetting component (B).

[0197]

[Thermosetting Component (B)]

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

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

[0198]

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

[0199]

(Epoxy-Based Thermosetting Resin)

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

5 The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one type or two or more types 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 types of the epoxy-based thermosetting resins, the combination and ratio thereof can be arbitrarily selected.

10 [0200]

· Epoxy Resin (B1)

As the epoxy resin (B1), well-known epoxy resins are exemplary examples. Examples thereof include polyfunctional epoxy resins, biphenyl compounds, bisphenol A diglycidyl ethers and hydrogenated substances thereof, orthocresol novolac epoxy resins, 15 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.

[0201]

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 20 more favorable 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 protective film forming sheet improves.

25 [0202]

Examples of the epoxy resin having an unsaturated hydrocarbon group include 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 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 groups are preferred.

[0203]

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 resin layer and the strength and thermal resistance of the first protective film after curing.

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

The epoxy equivalent of the epoxy resin (B1) is preferably 100 to 1,000 g/eq and more preferably 300 to 800 g/eq.

In the present specification, “the epoxy equivalent” refers to the number of grams (g/eq) of an epoxy compound including one gram equivalent of epoxy group and

can be measured according to the method of JIS K 7236:2001.

[0204]

One type of the epoxy resin (B1) may be used singly or two or more types thereof may be jointly used, and, in a case in which two or more types thereof are jointly
5 used, the combination and ratio thereof can be arbitrarily selected.

[0205]

· Thermal Curing Agent (B2)

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

10 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
15 acid group is turned into an anhydride are preferred, and phenolic hydroxyl groups or amino groups are more preferred.

[0206]

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

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

25 [0207]

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
5 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 unsaturated hydrocarbon group.

10 [0208]

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 of the first protective film from the first supporting sheet improves.

15 [0209]

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 aralkylphenol resin as the thermal curing agent (B2) is preferably 300 to 30,000, more preferably 400 to 10,000, and particularly preferably 500 to 3,000.

20 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.

[0210]

One type of the thermal curing agent (B2) may be used singly or two or more
25 types thereof may be jointly used, and, in a case in which two or more types thereof are

jointly used, the combination and ratio thereof can be arbitrarily selected.

[0211]

In the resin layer forming composition (III-1) and the thermosetting resin layer, the amount of the thermal curing agent (B2) is preferably 0.1 to 500 parts by mass and
5 more preferably 1 to 200 parts by mass of the total amount (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 absorptivity of the thermosetting resin
10 layer decreases, and thus the reliability of packages obtained using the protective film forming sheet further improves.

[0212]

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
15 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 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
20 suppressed, and thus the peeling property of the first supporting sheet improves.

[0213]

[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
25 for adjusting the curing rate of the resin layer forming composition (III-1).

Examples of preferred 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

5 2-methylimidazole, 2-phenyl imidazole, 2-phenyl-4-methylimidazole, 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; tetraphenyl boron salts such as

10 tetraphenyl phosphonium tetraphenyl borate and triphenyl phosphine tetraphenyl borate; and the like.

[0214]

The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one type or two or more types of the curing accelerators (C), and, in a

15 case in which the resin layer forming composition contains two or more types of the curing accelerators, the combination and ratio thereof can be arbitrarily selected.

[0215]

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

20 accelerator (C) is preferably 0.01 to 10 parts by mass and more preferably 0.1 to 5 parts by mass of the total 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, and, when the amount of the curing accelerator (C) is equal to or less than the

25 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 protective film forming sheet further improves.

5 [0216]

[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 adjustment of the thermal expansion coefficient of the first protective film obtained
10 by curing the thermosetting resin layer becomes easy, and, when this thermal expansion coefficient is optimized for a subject on which the first protective film is to be formed, the reliability of packages obtained using the protective film forming sheet 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 improve
15 the heat dissipation property.

[0217]

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

Examples of preferred inorganic fillers include powder of silica, alumina, talc,
20 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; single crystal fibers of these inorganic fibers; glass fibers; and the like. More specific examples thereof include spherical silica modified with an epoxy group and the like.

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

[0218]

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

[0219]

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
10 solvent is preferably 5% to 35% by mass and more preferably 7% to 25% by mass.

[0220]

[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
15 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, 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.

20 [0221]

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.

Examples of preferred silane coupling agents include

25 3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropylmethyldiethoxysilane,

- 3-glycidyloxypropyltriethoxysilane, 3-glycidyloxymethyldiethoxysilane,
 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
 3-methacryloyloxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane,
 3-(2-aminoethylamino)propyltrimethoxysilane,
 5 3-(2-aminoethylamino)propylmethyldiethoxysilane,
 3-(phenylamino)propyltrimethoxysilane, 3-anilinopropyltrimethoxysilane,
 3-ureidopropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane,
 3-mercaptopropylmethyldimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfane,
 methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane,
 10 vinyltriacetoxysilane, imidazolesilane, and the like.

[0222]

- The resin layer forming composition (III-1) and the thermosetting resin layer
 may contain only one type or two or more types of the coupling agents (E), and, in a case
 in which the resin layer forming composition and the curable resin layer contains two or
 15 more types of the coupling agents, the combination and ratio thereof can be arbitrarily
 selected.

[0223]

- In a case in which 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
 20 (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 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
 25 (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 suppressed.

[0224]

5 [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, or an isocyanate group which is capable of reacting with other compounds such as the above-described acrylic resin is used as the polymer component (A), the resin layer
10 forming composition (III-1) and the thermosetting resin layer may also contain a crosslinking agent (F) for bonding and crosslinking the functional group to other compounds. When the functional group is crosslinked to other compound using the crosslinking agent (F), it is possible to adjust the initial adhesiveness and the agglomerative force of the thermosetting resin layer.

15 [0225]

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 aziridinyl group), and the like.

20 [0226]

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
25 like”); timers, 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, and examples thereof include xylylene diisocyanate adducts of trimethylolpropane as described below and the like. In addition, “the terminal isocyanate urethane prepolymer” is as described above.

10 [0227]

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; 15 hexamethylene diisocyanate; isophorone diisocyanate; dicyclohexylmethane-4,4'-diisocyanate; dicyclohexylmethane-2,4'-diisocyanate; compounds obtained by adding any one or more types of tolylene diisocyanate, hexamethylene diisocyanate, and xylylene diisocyanate to all or some of hydroxyl groups in a polyol such as trimethylolpropane; lysine diisocyanate; and the like.

20 [0228]

Examples of the organic polyhydric imine compounds include N,N'-diphenylmethane-4,4'-bis(1-aziridinecarboxamide), trimethylolpropane tri- β -aziridinypropionate, tetramethylolmethane-tri- β -aziridinypropionate, N,N'-toluene-2,4-bis(1-aziridinecarboxamide) triethylene melamine, and the like.

25 [0229]

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 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
5 introduce a crosslinking structure into the thermosetting resin layer by a reaction between the crosslinking agent (F) and the polymer component (A).

[0230]

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

[0231]

In a case in which the crosslinking agent (F) is used, in the resin layer forming
15 composition (III-1), the amount of the crosslinking agent (F) 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 total 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.
20 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.

[0232]

[Energy Ray-Curable Resin (G)]

The resin layer forming composition (III-1) may also contain an energy
25 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.

[0233]

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 preferred.

[0234]

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.

[0235]

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

[0236]

Only one type or two or more types of the energy ray-curable compounds may

be used for polymerization, and, in a case in which two or more types of the energy ray-curable compounds are used, the combination and ratio thereof can be arbitrarily selected.

[0237]

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

[0238]

10 In the resin layer forming composition (III-1), the amount of the energy ray-curable resin (G) is preferably 1 to 95% by mass, more preferably 5 to 90% by mass, and particularly preferably 10 to 85% by mass of the total mass of the resin layer forming composition (III-1).

[0239]

15 [Photopolymerization Initiator (H)]

In the case of containing the energy ray-curable resin (G), the resin layer forming composition (III-1) 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.

20 [0240]

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).

[0241]

25 The resin layer forming composition (III-1) may contain only one type or two or

more types of the photopolymerization initiators (H), and, in a case in which the resin layer forming composition contains two or more types of the photopolymerization initiators, the combination and ratio thereof can be arbitrarily selected.

[0242]

5 In the resin layer forming composition (III-1), the amount of the photopolymerization initiator (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).

[0243]

10 [Versatile Additive (I)]

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

15 The versatile additive (I) may be a well-known versatile additive, can be arbitrarily selected depending on the purpose, and is not particularly limited, and examples of preferred versatile additives include a plasticizer, an antistatic agent, an antioxidant, a coloring agent (a pigment or a dye), a gettering agent, and the like.

[0244]

20 The resin layer forming composition (III-1) and the thermosetting resin layer may contain only one type or two or more types of the versatile additives (I), and, in a case in which the resin layer forming composition and the thermosetting resin layer contains two or more types of the versatile additives, the combination and ratio thereof can be arbitrarily selected.

25 The amount of the versatile additive (I) 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.

[0245]

[Solvent]

The resin layer forming composition (III-1) preferably further contains a solvent.

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

The solvent is not particularly limited, and examples of preferred solvents include hydrocarbons such as toluene and xylene; alcohols such as methanol, ethanol, 2-propanol, isobutyl alcohol (2-methyl propane-1-ol), and 1-butanol; esters such as ethyl
10 acetate; ketones such as acetone and methyl ethyl ketone; ethers such as tetrahydrofuran; amides (compounds having an amide bond) such as dimethylformamide and N-methyl pyrrolidone, and the like.

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

[0246]

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

[0247]

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

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

constituting the composition.

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

5 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.

10 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
15 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.

20 [0248]

◇ Method for Manufacturing First Protective Film Forming Sheet

The protective film forming sheet 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.

25 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.

[0249]

Meanwhile, for example, in a case in which the thermosetting resin layer is further stacked on the first pressure-sensitive adhesive layer that has been stacked on the first base material, the thermosetting resin layer can be directly formed by applying the thermosetting resin layer forming composition onto 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.

[0250]

For example, in a case in which a protective film forming sheet (the protective film forming sheet 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 thermosetting resin layer on the first pressure-sensitive adhesive layer is manufactured, the protective film forming sheet 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 onto the peeling film and drying the thermosetting resin layer forming composition as necessary so as to form the thermosetting resin layer on the peeling film, and attaching the exposed surface of the thermosetting 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 thermosetting resin layer on the first pressure-sensitive adhesive 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 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 protective film forming sheet can be obtained by, for example, separately, further applying the thermosetting resin layer forming composition onto the peeling film
5 and drying the thermosetting resin layer forming composition as necessary so as to form the thermosetting resin layer on the peeling film and attaching the exposed surface of the thermosetting 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 thermosetting resin layer on the first pressure-sensitive adhesive layer.

10 [0251]

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
15 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
20 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.

[0252]

25 As described above, all of the layers other than the first base material which

constitute the protective film forming sheet 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 protective film forming sheet may be manufactured by appropriately selecting layers for which the above-described steps are employed as necessary.

5 [0253]

Meanwhile, the protective film forming sheet is, generally, stored in a state in which the peeling film is attached to the surface of the outermost layer on the opposite side to the first supporting sheet (for example, the thermosetting resin layer). Therefore, the protective film forming sheet can also be obtained by applying a composition for forming a layer constituting the outermost layer such as the thermosetting resin layer forming composition onto the peeling film (preferably the peeling-treated surface thereof) and drying the thermosetting 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.

10
15

Examples

[0254]

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

20

[0255]

Components used to manufacture a thermosetting resin layer forming composition will be described below.

25 · Polymer Components

Polymer component (A)-1: An acrylic resin (the weight-average molecular weight: 800,000, the glass transition temperature: -28°C) obtained by copolymerizing butyl acrylate (hereinafter, abbreviated as “BA”) (55 parts by mass), methyl acrylate (hereinafter, abbreviated as “MA”) (10 parts by mass), glycidyl methacrylate (hereinafter, abbreviated as “GMA”) (20 parts by mass), and 2-hydroxyethyl acrylate (hereinafter, abbreviated as “HEA”) (15 parts by mass)

· Epoxy Resin

Epoxy resin (B1)-1: Liquid-form bisphenol F-type epoxy resin (“YL983U” manufactured by Mitsubishi Chemical Corporation)

10 Epoxy resin (B1)-2: Polyfunctional aromatic epoxy resin (“EPPN-502H” manufactured by Nippon Kayaku Co., Ltd.)

Epoxy resin (B1)-3: Dicyclopentadiene-type epoxy resin (“EPICLON HP-7200” manufactured by DIC Corporation)

· Thermal Curing Agent

15 Thermal curing agent (B2)-1: Novolac-type phenolic resin (“BRG-556” manufactured by Showa Denko K.K.)

· Curing Accelerator

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

20 · Filler

Filler (D)-1: Spherical silica modified with an epoxy group (“ADMANANO YA050C-MKK” manufactured by Admatechs)

[0256]

[Manufacturing Example 1]

(Manufacturing of Pressure-Sensitive Adhesive Resin (I-2a))

2-Ethylhexyl acrylate (hereinafter, abbreviated as “2EHA”) (80 parts by mass) and HEA (20 parts by mass) were used as raw materials of a copolymer, and a polymerization reaction was caused, thereby obtaining an acrylic polymer.

5 2-Methacryloyloxyethyl isocyanate (hereinafter, abbreviated as “MOI”) (22 parts by mass, approximately 80 mol% of HEA) was added to this acrylic polymer, and an addition reaction was caused in an air flow at 50°C for 48 hours, thereby obtaining an intended pressure-sensitive adhesive resin (I-2a).

[0257]

10 [Manufacturing Example 2]

(Manufacturing of Pressure-Sensitive Adhesive Resin (I-2a))

Butyl acrylate (hereinafter, abbreviated as “BA”) (52 parts by mass), methyl methacrylate (hereinafter, abbreviated as “MMA”) (20 parts by mass), and HEA (28 parts by mass) were used as raw materials of a copolymer, and a polymerization reaction was
15 caused, thereby obtaining an acrylic polymer.

2-Methacryloyloxyethyl isocyanate (hereinafter, abbreviated as “MOI”) (28 parts by mass, approximately 90 mol% of HEA) was added to this acrylic polymer, and an addition reaction was caused in an air flow at 50°C for 48 hours, thereby obtaining an intended pressure-sensitive adhesive resin (I-2a).

20 [0258]

[Manufacturing Example 3]

(Manufacturing of Pressure-Sensitive Adhesive Resin (I-2a))

Lauryl acrylate (hereinafter, abbreviated as “LA”) (80 parts by mass) and HEA (20 parts by mass) were used as raw materials of a copolymer, and a polymerization
25 reaction was caused, thereby obtaining an acrylic polymer.

MOI was added to this acrylic polymer so that the total mole number of isocyanate groups in MOI reached 0.8 times the total mole number of hydroxyl groups in HEA, and an addition reaction was caused in an air flow at 50°C for 48 hours, thereby obtaining an intended pressure-sensitive adhesive resin (I-2a).

5 [0259]

[Manufacturing Example 4]

(Manufacturing of Pressure-Sensitive Adhesive Resin (I-2a))

2EHA (40 parts by mass), vinyl acetate (hereinafter, abbreviated as “VAc”) (40 parts by mass), and HEA (20 parts by mass) were used as raw materials of a copolymer, and a polymerization reaction was caused, thereby obtaining an acrylic polymer.

MOI was added to this acrylic polymer so that the total mole number of isocyanate groups in MOI reached 0.8 times the total mole number of hydroxyl groups in HEA, and an addition reaction was caused in an air flow at 50°C for 48 hours, thereby obtaining an intended pressure-sensitive adhesive resin (I-2a).

15 [0260]

[Manufacturing Example 5]

(Manufacturing of Pressure-Sensitive Adhesive Resin (I-2a))

2EHA (80 parts by mass) and HEA (20 parts by mass) were used as raw materials of a copolymer, and a polymerization reaction was caused, thereby obtaining an acrylic polymer.

MOI was added to this acrylic polymer so that the total mole number of isocyanate groups in MOI reached 0.8 times the total mole number of hydroxyl groups in HEA, and an addition reaction was caused in an air flow at 50°C for 48 hours, thereby obtaining an intended pressure-sensitive adhesive resin (I-2a).

25 [0261]

[Example 1]

<Manufacturing of Protective Film Forming Sheet>

(Manufacturing of Thermosetting Resin Layer Forming Composition)

The polymer component (A)-1 (100 parts by mass), the epoxy resin (B1)-1 (135
5 parts by mass), the epoxy resin (B1)-2 (90 parts by mass), the epoxy resin (B1)-3 (150
parts by mass), the curing accelerator (C)-1 (180 parts by mass), the curing accelerator
(G)-1 (1 part by mass), and the filler (D)-1 (160 parts by mass) were dissolved in methyl
ethyl ketone and were stirred at 23°C, thereby obtaining a resin layer forming
composition (III-1) having a solid content concentration of 55% by mass as a
10 thermosetting resin layer forming composition.

[0262]

(Manufacturing of First Pressure-Sensitive Adhesive Composition)

A tolylene diisocyanate trimer adduct of trimethylolpropane (“CORONATE L”
manufactured by Tosoh Corporation) (0.5 parts by mass) was added as an
15 isocyanate-based crosslinking agent to the pressure-sensitive adhesive resin (I-2a)
obtained in Manufacturing Example 1 (100 parts by mass) and was stirred at 23°C,
thereby obtaining a first pressure-sensitive adhesive composition (I-2) having a solid
content concentration of 30% by mass as a first pressure-sensitive adhesive composition.
Meanwhile, the numbers of parts blended in the “manufacturing of the first
20 pressure-sensitive adhesive composition” are all solid content-equivalent values.

[0263]

(Manufacturing of First Protective Film Forming Sheet)

The above-obtained first pressure-sensitive adhesive composition was applied
onto a peeling-treated surface of a peeling film (“SP-PET381031” manufactured by
25 Lintec Corporation, thickness: 38 μm) obtained by carrying out a peeling treatment on a

single surface of a polyethylene terephthalate film with a silicone treatment and was heated and dried at 110°C for one minute, thereby forming a 30 µm-thick first pressure-sensitive adhesive layer on the peeling film.

Next, a 105 µm-thick stacked film formed by stacking a polyolefin film (thickness: 25 µm), an adhesive layer (thickness: 2.5 µm), a polyethylene terephthalate film (thickness: 50 µm), an adhesive layer (thickness: 2.5 µm), and a polyolefin film (thickness: 25 µm) in this order was attached as a first base material to an exposed surface of the first pressure-sensitive adhesive layer, thereby obtaining a first supporting sheet.

10 [0264]

The above-obtained thermosetting resin layer forming composition was applied to a peeling-treated surface of a peeling film (“SP-PET381031” manufactured by Lintec Corporation, thickness: 38 µm) obtained by carrying out a peeling treatment on a single surface of a polyethylene terephthalate film with a silicone treatment and was dried at 100°C for two minutes, thereby producing a 40 µm-thick thermosetting resin layer.

[0265]

Next, the peeling film was removed from the first pressure-sensitive adhesive layer of the above-obtained first supporting sheet, an exposed surface of the above-obtained thermosetting resin layer was attached to an exposed surface of the first pressure-sensitive adhesive layer, thereby obtaining a protective film forming sheet formed by stacking the first base material, the first pressure-sensitive adhesive layer, the thermosetting resin layer, and the peeling film in this order in the thickness direction.

[0266]

[Comparative Example 1]

(Manufacturing of First Pressure-Sensitive Adhesive Composition)

A tolylene diisocyanate trimer adduct of trimethylolpropane ("CORONATE L" manufactured by Tosoh Corporation) (1.0 part by mass) was added as an isocyanate-based crosslinking agent to the pressure-sensitive adhesive resin (I-2a) obtained in Manufacturing Example 2 (100 parts by mass) and was stirred at 23°C, thereby obtaining a first pressure-sensitive adhesive composition (I-2') having a solid content concentration of 30% by mass as a first pressure-sensitive adhesive composition. Meanwhile, the numbers of parts blended in the "manufacturing of the first pressure-sensitive adhesive composition" are all solid content-equivalent values.

10 [0267]

(Manufacturing of Protective Film Forming Sheet)

A first supporting sheet was obtained in the same manner as in Example 1 except for the fact that the first pressure-sensitive adhesive composition described in Example 1 was changed to the above-obtained first pressure-sensitive adhesive composition of Comparative Example 1.

15 [0268]

The above-obtained thermosetting resin layer forming composition was applied to a peeling-treated surface of a peeling film ("SP-PET381031" manufactured by Lintec Corporation, thickness: 38 μm) obtained by carrying out a peeling treatment on a single surface of a polyethylene terephthalate film with a silicone treatment and was dried at 100°C for two minutes, thereby producing a 40 μm -thick thermosetting resin layer.

20 [0269]

Next, the peeling film was removed from the first pressure-sensitive adhesive layer of the above-obtained first supporting sheet, an exposed surface of the above-obtained thermosetting resin layer, which was the same as that in Example 1, was

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attached to an exposed surface of the first pressure-sensitive adhesive layer, thereby obtaining a protective film forming sheet of Comparative Example 1 formed by stacking the first base material, the first pressure-sensitive adhesive layer, the thermosetting resin layer, and the peeling film in this order in the thickness direction.

5 [0270]

[Example 2]

(Manufacturing of First Pressure-Sensitive Adhesive Composition)

A tolylene diisocyanate trimer adduct of trimethylolpropane (“CORONATE L”
manufactured by Tosoh Corporation) (1.0 part by mass) was added as an
10 isocyanate-based crosslinking agent to the pressure-sensitive adhesive resin (I-2a)
obtained in Manufacturing Example 3 (100 parts by mass) and was stirred at 23°C,
thereby obtaining a first pressure-sensitive adhesive composition (I-2) having a solid
content concentration of 30% by mass as a first pressure-sensitive adhesive composition.
Meanwhile, the numbers of parts blended in the “manufacturing of the first
15 pressure-sensitive adhesive composition” are all solid content-equivalent values.

[0271]

(Manufacturing of Protective Film Forming Sheet)

A protective film forming sheet of Example 2 was obtained in the same manner
as in Example 1 except for the fact that the first pressure-sensitive adhesive composition
20 described in Example 1 was changed to the above-obtained first pressure-sensitive
adhesive composition of Example 2.

[0272]

[Example 3]

(Manufacturing of First Pressure-Sensitive Adhesive Composition)

25 A tolylene diisocyanate trimer adduct of trimethylolpropane (“CORONATE L”

manufactured by Tosoh Corporation) (1.0 part by mass) was added as an isocyanate-based crosslinking agent to the pressure-sensitive adhesive resin (I-2a) obtained in Manufacturing Example 4 (100 parts by mass) and was stirred at 23°C, thereby obtaining a first pressure-sensitive adhesive composition (I-2) having a solid content concentration of 30% by mass as a first pressure-sensitive adhesive composition. Meanwhile, the numbers of parts blended in the “manufacturing of the first pressure-sensitive adhesive composition” are all solid content-equivalent values.

[0273]

(Manufacturing of Protective Film Forming Sheet)

A protective film forming sheet of Example 3 was obtained in the same manner as in Example 1 except for the fact that the first pressure-sensitive adhesive composition described in Example 1 was changed to the above-obtained first pressure-sensitive adhesive composition of Example 3.

[0274]

[Example 4]

(Manufacturing of First Pressure-Sensitive Adhesive Composition)

A tolylene diisocyanate trimer adduct of trimethylolpropane (“CORONATE L” manufactured by Tosoh Corporation) (1.0 part by mass) was added as an isocyanate-based crosslinking agent to the pressure-sensitive adhesive resin (I-2a) obtained in Manufacturing Example 5 (100 parts by mass) and was stirred at 23°C, thereby obtaining a first pressure-sensitive adhesive composition (I-2) having a solid content concentration of 30% by mass as a first pressure-sensitive adhesive composition. Meanwhile, the numbers of parts blended in the “manufacturing of the first pressure-sensitive adhesive composition” are all solid content-equivalent values.

[0275]

(Manufacturing of Protective Film Forming Sheet)

A protective film forming sheet of Example 4 was obtained in the same manner as in Example 1 except for the fact that the first pressure-sensitive adhesive composition described in Example 1 was changed to the above-obtained first pressure-sensitive adhesive composition of Example 3.

[0276]

<Evaluation of Protective Film Forming Sheets>

Regarding the thermosetting resin layers and the first pressure-sensitive adhesive layers obtained in Example 1 and Comparative Example 1, the contact angles of pure water, diiodomethane, and 1-bromonaphthalene were obtained in an environment of a temperature of 23°C and a humidity of 50%, the respective surface free energies of a dispersion force component γ_s^d , a polar component γ_s^p , and a hydrogen bond component γ_s^h were obtained from the contact angles, and the surface free energy γ_s^{total} of the respective layer surfaces were obtained from the sum of the respective surface free energies.

The results are shown in Table 1.

In the respective protective film forming sheets of Example 1 and Comparative Example 1, the differences between γ_s^{total} of the thermosetting resin layer and γ_s^{total} of the first pressure-sensitive adhesive layer are as shown in Table 1.

In the respective protective film forming sheets of Example 1 and Comparative Example 1, the differences between the contact angle of the thermosetting resin layer with respect to water and the contact angle of the first pressure-sensitive adhesive layer with respect to water are also shown in Table 1.

[0277]

[Table 1]

		Thermosetting resin layer	First pressure-sensitive adhesive layer				
			Example 1	Comparative Example 1	Example 2	Example 3	Example 4
Contact angle [°]	H ₂ O	67.7	115.8	92.1	111.8	103.0	102.5
	CH ₂ I ₂	59.0	91.1	52.6	69.9	69.3	69.7
	C ₁₀ H ₇ Br	58.4	57.5	63.7	59.4	46.8	58.4
Surface free energy [mJ/m ²]	γ_s^d	24.4	18	20.2	23.5	28.1	25.5
	γ_s^p	5.4	0	25.5	0	0	0
	γ_s^h	10.3	0	0.6	0	0	0
	γ_s^{total}	40.1	18	46.3	23	28.1	25.5
Differences between γ_s^{total} of thermosetting resin layer and γ_s^{total} of first pressure-sensitive adhesive layer [mJ/m ²]			22.1	6.2	16.6	12.0	14.6
Differences between contact angle of thermosetting resin layer with respect to water and contact angle of first pressure-sensitive adhesive layer with respect to water [°]			48.1	24.4	44.1	35.3	34.8
Evaluation result			O	X	O	O	O

[0278]

The first pressure-sensitive adhesive layer obtained in each of Examples 1 to 4 and Comparative Example 1 was irradiated with UV under conditions of an illuminance of 230 mW/cm^2 and a light intensity of 760 mJ/cm^2 in a UV irradiation device (RAD-2000m/8 manufactured by Lintec Corporation), then, the contact angles of pure water, diiodomethane, and 1-bromonaphthalene were obtained in an environment of 23°C and a humidity of 50%, the respective surface free energies of the dispersion force component γ_s^d , the polar component γ_s^p , and the hydrogen bond component γ_s^h were obtained from the contact angles, and the surface free energy γ_s^{total} of the respective layer surfaces were obtained from the sum of the respective surface free energies.

The results are shown in Table 2 together with the results of non-cured thermosetting resin layers.

In the respective protective film forming sheets of Example 1 and Comparative Example 1, the differences between γ_s^{total} of the thermosetting resin layer and γ_s^{total} of the first pressure-sensitive adhesive layer after UV curing are as shown in Table 2.

In the respective protective film forming sheets of Example 1 and Comparative Example 1, the differences between the contact angle of the thermosetting resin layer with respect to water and the contact angle of the first pressure-sensitive adhesive layer with respect to water after UV curing are also as shown in Table 2.

[0279]

[Table 2]

		Thermosetting resin layer	First pressure-sensitive adhesive layer after UV curing				
			Example 1	Comparative Example 1	Example 2	Example 3	Example 4
Contact angle [°]	H ₂ O	67.7	86.9	89.4	108.1	89.7	91.7
	CH ₂ I ₂	59.0	49.3	43.7	70.0	46.7	48.5
	C ₁₀ H ₇ Br	58.4	42.2	30.8	59.8	40.0	43.0
Surface free energy [mJ/m ²]	γ_s^d	24.4	32.9	38.1	24.2	33.7	32.3
	γ_s^p	5.4	1.9	0.6	0	2.4	2.8
	γ_s^h	10.3	0.8	0.2	0	0.3	0.2
	γ_s^{total}	40.1	35.6	38.9	24.2	36.4	35.3
Differences between γ_s^{total} of thermosetting resin layer and γ_s^{total} of first pressure-sensitive adhesive layer after UV curing [mJ/m ²]			4.5	1.2	15.9	3.7	4.8
Differences between contact angle of thermosetting resin layer with respect to water and contact angle of first pressure-sensitive adhesive layer with respect to water after UV curing [°]			19.2	21.7	40.4	22.0	24.0

[0280]

<Evaluation of Peeling Property After UV Curing>

The peeling property after UV curing was evaluated in the following order after one week from the production of the protective film forming sheets of Examples 1 to 4 and Comparative Example 1.

The protective film forming sheet was attached onto a circuit surface of a 6 inch-sized bump-attached semiconductor wafer through thermal lamination at 70°C.

After the temperature of the attached protective film forming sheet returned to normal temperature (after approximately five minutes), the protective film forming sheet was irradiated with UV under conditions of an illuminance of 230 mW/cm² and a light intensity of 760 mJ/cm² in a UV irradiation device (RAD-2000m/8 manufactured by Lintec Corporation), thereby curing the first pressure-sensitive adhesive layer. After that, an attempt was made to peel the first supporting sheet from the thermosetting resin layer, and consequently, in the protective film forming sheets of Examples 1 to 4, it was possible to easily peel the first supporting sheet made up of the first base material and the first pressure-sensitive adhesive layer in the interface with the thermosetting resin layer (the peeling property was “favorable”); however, in the protective film forming sheet of Comparative Example 1, the first base material was peeled off while the first pressure-sensitive adhesive layer remained attached to the thermosetting resin layer or the first pressure-sensitive adhesive layer partially caused cohesion failure and remained on the surface of the thermosetting resin layer (the peeling property was “poor”).

[0281]

The difference between γ_s^{total} of the thermosetting resin layer and γ_s^{total} of the first pressure-sensitive adhesive layer after UV curing or the difference between the contact angle of the thermosetting resin layer with respect to water and the contact angle

of the first pressure-sensitive adhesive layer with respect to water after UV curing were not large differences as shown in Table 2, but a large difference appeared in terms of the peeling property between the first supporting sheet and the thermosetting resin layer.

That is, the difference between γ_s^{total} of the thermosetting resin layer and γ_s^{total} of the first pressure-sensitive adhesive layer before UV curing, not after UV curing, or the difference between the contact angle of the thermosetting resin layer with respect to water and the contact angle of the first pressure-sensitive adhesive layer before UV curing with respect to water has a significant influence on the peeling property between the first supporting sheet and the thermosetting resin layer.

10 [0282]

In the protective film forming sheets of Examples 1 to 4 and Comparative Example 1, the polymer component (A)-1 including butyl acrylate (BA) as a main component was used in the thermosetting resin layer. Therefore, in the first pressure-sensitive adhesive layers of Examples 1 to 4, the pressure-sensitive adhesive resin (I-2a) including 2-ethylhexyl acrylate (2EHA) or lauryl acrylate (LA) as a main component was used, and thus it was possible to set the difference in the surface free energy to 10 mJ/m² or more; in contrast, in the first pressure-sensitive adhesive layer of Comparative Example 1, the pressure-sensitive adhesive resin (I-2a) including butyl acrylate (BA) as a main component was used as in the thermosetting resin layer, and thus the difference in the surface free energy decreased.

20 [0283]

It is considered that approximately one week is taken to stabilize product qualities such as the pressure-sensitive adhesive force from the production of the protective film forming sheet. Therefore, in the protective film forming sheet of

25 Comparative Example 1 in which the difference between the surface free energy of the

thermosetting resin layer and the surface free energy of the first supporting sheet was small, it is considered that the components migrated in the interface between both elements, thus, the adhesive force abnormally increased, and consequently, poor peeling was caused.

5 In the protective film forming sheet of Example 1 in which the difference between the surface free energy of the thermosetting resin layer and the surface free energy of the first supporting sheet was large, it is considered that there was no migration of the components in the interface between both elements, the adhesive force was stabilized, and thus the easy peeling property became excellent in the interface between
10 the first supporting sheet and the thermosetting resin layer.

Industrial Applicability

[0284]

The present invention can be used to manufacture semiconductor chips and the
15 like having bumps in a connection pad portion which are used in a flip chip mounting method.

Reference Signs List

[0285]

20 1, 2, 3 ... protective film forming sheet, 11 ... first base material, 11a ... thermosetting resin layer-side surface of first base material, 12 ... curable resin layer, 12' ... first protective film, 13 ... first pressure-sensitive adhesive layer, 13a ... surface of first pressure-sensitive adhesive layer, 14 ... first interlayer, 101, 102, 103 ... first supporting sheet, 101a, 102a, 103a ... surface of first supporting sheet, 90 ... semiconductor wafer,

90a ... circuit surface of semiconductor wafer, 91 ... bump, 91a ... surface of bump, 911 ...
top of bump

CLAIMS

What is claimed is:

1. A protective film forming sheet formed by stacking a thermosetting resin layer on a first supporting sheet,
5 wherein the thermosetting resin layer is adhered to a surface having bumps of a semiconductor wafer and is cured by heat, whereby the first protective film is formed on the semiconductor wafer surface, and
a difference between a surface free energy of a first supporting sheet-side surface of the thermosetting resin layer before thermal curing and a surface free energy
10 of a thermosetting resin layer-side surface of the first supporting sheet is 10 mJ/m^2 or more.
2. The protective film forming sheet according to Claim 1,
wherein a difference between a contact angle of the first supporting sheet-side
15 surface of the thermosetting resin layer before thermal curing with respect to water and a contact angle of the thermosetting resin layer-side surface of the first supporting sheet with respect to water is 30° or more.