

## DESCRIPTION

## Title of Invention

## PROTECTIVE FILM-FORMING COMPOSITE SHEET

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## Technical Field

[0001]

The present invention relates to a protective film-forming composite sheet for forming a protective film on a rear surface of a semiconductor chip.

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Priority is claimed on Japanese Patent Application No. 2016-042689, filed on March 4, 2016, the content of which is incorporated herein by reference.

## Background Art

[0002]

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In recent years, semiconductor devices are manufactured using a mounting method which is referred to as a face down system. In a face down system, a semiconductor chip having an electrode such as a bump on a circuit surface is used so that the electrode and a substrate are bonded to each other. In some cases, the rear surface of the chip on a side opposite to the circuit surface is exposed.

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[0003]

A resin film formed of an organic material is formed on the exposed rear surface of the chip as a protective film and is occasionally taken into a semiconductor device as a semiconductor chip provided with a protective film. A protective film is used for preventing occurrence of cracks in a chip after a dicing step or packaging.

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[0004]

A protective film-forming composite sheet that includes a support sheet and a protective film-forming film on the support sheet is used for forming such a protective film. As the support sheet, for example, a base material made of a resin or a laminated structure of a base material, a pressure sensitive adhesive layer, and the like is used, and  
5 the lamination surface of the protective film-forming film or the pressure sensitive adhesive layer of the base material is subjected to a surface treatment in some cases. The protective film-forming composite sheet can be made into a sheet in which the protective film-forming film has a protective film-forming ability, the support sheet can function as a dicing sheet, and the protective film-forming film and the dicing sheet are  
10 integrated with each other.

[0005]

One or both surfaces of the base material before being processed to be used as a support sheet typically has an uneven shape. This is because, when the base material is wound to be formed as a roll, the contact surfaces between the base materials adhere to  
15 each other so that blocking occurs, and thus the base material becomes difficult to use in cases where the base material does not have an uneven shape. In a case where at least one of the contact surfaces between the base materials has an uneven shape, the area of the contact surfaces is decreased and thus the blocking is suppressed.

[0006]

20 In the related art, a protective film-forming composite sheet formed by using a base material having such an uneven surface typically has a configuration shown in FIG. 4. FIG. 4 is a cross-sectional view schematically showing an example of a protective film-forming composite sheet of the related art. In the accompanying drawings used for description below, in order to facilitate understanding of the characteristics of the  
25 protective film-forming composite sheet, portions serving as main portions are shown in

an enlarged manner in some cases for convenience so that the dimension ratios of respective constituent elements are not necessarily the same as the actual dimension ratios thereof.

[0007]

5           A protective film-forming composite sheet 9 of the related art shown here includes a support sheet 90; and a protective film-forming film 13 on the support sheet 90, the support sheet 90 has a laminated structure of a base material 91 and a pressure sensitive adhesive layer 12, and the protective film-forming film 13 is provided on the pressure sensitive adhesive layer 12. The protective film-forming film 13 becomes a  
10   protective film by being cured. Further, the protective film-forming composite sheet 9 includes a release film 15 on the protective film-forming film 13, and the release film 15 is removed at the time of using the protective film-forming composite sheet 9. In the protective film-forming composite sheet 9, a surface (rear surface) 90b of the support sheet 90 on a side opposite to a surface (front surface) 90a where the protective  
15   film-forming film 13 is provided, that is, a surface (rear surface) 91b of the base material 91 on a side opposite to a surface (front surface) 91a where the pressure sensitive adhesive layer 12 is provided is an uneven surface. In the protective film-forming composite sheet 9, since the rear surface 91b of the base material 91 is an uneven surface as described above, blocking is suppressed when the base material 91 is wound to be  
20   formed into a roll. In other words, adhesion between the laminated portions in the protective film-forming composite sheet 9, more specifically, adhesion between the rear surface 91b of the base material 91 and an exposed surface (front surface) 15a of the release film 15 is suppressed.

[0008]

25           In the protective film-forming composite sheet, the surface on the support sheet

side of the protective film formed of the protective film-forming film is printed (hereinafter, also referred to as “laser printing”) by being irradiated with laser light in some cases. The laser printing is performed by irradiating the surface with laser light from a side opposite to the side where the protective film of the support sheet is formed.

5 At this time, for example, in a case of the protective film-forming composite sheet 9, the protective film is irradiated with laser light through the support sheet 90 from the rear surface 91b side of the base material 91. However, since the rear surface 91b of the base material 91 is an uneven surface, there is a problem in that the light is irregularly reflected on the uneven surface so that the laser printing becomes unclear.

10 [0009]

As a protective film-forming composite sheet which is capable of preventing such irregular reflection of light, a protective film-forming composite sheet 8 having a configuration shown in FIG. 5 has been known (for example, see Patent Document 1).

FIG. 5 is a cross-sectional view schematically showing another example of a  
15 protective film-forming composite sheet of the related art.

[0010]

A protective film-forming composite sheet 8 of the related art shown here includes a support sheet 80; and a protective film-forming film 13 on the support sheet 90 similar to the protective film-forming composite sheet 9, the support sheet 80 has a  
20 laminated structure of a base material 81 and a pressure sensitive adhesive layer 12, and the protective film-forming film 13 is provided on the pressure sensitive adhesive layer 12. In this case of the support sheet 80, the disposition of an uneven surface on the base material 81 is opposite to that of the base material 91 in the support sheet 90. In other words, in the protective film-forming composite sheet 8, a surface (front surface) 81a of  
25 the base material 81 where the pressure sensitive adhesive layer 12 is provided is an

uneven surface, and a surface (rear surface) 81b of the base material 81 on a side opposite to the surface 81a is a smooth surface. The base material 81 in the support sheet 80, the protective film-forming film 13, and the release film 15 are respectively the same as the base material 91 in the support sheet 90, the protective film-forming film 13, and the release film 15.

[0011]

However, in the case of the protective film-forming composite sheet 8, since the rear surface 81b of the base material 81, that is, a surface (rear surface) 80b of the support sheet 80 on a side opposite to the surface (front surface) 80a where the pressure sensitive adhesive layer 12 is provided is a smooth surface, the rear surface 81b of the base material 81 and an exposed surface (front surface) 15a of the release film 15 adhere to each other, in other words, blocking cannot be suppressed when the protective film-forming composite sheet 8 is wound to be formed into a roll. In a case where blocking occurs, wrinkles are generated in the protective film-forming composite sheet 8 or the release film 15 is peeled off from the protective film-forming film 13 when the protective film-forming composite sheet 8 is fed from the roll. Further, the pressure sensitive adhesive layer 12 is required to have a sufficiently large thickness so as to eliminate the uneven shape from the surface 81a of the base material 81. In a case where the thickness thereof is not sufficiently large, since a surface (rear surface) 13b of the protective film-forming film 13 on the support sheet 80 side has an uneven shape by reflecting the uneven shape of the base material 81, there is a problem in that laser printing performed on the surface of the protective film formed from the protective film-forming film 13 on the support sheet side becomes unclear.

As described above, in the related art, a protective film-forming composite sheet which is capable of achieving both suppression of blocking and clear laser printing on a

protective film has not been present.

## Citation List

### Patent Literature

5 [0012]

[Patent Document 1] Japanese Patent No. 5432853

## Summary of Invention

### Technical Problem

10 [0013]

An object of the present invention is to provide a protective film-forming composite sheet which is used for forming a protective film on a rear surface of a semiconductor chip and is capable of suppressing blocking and performing clear laser printing on the protective film.

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### Solution to Problem

[0014]

According to the present invention, there is provided a protective film-forming composite sheet including: a support sheet; a protective film-forming film provided on one surface of the support sheet; and a coating layer provided on a surface of the support sheet on a side opposite to a side where the protective film-forming film is provided, in which a surface roughness Ra of a surface of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet is smaller than that of the surface of the support sheet on a side where the coating layer is provided.

25 [0015]

In the protective film-forming composite sheet of the present invention, a peeling force of a release film measured according to the following method using the protective film-forming composite sheet which further includes the release film on the protective film-forming film may be 10 mN/50 mm or less.

5 (Method of measuring peeling force of release film)

The protective film-forming composite sheet having a width of 50 mm and a length of 100 mm which includes the protective film-forming film on which the release film is provided is formed into a laminate whose one outermost layer is the coating layer and the other outermost layer is the release film by overlapping a plurality of the  
10 protective film-forming composite sheets such that all the coating layers are directed to the same direction and a total thickness of the coating layers is in a range of 10 to 60  $\mu\text{m}$ , the laminate is allowed to stand at 40°C for 3 days in a lamination direction of the protective film-forming composite sheet while a force of 980.665 mN is applied thereto, and the peeling force when the release film closest to the coating layer which is the  
15 outermost layer in the lamination direction is peeled off from the coating layer adjacent to the release film under conditions of a peeling rate of 300 mm/min and a peeling angle of 180° is measured.

[0016]

In the protective film-forming composite sheet of the present invention, the  
20 support sheet may include a base material and a pressure sensitive adhesive layer which are laminated on each other, and the protective film-forming composite sheet may be formed by laminating the coating layer, the base material, the pressure sensitive adhesive layer, and the protective film-forming film in this order.

In the protective film-forming composite sheet of the present invention, the  
25 pressure sensitive adhesive layer may be energy ray curable or non-energy ray curable.

In the protective film-forming composite sheet of the present invention, the protective film-forming film may be thermosetting or energy ray curable.

#### Advantageous Effects of Invention

5 [0017]

The protective film-forming composite sheet of the present invention is used for forming a protective film on a rear surface of a semiconductor chip. By using this protective film-forming composite sheet, blocking of the protective film-forming composite sheet can be suppressed and clear laser printing can be performed on the  
10 protective film.

#### Brief Description of Drawings

[0018]

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

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

FIG. 3 is a plan view showing a protective film-forming composite sheet produced in an example.

20 FIG. 4 is a cross-sectional view schematically showing an example of a protective film-forming composite sheet of the related art.

FIG. 5 is a cross-sectional view schematically showing another example of a protective film-forming composite sheet of the related art.

25 Description of Embodiments

[0019]

Protective film-forming composite sheet

A protective film-forming composite sheet according to the present invention includes a support sheet; a protective film-forming film provided on one surface of the support sheet; and a coating layer provided on the surface of the support sheet on a side opposite to a side where the protective film-forming film is provided, in which a surface roughness  $R_a$  of the surface of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet is smaller than that of the surface of the support sheet on a side where the coating layer is provided.

10 [0020]

In the protective film-forming composite sheet, the surface roughness  $R_a$  of the surface of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet is smaller than that of the surface of the support sheet on a side where the coating layer is provided. In other words, the surface of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet is a smooth surface or a surface with a degree of suppressed unevenness. Therefore, in a case where the surface of the coating layer with a low surface roughness  $R_a$  is irradiated with laser light, irregular reflection of laser light on the surface is suppressed.

15 Accordingly, the protective film obtained after the protective film-forming film is cured is irradiated with laser light through the support sheet from the coating layer side, clear laser printing can be performed on the protective film.

[0021]

Further, the coating layer in the protective film-forming composite sheet is easily and moderately slides against the material in contact with the coating layer and has antistatic properties. Therefore, adhesion between the laminated portions of the

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protective film-forming composite sheet, that is, blocking is suppressed when the protective film-forming composite sheet is wound to be formed into a roll.

[0022]

In the present specification, in a case where the protective film-forming film in  
5 the protective film-forming composite sheet is cured by being heated or being irradiated  
with energy rays to obtain a protective film, the sheet is referred to as a protective  
film-forming composite sheet as long as the laminated structure of the support sheet and  
the protective film is maintained. Further, in a case where the support sheet in the  
protective film-forming composite sheet has a laminated structure of the base material  
10 and the pressure sensitive adhesive layer, the sheet with a cured pressure sensitive  
adhesive layer is referred to as a protective film-forming composite sheet as long as the  
laminated structure of the base material, the cured product of the pressure sensitive  
adhesive layer, and the protective film-forming film or the protective film is maintained.

[0023]

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

A protective film-forming composite sheet 1 shown here includes a support  
sheet 10; a protective film-forming film 13 on one surface 10a of the support sheet 10;  
and a coating layer 14 on the other surface (rear surface) 10b of the support sheet 10.  
20 Further, the support sheet 10 is formed by a base material 11 and a pressure sensitive  
adhesive layer 12 being laminated on each other and includes the pressure sensitive  
adhesive layer 12 on one surface 11a of the base material 11; the coating layer 14 on the  
other surface (rear surface) 11b of the base material 11; and the protective film-forming  
film 13 on the pressure sensitive adhesive layer 12. Further, the protective film-forming  
25 composite sheet 1 further includes a release film 15 on the protective film-forming film

13, and the release film 15 is removed at the time of using the protective film-forming composite sheet 1. A protective film is obtained when the protective film-forming film 13 is cured.

[0024]

5 In the protective film-forming composite sheet 1, the pressure sensitive adhesive layer 12 is laminated on the surface 11a of the base material 11, and the protective film-forming film 13 is laminated on a part of the surface 12a of the pressure sensitive adhesive layer 12. Further, the release film 15 is laminated on the exposed surface on which the protective film-forming film 13 is not laminated in the surface 12a of the  
10 pressure sensitive adhesive layer 12 and a surface 13a (that is, the upper surface and the side surfaces) of the protective film-forming film 13.

A gap portion may be present between the release film 15 and the surface 12a of the pressure sensitive adhesive layer 12 or the surface 13a of the protective film-forming film 13. For example, the gap portion is likely to be generated in the side surfaces of  
15 the protective film-forming film 13 and in a region in the vicinity of the protective film-forming film 13 in the surface 12a of the pressure sensitive adhesive layer 12.

[0025]

In the protective film-forming composite sheet 1, the surface (rear surface) 10b of the support sheet 10 on a side opposite to the surface (front surface) 10a where the  
20 protective film-forming film 13 is provided, that is, the surface (rear surface) 11b of the base material 11 on a side opposite to the surface (front surface) 11a where the pressure sensitive adhesive layer 12 is provided is an uneven surface. In addition, the coating layer 14 is provided by covering this uneven surface. The surface roughness Ra of the surface (rear surface) 14b of the coating layer 14 on a side opposite to the surface (front  
25 surface) 14a where the coating layer 14 is in contact with the support sheet 10 (base

material 11) is smaller than that of the rear surface 10b of the support sheet 10 (that is, the rear surface 11b of the base material 11). In a case where laser printing is performed on the protective film (not shown) formed from the protective film-forming film 13, the surface of the protective film on the support sheet 10 side is irradiated with laser light from the coating layer 14 side. At this time, the surface roughness Ra of the rear surface 14b of the coating layer 14 is small, and thus irregular reflection of laser light on the coating layer 14 is suppressed. Therefore, clear laser printing can be performed on the protective film.

[0026]

10 In the present specification, the “surface roughness Ra” indicates a so-called arithmetic average roughness which is defined in JIS B0601:2001 unless otherwise noted.

[0027]

Further, since the protective film-forming composite sheet 1 includes the coating layer 14, adhesion between laminated portions of the protective film-forming composite sheet 1, that is, blocking is suppressed even in a case where the protective film-forming composite sheet 1 is wound to be formed into a roll. More specifically, adhesion between the rear surface 11b of the base material 11 and the exposed surface (front surface) 15a of the release film 15 is suppressed.

20 [0028]

The surface 11a of the base material 11 in the protective film-forming composite sheet 1 is a smooth surface here, but may be an uneven surface with a low smoothness. However, as described below, it is preferable that the surface 11a of the base material 11 is a smooth surface from the viewpoint that generation of a gap portion between the base material 11 and the pressure sensitive adhesive layer 12 is suppressed and the protective

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film-forming composite sheet 1 are likely to have preferable characteristics.

[0029]

When the protective film-forming composite sheet 1 shown in FIG. 1 is used, the release film 15 is removed and the rear surface of a semiconductor wafer (not shown) is allowed to adhere to the surface 13a of the protective film-forming film 13. Further, the exposed surface, in the surface 12a of the pressure sensitive adhesive layer 12, on which the protective film-forming film 13 is not laminated is allowed to adhere to a jig such as a ring frame.

[0030]

FIG. 2 is a cross-sectional view schematically showing another embodiment of a protective film-forming composite sheet according to the present invention. In FIG. 2, the same constituent elements as those shown in FIG. 1 are denoted by the same reference numerals as in FIG. 1 and the description thereof will not be repeated. The same applies to the accompanying drawings subsequent to FIG. 2.

[0031]

In a protective film-forming composite sheet 2 shown here, a protective film-forming film 23 is laminated on the entire surface 12a of a pressure sensitive adhesive layer 12, and an adhesive layer 16 for a jig is laminated on a part of a surface 23a of the protective film-forming film 23. Further, in the protective film-forming composite sheet 2, a release film 15 is laminated on the exposed surface on which the adhesive layer 16 for a jig is not laminated in the surface 23a of the protective film-forming film 23 and a surface 16a (the upper surface and the side surfaces) of the adhesive layer 16 for a jig. Except for these points, the protective film-forming composite sheet 2 is the same as the protective film-forming composite sheet 1 shown in FIG. 1.

[0032]

A gap portion may be present between the release film 15 and the surface 23a of the protective film-forming film 23 or the surface 16a of the adhesive layer 16 for a jig.

For example, the gap portion is likely to be generated in the side surfaces of the adhesive

5 layer 16 for a jig and in a region in the vicinity of the adhesive layer 16 for a jig in the surface 23a of the protective film-forming film 23.

[0033]

Even in the protective film-forming composite sheet 2, similar to the case of the

protective film-forming composite sheet 1, the rear surface 10b (the rear surface 11b of

10 the base material 11) of the support sheet 10 is an uneven surface, and the coating layer

14 is provided by covering the uneven surface. Accordingly, the surface roughness Ra

of the rear surface 14b of the coating layer 14 is smaller than that of the rear surface 10b

of the support sheet 10. Therefore, clear laser printing can be performed on the

protective film formed from the protective film-forming film 23.

15 [0034]

Since the protective film-forming composite sheet 2 includes the coating layer

14, adhesion between laminated portions of the protective film-forming composite sheet

2, that is, blocking is suppressed even in a case where the protective film-forming

composite sheet 2 is wound to be formed into a roll.

20 [0035]

When the protective film-forming composite sheet 2 shown in FIG. 2 is used, the

release film 15 is removed and the rear surface of the semiconductor wafer (not shown) is

allowed to adhere to the surface 23a of the protective film-forming film 23. Further, the

upper surface in the surface 16a of the adhesive layer 16 for a jig is allowed to adhere to

25 a jig such as a ring frame.

[0036]

The protective film-forming composite sheet of the present invention is not limited to those shown in FIGS. 1 and 2, a part of the configurations shown in FIGS. 1 and 2 may be changed or eliminated within the range not damaging the effects of the present invention, and other configurations may be added to the configurations which have been described so far.

Hereinafter, each configuration of the protective film-forming composite sheet according to the present invention will be described in more detail.

[0037]

10 Support sheet

The support sheet is not particularly limited as long as the protective film-forming film can be provided thereon. Examples of the support sheet include a sheet that plays a role of a release sheet used for preventing attachment of dust or the like to the surface of the protective film-forming film; and a sheet that plays a role of a dicing sheet used for protecting the surface of the protective film-forming film by performing a dicing step or the like.

Preferred examples of the support sheet include a sheet formed of only a base material which has been typically used in the field of processing sheets of semiconductor wafers; and a sheet formed by laminating a base material and a pressure sensitive adhesive layer on each other.

[0038]

The support sheet may be formed of one layer (single layer) or two or more layers (plurality of layers). In a case where the support sheet is formed of a plurality of layers, a plurality of these layers may be the same as or different from one another. In other words, all layers may be the same as or different from one another or only some

layers may be the same as one another. Further, in a case where a plurality of layers are different from one another, the combination of a plurality of these layers is not particularly limited. Here, the expression of “a plurality of layers are different from one another” means that at least one of the materials and the thicknesses of respective layers are different from one another.

[0039]

The thickness of the support sheet may be appropriately selected depending on the intended purpose thereof, but is preferably in a range of 10 to 500  $\mu\text{m}$ , more preferably in a range of 20 to 350  $\mu\text{m}$ , and particularly preferably in a range of 30 to 200  $\mu\text{m}$  from the viewpoints of performing clearer laser printing on the protective film, imparting sufficient flexibility to the protective film-forming composite sheet, and improving the adhesiveness of the support sheet to the semiconductor wafer. Further, for example, the thickness thereof may be in a range of 40 to 175  $\mu\text{m}$  or in a range of 50 to 150  $\mu\text{m}$ .

Here, the “thickness of the support sheet” indicates the total thickness of respective layers constituting the support sheet. For example, in a case where the support sheet is formed by laminating a base material and a pressure sensitive adhesive layer, the thickness of the support sheet indicates the total value of the thickness of the base material and the thickness of the pressure sensitive adhesive layer.

Further, at least one surface of the support sheet may be an uneven surface. In a portion having a projection in the uneven surface of the support sheet, the thickness of the support sheet can be calculated using the tip of this projection as one starting point.

[0040]

Base material

As the material of the base material, various resins are preferable.

Specific examples of the resins include polyethylene (such as low density polyethylene (LDPE), linear low density polyethylene (LLDPE), or high density polyethylene (HDPE)), polypropylene, an ethylene-propylene copolymer, polybutene, polybutadiene, polymethylpentene, polyvinyl chloride, a vinyl chloride copolymer, polyethylene terephthalate, polyethylene naphthalate, polybutylene terephthalate, polyurethane, polyurethane acrylate, polyimide, an ethylene-vinyl acetate copolymer, an ionomer resin, an ethylene-(meth)acrylic acid copolymer, an ethylene-(meth)acrylic acid ester copolymer, polystyrene, polycarbonate, a fluorine resin, and a water additive, a modified product, a cross-linked product, or a copolymer of any of these resins.

In the present specification, the concept “(meth)acrylic acid” includes both of “acrylic acid” and “methacrylic acid”.

[0041]

In a case where the support sheet is formed by laminating a base material and other layers such as a pressure sensitive adhesive layer, the thickness of the base material can be appropriately selected depending on the intended purpose thereof, but is preferably in a range of 15 to 300  $\mu\text{m}$  and more preferably in a range of 20 to 200  $\mu\text{m}$ . Further, for example, the thickness thereof may be in a range of 30 to 175  $\mu\text{m}$ , in a range of 40 to 150  $\mu\text{m}$ , or in a range of 50 to 125  $\mu\text{m}$ . In a case where the thickness of the base material is in the above-described range, the flexibility of the protective film-forming composite sheet and the adhesiveness of the base material to the semiconductor wafer or the semiconductor chip are further improved.

[0042]

The base material may be formed of one layer (single layer) or two or more layers (plurality of layers). In a case where the base material is formed of a plurality of

layers, a plurality of these layers may be the same as or different from one another.

Here, the expression of “a plurality of layers may be the same as or different from one another” has the same definition as in the case of the support sheet described above.

In the case where the base material is formed of a plurality of layers, the total  
5 thickness of respective layers may be set to be the above-described preferable thickness of the base material.

[0043]

The surface roughness Ra of the surface (front surface) of the base material on  
which the pressure sensitive adhesive layer is provided is preferably in a range of 0.001  
10 to 0.1  $\mu\text{m}$ , more preferably in a range of 0.005 to 0.08  $\mu\text{m}$ , and particularly preferably in  
a range of 0.01 to 0.04  $\mu\text{m}$ . In a case where the surface roughness Ra of the surface of  
the base material is less than or equal to the above-described upper limit, clear laser  
printing can be performed on the protective film.

The surface roughness Ra of the surface of the base material can be adjusted by  
15 changing conditions for forming the base material or conditions for the surface treatment  
of the base material.

[0044]

Examples of a method of dicing a semiconductor wafer to be individualized into  
a semiconductor chip include a method of using blade dicing for cutting a semiconductor  
20 wafer using a blade; a method of using laser dicing for cutting a semiconductor wafer  
through laser irradiation; and a method of using water dicing for cutting a semiconductor  
wafer by blowing water containing an abrasive.

Further, as the method of individualizing a semiconductor wafer into a  
semiconductor chip, a method of applying laser light in an infrared region so as to be  
25 focused on a focal point set in a semiconductor wafer and applying a force to the

semiconductor wafer after a modified layer is formed in the semiconductor wafer so that the semiconductor wafer is divided and individualized in the portion where the modified layer is formed is exemplary example not included in the methods using the above-described dicing.

- 5            In a case where the surface roughness Ra of the surface of the base material is in a range of 0.01 to 0.2  $\mu\text{m}$ , the protective film-forming composite sheet including such a base material is suitably used when the semiconductor wafer is individualized by forming a modified layer in the semiconductor wafer.

[0045]

- 10           The surface roughness Ra of the surface (rear surface) of the base material on a side opposite to the surface (front surface) where the pressure sensitive adhesive layer is provided, that is, the surface roughness Ra of the surface (rear surface) of the support sheet on a side opposite to the surface (front surface) where the protective film-forming film is provided is preferably in a range of 0.001 to 4  $\mu\text{m}$ , more preferably in a range of  
15   0.005 to 3.7  $\mu\text{m}$ , still more preferably in a range of 0.01 to 3.4  $\mu\text{m}$ , and particularly preferably in a range of 0.02 to 3.1  $\mu\text{m}$ . In a case where the surface roughness Ra of the rear surface of the base material is less than or equal to the above-described upper limit, the surface roughness Ra of the surface of the coating layer on a side opposite to the side where the coating layer is in contact with the support sheet can be easily decreased and  
20   clear laser printing can be more easily performed on the protective film.

The surface roughness Ra of the rear surface of the base material can be adjusted by changing the conditions for forming the base material and the conditions for the surface treatment of the base material.

[0046]

The resin serving as the material of the base material may be cross-linked.

Further, the base material using a resin as a constituent material may be formed into a sheet by extrusion forming of a thermoplastic resin, stretched, or formed into a sheet by being thinned or cured by known means for a curable resin.

5 Further, the base material may be colored or printed.

[0047]

From the viewpoint that the base material has expanding suitability and improved pick-up suitability in a case where the base material has excellent heat resistance and moderate flexibility, it is preferable that the base material contains  
10 polypropylene.

The base material containing polypropylene may be a base material formed of a single layer that is formed of only polypropylene or a plurality of layers or may be a base material formed by laminating a plurality of layers (two or more layers) of a polypropylene layer and resin layers other than polypropylene.

15 In a case where the protective film-forming film is thermosetting, deterioration of the base material due to heat is suppressed and occurrence of defects in the manufacturing process of a semiconductor device can be effectively suppressed by means of the base material having the heat resistance.

[0048]

20 In order to improve the adhesiveness between the pressure sensitive adhesive layer provided on the base material and the protective film-forming film, the surface of the base material may be subjected to a roughening treatment such as a sand blast treatment or a solvent treatment; or an oxidation treatment such as a corona discharge treatment, an electron beam irradiation treatment, a plasma treatment, an ozone and  
25 ultraviolet ray irradiation treatment, a flame treatment, a chromic acid treatment, or a hot

air treatment. In addition, the surface of the base material may be subjected to a primer treatment.

[0049]

Pressure sensitive adhesive layer

5 As the pressure sensitive adhesive layer, a known one can be used as appropriate.

The pressure sensitive adhesive layer can be formed using a pressure sensitive adhesive composition containing various components such as a pressure sensitive adhesive for constituting the pressure sensitive adhesive layer. The ratio of the amounts  
10 of components in the pressure sensitive adhesive composition that do not vaporize at ordinary temperature is typically the same as the ratio of the amounts of components in the pressure sensitive adhesive layer. In the present specification, “ordinary temperature” indicates a temperature which is not particularly cooled or heated, that is, normal temperature, and a temperature of 15°C to 25°C is an exemplary example.

15 [0050]

The thickness of the pressure sensitive adhesive layer can be appropriately selected depending on the intended purpose thereof, but is preferably in a range of 1 to 100 μm, more preferably in a range of 2 to 80 μm, and particularly preferably in a range of 3 to 50 μm. Further, for example, the thickness thereof may be in a range of 3 to 35  
20 μm, in a range of 3 to 20 μm, or in a range of 3 to 10 μm.

[0051]

The pressure sensitive adhesive layer may be formed of one layer (single layer) or two or more layers (plurality of layers). In a case where the pressure sensitive adhesive layer is formed of a plurality of layers, a plurality of these layers may be the

same as or different from one another. Here, the expression of “a plurality of layers may be the same as or different from one another” has the same definition as in the case of the support sheet described above.

In the case where the pressure sensitive adhesive layer is formed of a plurality of  
5 layers, the total thickness of respective layers may be set to be the above-described preferable thickness of the pressure sensitive adhesive layer.

[0052]

Examples of the pressure sensitive adhesive include a pressure sensitive  
adhesive resin such as an acrylic resin, a urethane-based resin, a rubber-based resin, a  
10 silicone-based resin, or a vinyl ether-based resin. In a case of classification from the viewpoint of the function of the resin, an energy ray curable resin or the like is an exemplary example of the pressure sensitive adhesive.

[0053]

In the present specification, the “energy ray” indicates one that has an energy  
15 quantum in an electromagnetic wave or a charged particle ray, and examples thereof include ultraviolet rays, radiation, and electron beams. Ultraviolet rays can be applied using a high pressure mercury lamp, a fusion H lamp, a xenon lamp, a black light, or an LED lamp as an ultraviolet ray source. The electron beams can be used by applying those generated by an electron beam accelerator or the like.

20 In the present specification, the term “energy ray curable” indicates the property of being cured by irradiation with energy rays and the term “non-energy ray curable” indicates the property of not being cured even by irradiation with energy rays.

[0054]

Examples of the energy ray curable resin include resins having polymerizable  
25 groups such as a (meth)acryloyl group and a vinyl group.

As the pressure sensitive adhesive resin, an acrylic resin is preferable and a (meth)acrylic acid ester copolymer having a constitutional unit derived from (meth)acrylic acid ester is more preferable.

[0055]

5           The pressure sensitive adhesive layer becomes energy ray curable in a case where the pressure sensitive adhesive layer contains components to be polymerized by irradiation with energy rays such as an energy ray curable resin, and a semiconductor chip provided with a protective film is likely to be picked up by irradiating the pressure sensitive adhesive layer with energy rays to decrease the tackiness thereof. Such a  
10   pressure sensitive adhesive layer can be formed using various pressure sensitive adhesive compositions containing components to be polymerized by irradiation with energy rays.

[0056]

<<Pressure sensitive adhesive composition>>

Preferred examples of the pressure sensitive adhesive composition include those  
15   containing components to be polymerized by irradiation with energy rays. Examples of such a pressure sensitive adhesive composition include a composition that contains an acrylic resin and an energy ray polymerizable compound (hereinafter, also abbreviated as a “pressure sensitive adhesive composition (i)); and a composition that contains an acrylic resin containing a hydroxyl group and a polymerizable group in a side chain and  
20   an isocyanate-based cross-linking agent (hereinafter, also abbreviated as a “pressure sensitive adhesive composition (ii)”). Examples of the acrylic resin which contains a hydroxyl group and a polymerizable group in a side chain include an acrylic resin which contains a hydroxyl group and a polymerizable group in a side chain through a urethane bond.

25           [0057]

<Pressure sensitive adhesive composition (i)>

The pressure sensitive adhesive composition (i) contains an acrylic resin and an energy ray polymerizable compound as indispensable components.

Hereinafter, each component will be described.

5 [0058]

[Acrylic resin]

Preferred examples of the acrylic resin in the pressure sensitive adhesive composition (i) include a (meth)acrylic acid ester copolymer obtained by polymerizing (meth)acrylic acid ester as a monomer and another monomer other than (meth)acrylic acid ester used as necessary.

[0059]

Examples of the (meth)acrylic acid ester include (meth)acrylic acid alkyl ester in which an alkyl group constituting alkyl ester has a chain structure having 1 to 18 carbon atoms such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, n-octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), a pentadecyl (meth)acrylate group, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, octadecyl (meth)acrylate (stearyl (meth)acrylate), or isooctadecyl (meth)acrylate (isostearyl (meth)acrylate); (meth)acrylic acid cycloalkyl ester such as isobornyl (meth)acrylate or dicyclopentanyl (meth)acrylate; (meth)acrylic acid aralkyl ester such as benzyl (meth)acrylate; (meth)acrylic acid cycloalkenyl ester such as (meth)acrylic acid dicyclopentenyl ester; (meth)acrylic acid cycloalkenyloxy alkyl ester such as

(meth)acrylic acid dicyclopentenyl ether; imide (meth)acrylate; glycidyl group-containing (meth)acrylic acid ester such as glycidyl (meth)acrylate; and hydroxyl group-containing (meth)acrylic acid ester 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, or 4-hydroxybutyl (meth)acrylate.

[0060]

Examples of the monomer other than (meth)acrylic acid ester include (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene, and N-methylol acrylamide.

[0061]

Various monomers such as (meth)acrylic acid ester constituting an acrylic resin, monomers other than the (meth)acrylic acid ester, and the like may be formed of only one or two or more kinds thereof.

[0062]

The acrylic resin contained in the pressure sensitive adhesive composition (i) may be formed of only one or two or more kinds thereof.

[0063]

The amount of the acrylic resin in the pressure sensitive adhesive composition (i) is preferably in a range of 40% to 99% by mass and more preferably in a range of 50% to 91% by mass with respect to the total amount of all components contained in the pressure sensitive adhesive composition (i) other than the solvent.

[0064]

[Energy ray polymerizable compound]

The energy ray polymerizable compound is a compound polymerized and cured

by irradiation with energy rays, and examples thereof include a compound containing an energy ray polymerizable group such as an energy ray curable double bond in a molecule.

[0065]

5           Examples of the energy ray polymerizable compound include a low-molecular-weight compound (a monofunctional or polyfunctional monomer or oligomer) containing an energy ray polymerizable group.

More specific examples of the energy ray polymerizable compound include acrylates such as acrylate such as trimethylolpropane triacrylate, tetramethylolmethane  
10   tetraacrylate, pentaerythritol triacrylate, dipentaerythritol monohydroxypentaacrylate, dipentaerythritol hexaacrylate, 1,4-butylene glycol diacrylate, or 1,6-hexanediol diacrylate; cyclic aliphatic skeleton-containing acrylate such as dicyclopentadiene dimethoxy diacrylate; and an acrylate-based compound such as polyethylene glycol diacrylate, oligoester acrylate, urethane acrylate oligomer, epoxy-modified acrylate,  
15   polyether acrylate, or itaconic acid oligomer.

[0066]

The molecular weight of the energy ray polymerizable compound is preferably in a range of 100 to 30000 and more preferably in a range of 300 to 10000.

[0067]

20           The energy ray polymerizable compound contained in the pressure sensitive adhesive composition (i) may be formed of only one or two or more kinds thereof.

[0068]

The amount of the energy ray polymerizable compound in the pressure sensitive adhesive composition (i) is preferably in a range of 1 to 125 parts by mass and more  
25   preferably in a range of 10 to 125 parts by mass with respect to 100 parts by mass of the

amount of the acrylic resin.

[0069]

[Photopolymerization initiator]

The pressure sensitive adhesive composition (i) may contain a  
 5 photopolymerization initiator other than the acrylic resin and the energy ray  
 polymerizable compound.

A known one may be used as the photopolymerization initiator.

Specific examples of the photopolymerization initiator include an  $\alpha$ -ketol-based  
 compound such as 4-(2-hydroxyethoxy)phenyl(2-hydroxy-2-propyl)ketone,  
 10  $\alpha$ -hydroxy- $\alpha,\alpha'$ -dimethylacetophenone, 2-methyl-2-hydroxypropiophenone,  
 1-hydroxycyclohexylphenylketone, or  
 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]phenyl}-2-methyl-propan-1-  
 one; an acetophenone-based compound such as methoxyacetophenone,  
 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxyacetophenone, or  
 15 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one; a benzoin ether-based  
 compound such as benzoin ethyl ether, benzoin isopropyl ether, or anisoin methyl ether; a  
 ketal-based compound such as benzyl dimethyl ketal; an aromatic sulfonyl  
 chloride-based compound such as 2-naphthalene sulfonyl chloride; a photoactive  
 oxime-based compound such as  
 20 1-phenone-1,1-propanedione-2-(o-ethoxycarbonyl)oxime; a benzophenone-based  
 compound such as benzophenone, benzoylbenzoic acid, or  
 3,3'-dimethyl-4-methoxybenzophenone; a thioxanthone-based compound such as  
 thioxanthone, 2-chlorothioxanthone, 2-methylthioxanthone, 2,4-dimethylthioxanthone,  
 isopropylthioxanthone, 2,4-dichlorothioxanthone, 2,4-diethylthioxanthone, or  
 25 2,4-diisopropylthioxanthone; camphor quinone; halogenated ketone; acyl phosphine

oxide; and acyl phosphonate.

[0070]

The photopolymerization initiator contained in the pressure sensitive adhesive composition (i) may be formed of only one or two or more kinds thereof.

5 [0071]

In a case of using the photopolymerization initiator, the amount of the photopolymerization initiator in the pressure sensitive adhesive composition (i) is preferably in a range of 0.1 to 10 parts by mass and more preferably in a range of 1 to 5 parts by mass with respect to 100 parts by mass of the amount of the energy ray  
10 polymerizable compound. In a case where the amount of the photopolymerization initiator is greater than or equal to the above-described lower limit, the effects obtained by using a photopolymerization initiator can be sufficiently obtained. Further, in a case where the amount of the photopolymerization initiator is less than or equal to the above-described upper limit, generation of by-products due to an excessive amount of  
15 photopolymerization initiator is suppressed and the pressure sensitive adhesive layer is more satisfactorily cured.

[0072]

[Cross-linking agent]

The pressure sensitive adhesive composition (i) may contain a cross-linking  
20 agent other than the acrylic resin and the energy ray polymerizable compound.

Examples of the cross-linking agent include an organic polyvalent isocyanate compound and an organic polyvalent imine compound.

[0073]

Examples of the organic polyvalent isocyanate compound include an aromatic  
25 polyvalent isocyanate compound, an aliphatic polyvalent isocyanate compound, an

alicyclic polyvalent isocyanate compound, trimers of these compounds, an isocyanurate product, an adduct product, and a terminal isocyanate urethane prepolymer obtained by reacting the aromatic polyvalent isocyanate compound, the aliphatic polyvalent isocyanate compound or the alicyclic polyvalent isocyanate compound, and a polyol compound. The adduct product indicates a reactant of the aromatic polyvalent isocyanate compound, the aliphatic polyvalent isocyanate compound or the alicyclic polyvalent isocyanate compound, and a low-molecular active hydrogen-containing compound such as ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane, or castor oil.

10 [0074]

More specific examples of the organic polyvalent 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-methyl diphenylmethane diisocyanate; hexamethylene diisocyanate; isophorone diisocyanate; dicyclohexylmethane-4,4'-diisocyanate; dicyclohexylmethane-2,4'-diisocyanate; a compound obtained by adding any or both of tolylene diisocyanate and hexamethylene diisocyanate to all or some hydroxyl groups in a polyol such as trimethylolpropane; and lysine diisocyanate.

20 [0075]

Examples of the organic polyvalent imine compound include N,N-diphenylmethane-4,4'-bis(1-aziridinecarboxamide), trimethylolpropane-tri- $\beta$ -aziridinyl propionate, tetramethylolmethane-tri- $\beta$ -aziridinyl propionate, and N,N'-toluene-2,4-bis(1-aziridinecarboxamide)triethylene melamine.

25 [0076]

In a case where an isocyanate compound is used as a cross-linking agent, it is preferable to use a hydroxyl group-containing polymer as an acrylic resin. In a case where the cross-linking agent contains an isocyanate group and the acrylic resin contains a hydroxyl group, a cross-linked structure can be easily introduced into the pressure sensitive adhesive layer by reacting the isocyanate group with the hydroxyl group.

[0077]

The cross-linking agent contained in the pressure sensitive adhesive composition (i) may be formed of only one or two or more kinds thereof.

[0078]

In a case of using a cross-linking agent, the amount of the cross-linking agent in the pressure sensitive adhesive composition (i) is preferably in a range of 0.01 to 20 parts by mass and more preferably in a range of 0.1 to 16 parts by mass with respect to 100 parts by mass of the amount of the acrylic resin.

[0079]

[Solvent]

It is preferable that the pressure sensitive adhesive composition (i) further contain a solvent other than the acrylic resin and the energy ray polymerizable compound.

The solvent is not particularly limited.

Preferred examples thereof include a hydrocarbon such as toluene or xylene; an alcohol such as methanol, ethanol, 2-propanol, isobutyl alcohol (2-methylpropan-1-ol), or 1-butanol; an ester such as ethyl acetate; a ketone such as acetone or methyl ethyl ketone; an ether such as tetrahydrofuran; and an amide (a compound having an amide bond) such as dimethylformamide or N-methylpyrrolidone.

The solvent contained in the pressure sensitive adhesive composition (i) may be

formed of only one or two or more kinds thereof.

[0080]

The amount of the solvent in the pressure sensitive adhesive composition (i) in a case where the pressure sensitive adhesive composition (i) contains a solvent is

5 preferably in a range of 40% to 90% by mass and more preferably in a range of 50% to 80% by mass.

[0081]

[Other components]

The pressure sensitive adhesive composition (i) may contain other components  
10 which do not correspond to the photopolymerization initiator, the cross-linking agent, and the solvent other than the acrylic resin and the energy ray polymerizable compound within the range not damaging the effects of the present invention.

Other components may be known, can be appropriately selected depending on the intended purpose thereof, and is not particularly limited. Preferred examples of  
15 other components include various additives such as a dye, a pigment, a deterioration inhibitor, an antistatic agent, a flame retardant, a silicone compound, and a chain transfer agent.

Other components contained in the pressure sensitive adhesive composition (i) may be formed of only one or two or more kinds thereof.

20 [0082]

<Pressure sensitive adhesive composition (ii)>

The pressure sensitive adhesive composition (ii) contains an acrylic resin containing a hydroxyl group and a polymerizable group in a side chain; and an isocyanate-based cross-linking agent as indispensable components. Here, as the acrylic  
25 resin, an acrylic resin containing a hydroxyl group and a polymerizable group in a side

chain through a urethane bond is an exemplary example.

In a case of using the pressure sensitive adhesive composition (ii), since the acrylic resin contains a polymerizable group in a side chain, peeling properties from an adherend due to degradation of tackiness of the pressure sensitive adhesive layer after the polymerization reaction (curing) are improved and the pick-up properties of the semiconductor chip provided with a protective film are improved compared to a case of a polymerization reaction through irradiation with energy rays using the energy ray polymerizable compound as in the pressure sensitive adhesive composition (i).

In the present specification, the description of “acrylic resin” in the pressure sensitive adhesive composition (ii) indicates the “acrylic resin containing a polymerizable group in a side chain” unless otherwise noted.

[0083]

[Acrylic resin]

Examples of the acrylic resin containing a polymerizable group in a side chain include those obtained by reacting an isocyanate group of a compound, which contains an isocyanate group and a polymerizable group, with a hydroxyl group of a hydroxyl group-containing copolymer obtained by copolymerizing (meth)acrylic acid ester free from a hydroxyl group (in the present specification, also referred to as “(meth)acrylic acid ester free from a hydroxyl group”) and a hydroxyl group-containing compound such as (meth)acrylic acid ester containing a hydroxyl group (in the present specification, also referred to as “hydroxyl group-containing (meth)acrylic acid ester”) as monomers and forming a urethane bond.

[0084]

Examples of the (meth)acrylic acid ester free from a hydroxyl group include those other than the hydroxyl group-containing (meth)acrylic acid ester among examples

of the (meth)acrylic acid ester in the pressure sensitive adhesive composition (i).

Examples of the hydroxyl group-containing compound are the same as those for the hydroxyl group-containing (meth)acrylic acid ester in the pressure sensitive adhesive composition (i).

- 5           The (meth)acrylic acid ester free from a hydroxyl group and the hydroxyl group-containing compound constituting the acrylic resin may be respectively formed of only one or two or more kinds thereof.

[0085]

- 10           Examples of the compound containing an isocyanate group and a polymerizable group include isocyanate group-containing (meth)acrylic acid ester such as 2-metacryloyloxy ethyl isocyanate.

The compound containing an isocyanate group and a polymerizable group constituting the acrylic resin may be formed of only one or two or more kinds thereof.

[0086]

- 15           The acrylic resin contained in the pressure sensitive adhesive composition (ii) may be formed of only one or two or more kinds thereof.

[0087]

- 20           The amount of the acrylic resin of the pressure sensitive adhesive composition (ii) is preferably in a range of 80% to 99% by mass and more preferably in a range of 90% to 97% by mass with respect to the total amount of all components contained in the pressure sensitive adhesive composition (ii) other than the solvent.

[0088]

[Isocyanate-based cross-linking agent]

- 25           Examples of the isocyanate-based cross-linking agent are the same as those for the organic polyvalent isocyanate compound which is the cross-linking agent in the

pressure sensitive adhesive composition (i).

[0089]

The isocyanate-based cross-linking agent contained in the pressure sensitive adhesive composition (ii) may be formed of only one or two or more kinds thereof.

5 [0090]

The number of moles of the isocyanate group contained in the isocyanate-based cross-linking agent in the pressure sensitive adhesive composition (ii) is preferably 0.2 to 3 times the number of moles of the hydroxyl group contained in the acrylic resin in the pressure sensitive adhesive composition (ii). In a case where the number of moles of  
10 the isocyanate group is greater than or equal to the above-described lower limit, peeling properties from an adherend due to degradation of tackiness of the pressure sensitive adhesive layer after curing are improved and the pick-up properties of the semiconductor chip provided with a protective film are improved. Further, in a case where the number of moles of the isocyanate group is less than or equal to the above-described upper limit,  
15 generation of by-products due to the reaction between isocyanate-based cross-linking agents can be further suppressed.

[0091]

It is preferable that the amount of the isocyanate-based cross-linking agent in the pressure sensitive adhesive composition (ii) is appropriately adjusted such that the  
20 number of moles of the isocyanate group is set to be in the above-described range.

In a case where such a condition for the number of moles of the isocyanate group is satisfied, the amount of the isocyanate-based cross-linking agent of the pressure sensitive adhesive composition (ii) is preferably in a range of 0.01 to 20 parts by mass, more preferably in a range of 0.1 to 15 parts by mass, and particularly preferably in a  
25 range of 0.3 to 12 parts by mass with respect to 100 parts by mass of the amount of the

acrylic resin.

[0092]

[Photopolymerization initiator]

The pressure sensitive adhesive composition (ii) may contain a  
5 photopolymerization initiator other than the acrylic resin and the isocyanate-based  
cross-linking agent.

Examples of the photopolymerization initiator are the same as in case of the  
pressure sensitive adhesive composition (i).

The photopolymerization initiator contained in the pressure sensitive adhesive  
10 composition (ii) may be formed of only one or two or more kinds thereof.

[0093]

In a case of using the photopolymerization initiator, the amount of the  
photopolymerization initiator in the pressure sensitive adhesive composition (ii) is  
preferably in a range of 0.05 to 20 parts by mass with respect to 100 parts by mass of the  
15 amount of the acrylic resin.

In a case where the amount of the photopolymerization initiator is greater than  
or equal to the above-described lower limit, the effects obtained by using a  
photopolymerization initiator can be sufficiently obtained. Further, in a case where the  
amount of the photopolymerization initiator is less than or equal to the above-described  
20 upper limit, generation of by-products due to an excessive amount of  
photopolymerization initiator is suppressed and the pressure sensitive adhesive layer is  
more satisfactorily cured.

[0094]

[Solvent]

25 It is preferable that the pressure sensitive adhesive composition (ii) further

contains a solvent other than the acrylic resin and the isocyanate-based cross-linking agent.

Examples of the solvent are the same as in the case of the pressure sensitive adhesive composition (i).

5           The solvent contained in the pressure sensitive adhesive composition (ii) may be formed of only one or two or more kinds thereof.

[0095]

The amount of the solvent in the pressure sensitive adhesive composition (ii) in a case where the pressure sensitive adhesive composition (ii) contains a solvent is  
10   preferably in a range of 40% to 90% by mass and more preferably in a range of 50% to 80% by mass.

[0096]

[Other components]

The pressure sensitive adhesive composition (ii) may contain other components  
15   which do not correspond to the photopolymerization initiator and the solvent other than the acrylic resin and the isocyanate-based cross-linking agent within the range not damaging the effects of the present invention.

Examples of other components are the same as in the case of the pressure sensitive adhesive composition (i).

20           Other components contained in the pressure sensitive adhesive composition (ii) may be formed of only one or two or more kinds thereof.

[0097]

Hereinbefore, the pressure sensitive adhesive composition containing components to be polymerized by irradiation with energy rays has been described, but  
25   the pressure sensitive adhesive layer may be formed using a pressure sensitive adhesive

composition that does not contain the components to be polymerized by irradiation with energy rays. In other words, the pressure sensitive adhesive layer may be a non-energy ray curable layer that does not have energy ray curability.

Preferred examples of such a non-energy ray curable pressure sensitive adhesive composition include a composition containing an acrylic resin and a cross-linking agent (hereinafter, also abbreviated as a “pressure sensitive adhesive composition (iii)”). The pressure sensitive adhesive composition (iii) may contain optional components such as a solvent and other components that do not correspond to the solvent.

[0098]

<Pressure sensitive adhesive composition (iii)>

The acrylic resin, the cross-linking agent, the solvent, and other components contained in the pressure sensitive adhesive composition (iii) have the same definitions as the acrylic resin, the cross-linking agent, the solvent, and other components in the pressure sensitive adhesive composition (i).

[0099]

The amount of the acrylic resin in the pressure sensitive adhesive composition (iii) is preferably in a range of 40% to 99% by mass and more preferably in a range of 50% to 93% by mass with respect to the total amount of all components contained in the pressure sensitive adhesive composition (iii) other than the solvent.

[0100]

The amount of the cross-linking agent in the pressure sensitive adhesive composition (iii) is preferably in a range of 3 to 30 parts by mass and more preferably in a range of 5 to 25 parts by mass with respect to 100 parts by mass of the amount of the acrylic resin.

[0101]

The pressure sensitive adhesive composition (iii) has the same definition as the pressure sensitive adhesive composition (i) other than the above-described points.

[0102]

<<Method of producing pressure sensitive adhesive composition>>

5       The pressure sensitive adhesive compositions (i) to (iii) are obtained by blending components for constituting each pressure sensitive adhesive composition such as the pressure sensitive adhesive and components other than the pressure sensitive adhesive as necessary.

10       The order of each component to be added at the time of blending is not particularly limited, and two or more components may be added at the same time.

15       The method of mixing respective components at the time of blending is not particularly limited and may be appropriately selected from known methods such as a method of mixing components by rotating a stirrer or a stirring blade; a method of mixing components using a mixer; and a method of mixing components by adding ultrasonic waves thereto.

      The temperature and the time for the addition and the mixing of respective components are not particularly limited as long as the blending components are not deteriorated and may be appropriately adjusted, but the temperature is preferably in a range of 15°C to 30°C.

20       [0103]

Protective film-forming film

      The protective film-forming film may be thermosetting or energy ray curable. The protective film-forming film finally becomes a protective film having high impact resistance after being cured. This protective film prevents occurrence of cracks in the semiconductor chip after the dicing step.

25

The protective film-forming film can be formed using a thermosetting protective film-forming composition or an energy ray curable protective film-forming composition (hereinafter, these are collectively referred to as a “protective film-forming composition”) described below.

5 [0104]

The protective film-forming film may be formed of one layer (single layer) or two or more layers (plurality of layers). In a case where the protective film-forming film is formed of a plurality of layers, a plurality of these layers may be the same as or different from one another, and the combination of a plurality of these layers is not

10 particularly limited.

[0105]

The thickness of the protective film-forming film is not particularly limited, but is preferably in a range of 1 to 100  $\mu\text{m}$ , more preferably in a range of 5 to 75  $\mu\text{m}$ , and particularly preferably in a range of 5 to 50  $\mu\text{m}$ . In a case where the thickness of the

15 protective film-forming film is greater than or equal to the above-described lower limit, the adhesive strength of the protective film-forming film to a semiconductor wafer or a semiconductor chip serving as an adherend is increased. Further, in a case where the thickness of the protective film-forming film is less than or equal to the above-described upper limit, the protective film which is a cured product can be more easily cut using the

20 shearing force at the time of picking up the semiconductor chip.

[0106]

Thermosetting protective film-forming film

Preferred examples of the thermosetting protective film-forming film include those containing a polymer component (A) and a thermosetting component (B). The

25 polymer component (A) is a component to be considered as being formed by a

polymerization reaction of a polymerizable compound. Further, the thermosetting component (B) is a component that can be cured (polymerized) using heat as a trigger of the reaction. In addition, the concept of the polymerization reaction of the present invention also includes a polycondensation reaction.

5 [0107]

<<Thermosetting protective film-forming composition>>

The thermosetting protective film-forming film can be formed using a thermosetting protective film-forming composition containing the constituent material thereof. For example, a thermosetting protective film-forming film can be formed on a  
10 target portion by coating a target surface, on which the thermosetting protective film-forming film is to be formed, with the thermosetting protective film-forming composition and drying the surface as necessary. The ratio of the amounts of components in the thermosetting protective film-forming composition that do not vaporize at ordinary temperature is typically the same as the ratio of the amounts of  
15 components in the thermosetting protective film-forming film. Here, “ordinary temperature” is as described above.

[0108]

The thermosetting protective film-forming composition may be applied according to a known method, and examples thereof include methods using various  
20 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 Meyer bar coater, and a kiss coater.

[0109]

The conditions for drying the thermosetting protective film-forming composition  
25 are not particularly limited, but it is preferable that the thermosetting protective

film-forming composition is heated and dried in a case of containing a solvent described below. In this case, it is preferable that the thermosetting protective film-forming composition containing a solvent is dried under a temperature condition of 70°C to 130°C for 10 seconds to 5 minutes.

5 [0110]

<Protective film-forming composition (III-1)>

Examples of the thermosetting protective film-forming composition include a thermosetting protective film-forming composition (III-1) that contains a polymer component (A) and a thermosetting component (B) (in the present specification, also  
10 abbreviated as a “protective film-forming composition (III-1)”).

[0111]

[Polymer component (A)]

The polymer component (A) is a polymer compound for imparting film-forming properties or flexibility to the thermosetting protective film-forming film.

15 The polymer component (A) contained in the protective film-forming composition (III-1) and the thermosetting protective film-forming film may be formed of only one or two or more kinds thereof, and in a case where the polymer component (A) is formed of two or more kinds thereof, the combination and the ratio of these components can be optionally selected.

20 [0112]

Examples of the polymer component (A) include an acrylic resin (a resin containing a (meth)acryloyl group), polyester, a urethane-based resin (a resin having a urethane bond), an acrylurethane resin, a silicone-based resin (a resin having a siloxane bond), a rubber-based resin (a resin having a rubber structure), a phenoxy resin, and a  
25 thermosetting polyimide. Among these, an acrylic resin is preferable.

[0113]

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

The weight-average molecular weight ( $M_w$ ) of the acrylic resin is preferably in  
5 a range of 10000 to 2000000 and more preferably in a range of 100000 to 1500000. In  
a case where the weight-average molecular weight of the acrylic resin is greater than or  
equal to the above-described lower limit, the shape stability (temporal stability during  
storage) of the thermosetting protective film-forming film is improved. Further, in a  
case where the weight-average molecular weight of the acrylic resin is less than or equal  
10 to the above-described upper limit, the thermosetting protective film-forming film is  
likely to follow the uneven surface of the adherend so that occurrence of voids between  
the adherend and the thermosetting protective film-forming film is further suppressed.

[0114]

The glass transition temperature ( $T_g$ ) of the acrylic resin is preferably in a range  
15 of  $-60^{\circ}\text{C}$  to  $70^{\circ}\text{C}$  and more preferably in a range of  $-30^{\circ}\text{C}$  to  $50^{\circ}\text{C}$ . In a case where the  
 $T_g$  of the acrylic resin is higher than or equal to the above-described lower limit, the  
adhesive strength between the protective film and the support sheet is suppressed and  
thus the peeling properties of the support sheet are improved. Further, in a case where  
the  $T_g$  of the acrylic resin is lower than or equal to the above-described upper limit, the  
20 adhesive strength between the thermosetting protective film-forming film and the  
adherend of the protective film is improved.

[0115]

Examples of the acrylic resin include a polymer of one or two or more  
(meth)acrylic acid esters; and a copolymer of two or more monomers selected from  
25 (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene, and N-methylol

acrylamide.

[0116]

Examples of the (meth)acrylic acid ester constituting an acrylic resin include (meth)acrylic acid alkyl ester in which an alkyl group constituting alkyl ester has a chain structure having 1 to 18 carbon atoms such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), a pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, or octadecyl (meth)acrylate (stearyl (meth)acrylate); (meth)acrylic acid cycloalkyl ester such as isobornyl (meth)acrylate or dicyclopentanyl (meth)acrylate; (meth)acrylic acid aralkyl ester such as benzyl (meth)acrylate; (meth)acrylic acid cycloalkenyl ester such as (meth)acrylic acid dicyclopentenyl ester; (meth)acrylic acid cycloalkenyloxy alkyl ester such as (meth)acrylic acid dicyclopentenylloxy ethyl ester; imide (meth)acrylate; glycidyl group-containing (meth)acrylic acid ester such as glycidyl (meth)acrylate; hydroxyl group-containing (meth)acrylic acid ester 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, or 4-hydroxybutyl (meth)acrylate; and substituted amino group-containing (meth)acrylic acid ester such as N-methylaminoethyl (meth)acrylate. Here, the “substituted amino group” indicates a group formed by one or two hydrogen atoms in an amino group being

substituted with a group other than a hydrogen atom.

[0117]

The acrylic resin may be formed by copolymerizing one or two or more monomers selected from (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene, and N-methylolacrylamide other than the (meth)acrylic acid ester.

[0118]

The monomer constituting the acrylic resin may be formed of only one or two or more kinds thereof. In a case where the monomer is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

10 [0119]

The acrylic resin may contain a functional group which can be bonded to another compound 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 another compound through a cross-linking agent (F) described below or may be directly bonded to another compound without interposing the cross-linking agent (F) therebetween. In a case where the acrylic resin is bonded to another compound using the functional group, the reliability of a package obtained using the protective film-forming composite sheet tends to be improved.

[0120]

20 In the present invention, as the polymer component (A), a thermoplastic resin (hereinafter, also simply referred to as a “thermoplastic resin”) other than the acrylic resin may be used together with the acrylic resin.

By using the thermoplastic resin, the peeling properties of the protective film from the support sheet are improved, and the thermosetting protective film-forming film is likely to follow the uneven surface of the adherend. Therefore, occurrence of voids

25

between the adherend and the thermosetting protective film-forming film is further suppressed.

[0121]

The weight-average molecular weight of the thermoplastic resin is preferably in a range of 1000 to 100000 and more preferably in a range of 3000 to 80000.

[0122]

The glass transition temperature (T<sub>g</sub>) of the thermoplastic resin is preferably in a range of -30°C to 150°C and more preferably in a range of -20°C to 120°C.

[0123]

Examples of the thermoplastic resin include polyester, polyurethane, a phenoxy resin, polybutene, polybutadiene, and polystyrene.

[0124]

The thermoplastic resin contained in the protective film-forming composition (III-1) and the thermosetting protective film-forming film may be formed of only one or two or more kinds thereof. In a case where the thermoplastic resin is formed of two or more kinds thereof, the combination and the ratio can be optionally selected.

[0125]

The ratio of the amount of the polymer component (A) to the total amount of all components other than the solvent in the protective film-forming composition (III-1) (that is, the amount of the polymer component (A) in the thermosetting protective film-forming film) is preferably in a range of 5% to 50% by mass, more preferably in a range of 10% to 40% by mass, and particularly preferably in a range of 15% to 35% by mass regardless of the kind of the polymer component (A).

[0126]

The polymer component (A) corresponds to the thermosetting component (B) in

some cases. In the present invention, in a case where the protective film-forming composition (III-1) contains a component that corresponds to both of the polymer component (A) and the thermosetting component (B), the protective film-forming composition (III-1) is considered to contain the polymer component (A) and the thermosetting component (B).

[0127]

[Thermosetting component (B)]

The thermosetting component (B) is a component for curing the thermosetting protective film-forming film to form a hard protective film.

The thermosetting component (B) contained in the protective film-forming composition (III-1) and the thermosetting protective film-forming film may be formed of only one or two or more kinds thereof. In a case where the thermosetting component (B) is formed of two or more kinds thereof, the combination and the ratio can be optionally selected.

[0128]

Examples of the thermosetting component (B) include an epoxy-based thermosetting resin, thermosetting polyimide, polyurethane, unsaturated polyester, and a silicone resin. Among these, an epoxy-based thermosetting resin is preferable.

[0129]

(Epoxy-based thermosetting resin)

The epoxy-based thermosetting resin contains an epoxy resin (B1) and a thermosetting agent (B2).

The epoxy-based thermosetting resin contained in the protective film-forming composition (III-1) and the thermosetting protective film-forming film may be formed of only one or two or more kinds thereof. In a case where the epoxy-based thermosetting

resin is formed of two or more kinds thereof, the combination and the ratio can be optionally selected.

[0130]

Epoxy resin (B1)

5           As the epoxy resin (B1), known resins are exemplary examples, and examples thereof include a bi- or higher functional epoxy compound such as a polyfunctional epoxy resin, a biphenyl compound, a bisphenol A diglycidyl ether and a hydrogenated product thereof, an orthocresol novolak epoxy resin, a dicyclopentadiene type epoxy resin, a biphenyl type epoxy resin, a bisphenol A type epoxy resin, a bisphenol F type  
10 epoxy resin, or a phenylene skeleton type epoxy resin.

[0131]

          As the epoxy resin (B1), an epoxy resin having an unsaturated hydrocarbon group may be used. The epoxy resin containing an unsaturated hydrocarbon group has a higher compatibility with an acrylic resin than the compatibility of the epoxy resin that  
15 does not contain an unsaturated hydrocarbon group. Therefore, by using the epoxy resin containing an unsaturated hydrocarbon group, the reliability of a package obtained using the protective film-forming composite sheet is improved.

[0132]

          Examples of the epoxy resin containing an unsaturated hydrocarbon group  
20 include a compound formed by some epoxy groups in a polyfunctional epoxy resin being substituted with groups containing an unsaturated hydrocarbon group. Such a compound is obtained by adding (meth)acrylic acid or a derivative thereof to an epoxy group to cause a reaction.

          Further, examples of the epoxy resin containing an unsaturated hydrocarbon  
25 group include a compound obtained by directly bonding a group that contains an

unsaturated hydrocarbon group to an aromatic ring or the like constituting an epoxy resin.

The unsaturated hydrocarbon group is a polymerizable unsaturated group, and specific examples thereof include an ethenyl group (vinyl group), a 2-propenyl group (allyl group), a (meth)acryloyl group, and a (meth)acrylamide group. Among these, an acryloyl group is preferable.

Further, the “derivative” in the present specification indicates a derivative formed by one or more hydrogen atoms in an original compound being substituted with groups (substituents) other than a hydrogen atom.

10 [0133]

The number average molecular weight of the epoxy resin (B1) is not particularly limited, but is preferably in a range of 300 to 30000, more preferably in a range of 300 to 10000, and particularly preferably in a range of 300 to 3000 from the viewpoints of the curability of the thermosetting protective film-forming film and the strength and the heat resistance of the protective film obtained after the thermosetting protective film-forming film is cured.

The epoxy equivalent of the epoxy resin (B1) is preferably in a range of 100 to 1100 g/eq and more preferably in a range of 150 to 1000 g/eq.

[0134]

20 The epoxy resin (B1) may be used alone or in combination of two or more kinds thereof. In a case where a combination of two or more kinds thereof is used, the combination and the ratio of these can be optionally selected.

[0135]

Thermosetting agent (B2)

25 The thermosetting agent (B2) functions as a curing agent with respect to the

epoxy resin (B1).

As the thermosetting agent (B2), a compound containing two or more functional groups which can react with an epoxy group in one molecule is an exemplary example.

Examples of the functional group include a phenolic hydroxyl group, an alcoholic

5 hydroxyl group, an amino group, a carboxy group, and a group obtained by forming an acid group into an anhydride. Among these, a phenolic hydroxyl group, an amino group, or a group obtained by forming an acid group into an anhydride is preferable, and a phenolic hydroxyl group or an amino group is more preferable.

[0136]

10 Among examples of the thermosetting agent (B2), examples of a phenol-based curing agent containing a phenolic hydroxyl group include a polyfunctional phenol resin, biphenol, a novolak type phenol resin, a dicyclopentadiene-based phenol resin, and an aralkyl phenol resin.

Among examples of the thermosetting agent (B2), examples of an amine-based  
15 curing agent containing an amino group include dicyandiamide (hereinafter, also abbreviated as "DICY").

[0137]

The thermosetting agent (B2) may contain an unsaturated hydrocarbon group.

Examples of the thermosetting agent (B2) containing an unsaturated  
20 hydrocarbon group include a compound formed by some hydroxyl groups in a phenol resin being substituted with groups containing an unsaturated hydrocarbon group; and a compound formed by directly bonding a group containing an unsaturated hydrocarbon group to an aromatic ring of a phenol resin.

The unsaturated hydrocarbon group in the thermosetting agent (B2) is the same  
25 as an unsaturated hydrocarbon group contained in the above-described epoxy resin

containing an unsaturated hydrocarbon group.

[0138]

In a case where a phenol-based curing agent is used as the thermosetting agent (B2), it is preferable that the thermosetting agent (B2) has a high softening point or glass transition temperature from the viewpoint of improving peeling properties of the protective film from the support sheet.

[0139]

It is preferable that the thermosetting agent (B2) is a thermosetting agent which is in a solid state at ordinary temperature and does not exhibit curing activity with respect to the epoxy resin (B1), but is dissolved when heated and exhibits curing activity with respect to the epoxy resin (B1) (hereinafter, also abbreviated as a “thermally active latent epoxy resin curing agent”).

In the thermosetting protective film-forming film, the thermally active latent epoxy resin curing agent is stably dispersed in the epoxy resin (B1) at ordinary temperature, but is compatible with the epoxy resin (B1) when heated and reacts with the epoxy resin (B1). The storage stability of the protective film-forming composite sheet is significantly improved by using the thermally active latent epoxy resin curing agent. For example, movement of the curing agent from the protective film-forming film to the support sheet adjacent to the curing agent is suppressed, and degradation of thermosetting properties of the thermosetting protective film-forming film is effectively suppressed. Further, since the thermosetting degree of the thermosetting protective film-forming film is further increased when heated and the peak-up properties of the semiconductor chip provided with a protective film described below are further improved.

[0140]

Examples of the thermally active latent epoxy resin curing agent include an

onium salt, dibasic acid hydrazide, dicyandiamide, and an amine adduct of a curing agent.

[0141]

The number average molecular weight of resin components such as a  
5 polyfunctional phenol resin, a novolak type phenol resin, a dicyclopentadiene-based phenol resin, and an aralkyl phenol resin in the thermosetting agent (B2) is preferably in a range of 300 to 30000, more preferably in a range of 400 to 10000, and particularly preferably in a range of 500 to 3000.

The molecular weight of the non-resin components such as biphenol and  
10 dicyandiamide in the thermosetting agent (B2) is not particularly limited, but is preferably in a range of 60 to 500.

[0142]

The thermosetting agent (B2) may be used alone or in combination of two or more kinds thereof. In a case where a combination of two or more kinds thereof is used,  
15 the combination and the ratio of these can be optionally selected.

[0143]

The amount of the thermosetting agent (B2) in the protective film-forming composition (III-1) and the thermosetting protective film-forming film is preferably in a range of 0.1 to 500 parts by mass and more preferably in a range of 1 to 200 parts by  
20 mass with respect to 100 parts by mass of the amount of the epoxy resin (B1). In a case where the amount of the thermosetting agent (B2) is greater than or equal to the above-described lower limit, the thermosetting protective film-forming film is more easily cured. Further, in a case where the amount of the thermosetting agent (B2) is less than or equal to the upper limit, the moisture absorption rate of the thermosetting  
25 protective film-forming film is decreased and the reliability of a package to be obtained

using the protective film-forming composite sheet is further improved.

[0144]

The amount of the thermosetting component (B) (for example, the total amount of the epoxy resin (B1) and the thermosetting agent (B2)) in the protective film-forming composition (III-1) and the thermosetting protective film-forming film is preferably in a range of 1 to 100 parts by mass, more preferably in a range of 1.5 to 85 parts by mass, and particularly preferably in a range of 2 to 70 parts by mass with respect to 100 parts by mass of the amount of the polymer component (A). In a case where the amount of the thermosetting component (B) is in the above-described range, the adhesive strength between the protective film and the support sheet is suppressed and the peeling properties of the support sheet are improved.

[0145]

[Curing accelerator (C)]

The protective film-forming composition (III-1) and the thermosetting protective film-forming film may contain a curing accelerator (C). The curing accelerator (C) is a component for adjusting the curing rate of the protective film-forming composition (III-1).

Preferred examples of the curing accelerator (C) include a tertiary amine such as triethylenediamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol, or tris(dimethylaminomethyl)phenol; imidazoles (imidazole in which one or more hydrogen atoms are substituted with groups other than a hydrogen atom) such as 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole, and 2-phenyl-4-methyl-5-hydroxymethylimidazole; organic phosphines (phosphine in which one or more hydrogen atoms are substituted with organic groups) such as

tributylphosphine, diphenylphosphine, and triphenylphosphine; and tetraphenylboron salt such as tetraphenylphosphonium tetraphenyl borate or triphenylphosphine tetraphenyl borate.

[0146]

5           The curing accelerator (C) contained in the protective film-forming composition (III-1) and the thermosetting protective film-forming film may be formed of only one or two or more kinds thereof. In a case where the curing accelerator (C) is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0147]

10           In a case where the curing accelerator (C) is used, the amount of the curing accelerator (C) in the protective film-forming composition (III-1) and the thermosetting protective film-forming film is preferably in a range of 0.01 to 10 parts by mass and more preferably in a range of 0.1 to 5 parts by mass with respect to 100 parts by mass of the amount of the thermosetting component (B). In a case where the amount of the curing  
15    accelerator (C) is greater than or equal to the above-described lower limit, the effects to be obtained by using the curing accelerator (C) are sufficiently obtained. Further, in a case where the amount of the curing accelerator (C) is lower than or equal to the above-described upper limit, the effect of suppressing movement of the curing  
20    accelerator (C) having a high polarity to an adhesive interface side between the adherend and the curing accelerator (C) to be segregated in the thermosetting protective film-forming film under high temperature and high humidity conditions, and the reliability of a package obtained by using the protective film-forming composite sheet is further improved.

[0148]

25           [Filler (D)]

The protective film-forming composition (III-1) and the thermosetting protective film-forming film may contain a filler (D). In a case where the thermosetting protective film-forming film contains the filler (D), the thermal expansion coefficient of the protective film obtained by curing the thermosetting protective film-forming film is easily adjusted. In addition, the reliability of a package obtained by using the protective film-forming composite sheet is further improved by optimizing the thermal expansion coefficient for a target on which a protective film is to be formed. Moreover, in a case where the thermosetting protective film-forming film contains the filler (D), the moisture absorption rate of the protective film can be decreased or heat radiation can be improved.

10 [0149]

The filler (D) may be an organic filler or an inorganic filler, but an inorganic filler is preferable.

Preferred examples of the inorganic filler include powder such as silica, alumina, talc, calcium carbonate, titanium white, red oxide, silicon carbide, or boron nitride; beads obtained by forming these inorganic fillers in a spherical shape; surface modified products of these inorganic fillers; single crystal fibers of these inorganic fillers; and glass fibers.

Among these, silica or alumina is preferable as the inorganic filler.

[0150]

20 The filler (D) contained in the protective film-forming composition (III-1) and the thermosetting protective film-forming film may be formed of only one or two or more kinds thereof. In a case where the filler (D) is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0151]

25 In a case of using the filler (D), the ratio of the amount of the filler (D) to the

total amount of all components contained in the protective film-forming composition (III-1) other than the solvent (in other words, the amount of the filler (D) in the thermosetting protective film-forming film) is preferably in a range of 5% to 80% by mass and more preferably in a range of 7% to 60% by mass. In a case where the amount of the filler (D) is in the above-described range, the above-described thermal expansion coefficient can be more easily adjusted.

[0152]

[Coupling agent (E)]

The protective film-forming composition (III-1) and the thermosetting protective film-forming film may contain a coupling agent (E). By using a coupling agent containing a functional group which can react with an inorganic compound or an organic compound as the coupling agent (E), the adhesiveness and adhesion properties of the thermosetting protective film-forming film to the adherend can be improved. Further, by using the coupling agent (E), the water resistance of the protective film obtained by curing the thermosetting protective film-forming film is improved without damaging the heat resistance.

[0153]

It is preferable that the coupling agent (E) is a compound containing a functional group which can react with the functional group contained in the polymer component (A), the thermosetting component (B), or the like and more preferable that the coupling agent (E) is a silane coupling agent.

Preferred examples of the silane coupling agent include

3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropylmethyldiethoxysilane,

3-glycidyloxypropyltriethoxysilane, 3-glycidyloxymethyldiethoxysilane,

2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,

3-methacryloyloxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane,  
3-(2-aminoethylamino)propyltrimethoxysilane,  
3-(2-aminoethylamino)propylmethyldiethoxysilane,  
3-(phenylamino)propyltrimethoxysilane, 3-anilinopropyltrimethoxysilane,  
5 3-ureidopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane,  
3-mercaptopropylmethyldimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfane,  
methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane,  
vinyltriacetoxysilane, and imidazole silane.

[0154]

10 The coupling agent (E) contained in the protective film-forming composition  
(III-1) and the thermosetting protective film-forming film may be formed of only one or  
two or more kinds thereof. In a case where the coupling agent (E) is formed of two or  
more kinds thereof, the combination and the ratio of these can be optionally selected.

[0155]

15 In a case of using the coupling agent (E), the amount of the coupling agent (E) in  
the protective film-forming composition (III-1) and the thermosetting protective  
film-forming film is preferably in a range of 0.03 to 20 parts by mass, more preferably in  
a range of 0.05 to 10 parts by mass, and particularly preferably in a range of 0.1 to 5 parts  
by mass with respect to 100 parts by mass of the total amount of the polymer component  
20 (A) and the thermosetting component (B). In a case where the amount of the coupling  
agent (E) is greater than or equal to the above-described lower limit, the effects to be  
obtained by using the coupling agent (E), such as improvement of dispersity of the filler  
(D) in a resin and improvement of adhesiveness of the thermosetting protective  
film-forming film to the adherend, are sufficiently obtained. Further, in a case where  
25 the amount of the coupling agent (E) is less than or equal to the above-described upper

limit, generation of outgas is further suppressed.

[0156]

[Cross-linking agent (F)]

In a case where a component containing a functional group such as a vinyl group,  
5 a (meth)acryloyl group, an amino group, a hydroxyl group, a carboxy group, or an  
isocyanate group which can be bonded to another compound such as the above-described  
acrylic resin is used as the polymer component (A), the protective film-forming  
composition (III-1) and the thermosetting protective film-forming film may contain a  
cross-linking agent (F). The cross-linking agent (F) is a component for bonding the  
10 functional group in the polymer component (A) to another compound so as to be  
cross-linked, and the initial adhesive strength and the cohesive force of the thermosetting  
protective film-forming film can be adjusted by the cross-linking.

[0157]

Examples of the cross-linking agent (F) include an organic polyvalent  
15 isocyanate compound, an organic polyvalent imine compound, a metal chelate-based  
cross-linking agent (a cross-linking agent having a metal chelate structure), and an  
aziridine-based cross-linking agent (a cross-linking agent having an aziridinyl group).

[0158]

Examples of the organic polyvalent isocyanate compound include an aromatic  
20 polyvalent isocyanate compound, an aliphatic polyvalent isocyanate compound, and an  
alicyclic polyvalent isocyanate compound (hereinafter, these compounds are collectively  
abbreviated as “an aromatic polyvalent isocyanate compound and the like”); trimers of  
the aromatic polyvalent isocyanate compound and the like; an isocyanurate product and  
an adduct product; and a terminal isocyanate urethane prepolymer obtained by reacting  
25 the aromatic polyvalent isocyanate compound and the like with a polyol compound.

The adduct product indicates a reactant of the aromatic polyvalent isocyanate compound, the aliphatic polyvalent isocyanate compound or the alicyclic polyvalent isocyanate compound, and a low-molecular active hydrogen-containing compound such as ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane, or castor oil. Examples of the adduct product include a xylylene diisocyanate adduct of trimethylolpropane described below. Further, the “terminal isocyanate urethane prepolymer” is as described above.

[0159]

More specific examples of the organic polyvalent 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-methyl diphenylmethane diisocyanate; hexamethylene diisocyanate; isophorone diisocyanate; dicyclohexylmethane-4,4'-diisocyanate; dicyclohexylmethane-2,4'-diisocyanate; a compound obtained by adding any one or two or more kinds from among tolylene diisocyanate, hexamethylene diisocyanate, and xylylene diisocyanate to all or some hydroxyl groups in a polyol such as trimethylolpropane; and lysine diisocyanate.

[0160]

Examples of the organic polyvalent imine compound include N,N-diphenylmethane-4,4'-bis(1-aziridinecarboxamide), trimethylolpropane-tri- $\beta$ -aziridinyl propionate, tetramethylolmethane-tri- $\beta$ -aziridinyl propionate, and N,N'-toluene-2,4-bis(1-aziridinecarboxamide)triethylene melamine.

[0161]

In a case where an organic polyvalent isocyanate compound is used as the cross-linking agent (F), it is preferable to use a hydroxyl group-containing polymer as the

polymer component (A). In a case where the cross-linking agent (F) contains an isocyanate group and the polymer component (A) contains a hydroxyl group, a cross-linked structure can be easily introduced into the thermosetting protective film-forming film by reacting the cross-linking agent (F) with the polymer component (A).

[0162]

The cross-linking agent (F) contained in the protective film-forming composition (III-1) and the thermosetting protective film-forming film may be formed of only one or two or more kinds thereof. In a case where the cross-linking agent (F) is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0163]

In a case of using the cross-linking agent (F), the amount of the cross-linking agent (F) in the protective film-forming composition (III-1) is preferably in a range of 0.01 to 20 parts by mass, more preferably in a range of 0.1 to 10 parts by mass, and particularly preferably in a range of 0.5 to 5 parts by mass with respect to 100 parts by mass of the amount of the polymer component (A). In a case where the amount of the cross-linking agent (F) is greater than or equal to the above-described lower limit, the effects obtained by using the cross-linking agent (F) can be sufficiently obtained.

Further, in a case where the amount of the cross-linking agent (F) is less than or equal to the above-described upper limit, an extreme decrease in adhesive strength of the thermosetting protective film-forming film to the support sheet or adhesive strength of the thermosetting protective film-forming film to the semiconductor wafer or the semiconductor chip is suppressed.

In the present invention, the effects of the present invention can be sufficiently

obtained without using the cross-linking agent (F).

[0164]

[Energy ray curable resin (G)]

The protective film-forming composition (III-1) may contain the energy ray  
5 curable resin (G). In a case where the thermosetting protective film-forming film  
contains the energy ray curable resin (G), the characteristics thereof can be changed by  
irradiation with energy rays.

[0165]

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

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

[0166]

15 Examples of the acrylate-based compound include chain aliphatic  
skeleton-containing (meth)acrylate such as trimethylolpropane tri(meth)acrylate,  
tetramethylolmethane tetra(meth)acrylate, pentaerythritol tri(meth)acrylate,  
pentaerythritol tetra(meth)acrylate, dipentaerythritol monohydroxypenta(meth)acrylate,  
dipentaerythritol hexa(meth)acrylate, 1,4-butylene glycol di(meth)acrylate, or  
20 1,6-hexanediol di(meth)acrylate; cyclic aliphatic skeleton-containing (meth)acrylate such  
as dicyclopentanyl di(meth)acrylate; polyalkylene glycol (meth)acrylate such as  
polyethylene glycol di(meth)acrylate; oligoester(meth)acrylate; urethane (meth)acrylate  
oligomer; epoxy-modified (meth)acrylate; polyether (meth)acrylate other than the  
polyalkylene glycol (meth)acrylate; and itaconic acid oligomer.

25 [0167]

The weight-average molecular weight of the energy ray curable compound is preferably in a range of 100 to 30000 and more preferably 300 to 10000.

[0168]

The energy ray curable compound used for polymerization may be formed of only one or two or more kinds thereof. In a case where the energy ray curable compound is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0169]

The energy ray curable resin (G) contained in the protective film-forming composition (III-1) may be formed of only one or two or more kinds thereof. In a case where the energy ray curable resin (G) is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0170]

In a case of using the energy ray curable resin (G), the amount of the energy ray curable resin (G) in the protective film-forming composition (III-1) is preferably in a range of 1% to 95% by mass, more preferably in a range of 2% to 90% by mass, and particularly preferably in a range of 3% to 85% by mass.

[0171]

[Photopolymerization initiator (H)]

In a case where the protective film-forming composition (III-1) contains the energy ray curable resin (G), the protective film-forming composition (III-1) may contain a photopolymerization initiator (H) in order to efficiently proceed the polymerization reaction of the energy ray curable resin (G).

[0172]

Examples of the photopolymerization initiator (H) in the protective film-forming

composition (III-1) are the same as those for the photopolymerization initiator in the pressure sensitive adhesive composition (ii).

[0173]

The photopolymerization initiator (H) contained in the protective film-forming composition (III-1) may be formed of only one or two or more kinds thereof. In a case where the photopolymerization initiator is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0174]

In a case of using the photopolymerization initiator (H), the amount of the photopolymerization initiator (H) in the protective film-forming composition (III-1) is preferably in a range of 0.1 to 20 parts by mass, more preferably in a range of 1 to 10 parts by mass, and particularly preferably in a range of 2 to 5 parts by mass with respect to 100 parts by mass of the amount of the energy ray curable resin (G).

[0175]

[Colorant (I)]

The protective film-forming composition (III-1) and the thermosetting protective film-forming film may contain a colorant (I).

Examples of the colorant (I) include inorganic pigments, organic pigments, organic dyes, and known ones.

[0176]

Examples of the organic pigments and the organic dyes include an aluminum-based dye, a cyanine-based dye, a merocyanine-based dye, a croconium-based dye, a squarylium-based dye, an azulenium-based dye, a polymethine-based dye, a naphthoquinone-based dye, a pyrylium-based dye, a phthalocyanine-based dye, a naphthalocyanine-based dye, a naphtholactam-based dye, an azo-based dye, a condensed

azo-based dye, an indigo-based dye, a perinone-based dye, a perylene-based dye, a dioxazine-based dye, a quinacridone-based dye, an isoindolinone-based dye, a quinophthalone-based dye, a pyrrole-based dye, a thioindigo-based dye, a metal complex-based dye (metal complex salt dye), a dithiol metal complex-based dye, an indole phenol-based dye, a triallylmethane-based dye, an anthraquinone-based dye, a dioxazine-based dye, a naphthol-based dye, an azomethine-based dye, a benzimidazolone-based dye, a pyranthrone-based dye, and a threne-based dye.

[0177]

Examples of the inorganic pigment include carbon black, a cobalt-based dye, an iron-based dye, a chromium-based dye, a titanium-based dye, a vanadium-based dye, a zirconium-based dye, a molybdenum-based dye, a ruthenium-based dye, a platinum-based dye, an indium tin oxide (ITO)-based dye, and an antimony tin oxide (ATO)-based dye.

[0178]

The colorant (I) contained in the protective film-forming composition (III-1) and the thermosetting protective film-forming film may be formed of only one or two or more kinds thereof. In a case where the colorant (I) is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0179]

In a case of using the colorant (I), the amount of the colorant (I) of the thermosetting protective film-forming film may be appropriately adjusted depending on the intended purpose thereof. For example, there is a case where the protective film is printed by irradiation with laser so that printing visibility can be adjusted by adjusting the amount of the colorant (I) in the thermosetting protective film-forming film and adjusting the optical transparency of the protective film. In addition, by adjusting the amount of

the colorant (I) in the thermosetting protective film-forming film, design properties of the protective film can be improved or grinding marks on the rear surface of the semiconductor wafer can be made less visible. In consideration of the above-described points, the ratio of the amount of the colorant (I) to the total amount of all components in the protective film-forming composition (III-1) other than the solvent (that is, the amount of the colorant (I) in the thermosetting protective film-forming film) is preferably in a range of 0.1% to 10% by mass, more preferably in a range of 0.1% to 7.5% by mass, and particularly preferably in a range of 0.1% to 5% by mass. For example, the ratio thereof may be in a range of 0.1% to 3% by mass or in a range of 0.1% to 1% by mass. In a case where the amount of the colorant (I) is greater than or equal to the above-described lower limit, the effects to be obtained by using the colorant (I) are sufficiently obtained. Further, in a case where the amount of the colorant (I) is less than or greater than the above-described upper limit, an extreme decrease in optical transparency of the thermosetting protective film-forming film is suppressed.

[0180]

[General-purpose additive (J)]

The protective film-forming composition (III-1) and the thermosetting protective film-forming film may contain a general-purpose additive (J) within the range not damaging the effects of the present invention.

The general-purpose additive (J) may be known, can be optionally selected from known additives depending on the intended purpose thereof, and is not particularly limited. Preferred examples of the general-purpose additive (J) include a plasticizer, an antistatic agent, an antioxidant, and a gettering agent.

[0181]

The general-purpose additive (I) contained in the protective film-forming

composition (III-1) and the thermosetting protective film-forming film may be formed of only one or two or more kinds thereof. In a case where the general-purpose additive (I) is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

5           The amount of the general-purpose additive (I) in the protective film-forming composition (III-1) and the thermosetting protective film-forming film is not particularly limited and may be appropriately selected depending on the intended purpose thereof.

[0182]

[Solvent]

10           It is preferable that the protective film-forming composition (III-1) may further contain a solvent. In a case where the protective film-forming composition (III-1) contains a solvent, handling properties thereof are improved.

The solvent is not particularly limited.

Preferred examples thereof include a hydrocarbon such as toluene or xylene; an  
15 alcohol such as methanol, ethanol, 2-propanol, isobutyl alcohol (2-methylpropan-1-ol), or 1-butanol; an ester such as ethyl acetate or butyl acetate; a ketone such as acetone or methyl ethyl ketone; an ether such as tetrahydrofuran; and an amide (a compound having an amide bond) such as dimethylformamide or N-methylpyrrolidone.

The solvent contained in the protective film-forming composition (III-1) may be  
20 formed of only one or two or more kinds thereof. In a case where the solvent is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0183]

From the viewpoint that the components contained in the protective  
25 film-forming composition (III-1) can be uniformly mixed, it is preferable that the solvent

contained in the protective film-forming composition (III-1) is methyl ethyl ketone or the like.

[0184]

<<Method of producing thermosetting protective film-forming composition>>

5       The thermosetting protective film-forming composition such as the protective film-forming composition (III-1) is obtained by blending respective components for constituting the composition.

The order of each component to be added at the time of blending is not particularly limited, and two or more components may be added at the same time.

10       In a case of using a solvent, the solvent may be used by being mixed with any of blending components other than the solvent and diluting the blending components in advance or may be used by being mixed with these blending components without diluting any of blending components other than the solvent in advance.

The method of mixing respective components at the time of blending is not particularly limited and may be appropriately selected from known methods such as a method of mixing components by rotating a stirrer or a stirring blade; a method of mixing components using a mixer; and a method of mixing components by adding ultrasonic waves thereto.

15       The temperature and the time for the addition and the mixing of respective components are not particularly limited as long as the blending components are not deteriorated and may be appropriately adjusted, but the temperature is preferably in a range of 15°C to 30°C.

[0185]

Energy ray curable protective film-forming film

25       The energy ray curable protective film-forming film contains an energy ray

curable component (a).

It is preferable that the energy ray curable component (a) is uncured or has tackiness and more preferable that the energy ray curable component (a) is uncured and has tackiness. Here, the terms “energy ray” and “energy ray curable” have the same definitions as those described above.

[0186]

<<Energy ray curable protective film-forming composition>>

The energy ray curable protective film-forming film can be formed using an energy ray curable protective film-forming composition containing the constituent material thereof. For example, an energy ray curable protective film-forming film can be formed on a target portion by coating a target surface, on which the energy ray curable protective film-forming film is to be formed, with the energy ray curable protective film-forming composition and drying the surface as necessary. The ratio of the amounts of components in the energy ray curable protective film-forming composition that do not vaporize at ordinary temperature is typically the same as the ratio of the amounts of components in the energy ray curable protective film-forming film. Here, “ordinary temperature” is as described above.

[0187]

The energy ray curable protective film-forming composition may be applied according to a known method, and examples thereof include methods using various 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 Meyer bar coater, and a kiss coater.

[0188]

The conditions for drying the energy ray curable protective film-forming

composition are not particularly limited, but it is preferable that the energy ray curable protective film-forming composition is heated and dried in a case of containing a solvent described below. It is preferable that the energy ray curable protective film-forming composition containing a solvent is dried under a temperature condition of 70°C to

5 130°C for 10 seconds to 5 minutes.

[0189]

<Protective film-forming composition (IV-1)>

Examples of the energy ray curable protective film-forming composition include an energy ray curable protective film-forming composition (IV-1) that contains an energy ray curable component (a) (in the present specification, also abbreviated as a “protective film-forming composition (IV-1)”).

10

[0190]

[Energy ray curable component (a)]

The energy ray curable component (a) is a component cured by irradiation with energy rays and used for imparting film-forming properties or flexibility to the energy ray curable protective film-forming film.

15

Examples of the energy ray curable component (a) include a polymer (a1) containing an energy ray curable group and having a weight-average molecular weight of 80000 to 2000000; and a compound (a2) containing an energy ray curable group and having a molecular weight of 100 to 80000. The polymer (a1) may have at least a portion that is cross-linked by a cross-linking agent or may not be cross-linked.

20

[0191]

(Polymer (a1) containing energy ray curable group and having weight-average molecular weight of 80000 to 2000000)

25

Examples of the polymer (a1) containing an energy ray curable group and a

weight-average molecular weight of 80000 to 2000000 include an acrylic resin (a1-1) formed by causing an addition reaction between an acrylic polymer (a11) containing a functional group which can react with a group contained in another compound and an energy ray curable compound (a12) containing a group that reacts with the functional group and an energy ray curable group such as an energy ray curable double bond.

[0192]

Examples of the functional group that can react with a group contained in another compound include a hydroxyl group, a carboxy group, an amino group, a substituted amino group (group formed by one or two hydrogen atoms in an amino group being substituted with groups other than a hydrogen atom), and an epoxy group. Here, from the viewpoint of preventing corrosion of a circuit such as a semiconductor wafer or a semiconductor chip, it is preferable that the functional group is a group other than a carboxy group.

Among these, it is preferable that the functional group is a hydroxyl group.

[0193]

Acrylic polymer (a11) containing functional group

Examples of the acrylic polymer (a11) containing the functional group include those obtained by copolymerizing an acrylic monomer containing the functional group and an acrylic monomer which does not have the functional group. In addition to these monomers, monomers other than the acrylic monomer (non-acrylic monomers) may be copolymerized.

Further, the acrylic polymer (a11) may be a random copolymer or a block copolymer.

[0194]

Examples of the acrylic monomer containing the functional group include a

hydroxyl group-containing monomer, a carboxy group-containing monomer, an amino group-containing monomer, a substituted amino group-containing monomer, and an epoxy group-containing monomer.

[0195]

- 5           Examples of the hydroxyl group-containing monomer include hydroxyalkyl (meth)acrylate 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, or 4-hydroxybutyl (meth)acrylate; and non-(meth)acrylic unsaturated alcohol (unsaturated alcohol that does not have a
- 10 (meth)acryloyl skeleton) such as vinyl alcohol or allyl alcohol.

[0196]

- Examples of the carboxyl group-containing monomer include an ethylenically unsaturated monocarboxylic acid (monocarboxylic acid having an ethylenically unsaturated bond) such as (meth)acrylic acid or crotonic acid; ethylenically unsaturated
- 15 dicarboxylic acid (dicarboxylic acid having an ethylenically unsaturated bond) such as fumaric acid, itaconic acid, maleic acid, or citraconic acid; an anhydride of the ethylenically unsaturated dicarboxylic acid; and (meth)acrylic acid carboxy alkyl ester such as 2-carboxyethyl methacrylate.

[0197]

- 20           As the acrylic monomer containing the functional group, a hydroxyl group-containing monomer or a carboxy group-containing monomer is preferable and a hydroxyl group-containing monomer is more preferable.

[0198]

- The acrylic monomer containing the functional group that constitutes the acrylic
- 25 polymer (a11) may be formed of only one or two or more kinds thereof. In a case

where the acrylic monomer is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0199]

Examples of the acrylic monomer that does not contain the functional group

5 include (meth)acrylic acid alkyl ester in which an alkyl group constituting alkyl ester has a chain structure having 1 to 18 carbon atoms such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate,

10 isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, or octadecyl (meth)acrylate (stearyl

15 (meth)acrylate).

[0200]

Further, other examples of the acrylic monomer that does not contain the functional group include alkoxyalkyl group-containing (meth)acrylic acid ester such as methoxymethyl (meth)acrylate, methoxyethyl (meth)acrylate, ethoxymethyl

20 (meth)acrylate, or ethoxyethyl (meth)acrylate; (meth)acrylic acid ester containing an aromatic group which contains (meth)acrylic acid aryl ester such as phenyl (meth)acrylate; noncrosslinkable (meth)acrylamide and a derivative thereof; and (meth)acrylic acid ester containing a noncrosslinkable tertiary amino group such as N,N-dimethylaminoethyl (meth)acrylate or N,N-dimethylaminopropyl (meth)acrylate.

25 [0201]

The acrylic monomer that constitutes the acrylic polymer (a11) and does not contain the functional group may be formed of only one or two or more kinds thereof.

In a case where the acrylic monomer is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

5 [0202]

Examples of the non-acrylic monomer include olefin such as ethylene or norbornene; vinyl acetate; and styrene.

The non-acrylic monomer constituting the acrylic polymer (a11) may be formed of only one or two or more kinds thereof. In a case where the non-acrylic monomer is  
10 formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0203]

In the acrylic polymer (a11), the ratio of the amount (content) of a constitutional unit derived from the acrylic monomer containing the functional group to the total  
15 amount of the constitutional unit constituting the acrylic polymer (a11) is preferably in a range of 0.1% to 50% by mass, more preferably in a range of 1% to 40% by mass, and particularly preferably in a range of 3% to 30% by mass. In a case where the ratio thereof is in the above-described range, the amount of the energy ray curable group in the acrylic resin (a1-1) obtained by copolymerization of the acrylic polymer (a11) and the  
20 energy ray curable compound (a12) can be easily adjusted such that the degree of curing the protective film is in a preferable range.

[0204]

The acrylic polymer (a11) constituting the acrylic resin (a1-1) may be formed of only one or two or more kind thereof. In a case where the acrylic polymer (a11) is  
25 formed of two or more kinds thereof, the combination and the ratio can be optionally

selected.

[0205]

The amount of the acrylic resin (a1-1) in the protective film-forming composition (IV-1) is preferably in a range of 1% to 40% by mass, more preferably in a range of 2% to 30% by mass, and particularly preferably in a range of 3% to 20% by mass.

[0206]

Energy ray curable compound (a12)

It is preferable that the energy ray curable compound (a12) contains one or two or more selected from the group consisting of an isocyanate group, an epoxy group, and a carboxy group as a group which can react with the functional group contained in the acrylic polymer (a11) and more preferable that the energy ray curable compound (a12) contains an isocyanate group as the group. In a case where the energy ray curable compound (a12) contains an isocyanate group as the group, the isocyanate group easily reacts with a hydroxyl group of the acrylic polymer (a11) that contains a hydroxyl group as the functional group.

[0207]

It is preferable that the energy ray curable compound (a12) contains one to five energy ray curable groups in one molecule and more preferable that the energy ray curable compound (a12) contains one or two energy ray curable groups in one molecule.

[0208]

Examples of the energy ray curable compound (a12) include

2-methacryloyloxyethyl isocyanate, meth-isopropenyl- $\alpha,\alpha$ -dimethylbenzylisocyanate, methacryloyl isocyanate, allyl isocyanate, 1,1-(bisacryloyloxymethyl)ethyl isocyanate; an acryloyl monoisocyanate compound obtained by reacting a diisocyanate compound or a

polyisocyanate compound with hydroxyethyl (meth)acrylate; and an acryloyl monoisocyanate compound obtained by reacting a diisocyanate compound or a polyisocyanate compound, a polyol compound, and hydroxyethyl (meth)acrylate.

Among these, 2-methacryloyloxy ethyl isocyanate is preferable as the energy ray curable compound (a12).

[0209]

The energy ray curable compound (a12) constituting the acrylic resin (a1-1) may be formed of only one or two or more kinds thereof. In a case where the energy ray curable compound (a12) is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0210]

The ratio of the amount of the energy ray curable group derived from the energy ray curable compound (a12) to the amount of the functional group derived from the acrylic polymer (a11) in the acrylic resin (a1-1) is preferably in a range of 20% to 120% by mole, more preferably in a range of 35% to 100% by mole, and particularly preferably in a range of 50% to 100% by mole. In a case where the content ratio is in the above-described range, the adhesive strength of the protective film after curing is further increased. In a case where the energy ray curable compound (a12) is a monofunctional (one group is contained in one molecule) compound, the upper limit of the content ratio becomes 100% by mole. In addition, in a case where the energy ray curable compound (a12) is a polyfunctional (two or more groups are contained in one molecule) compound, the upper limit of the content ratio exceeds 100% by mole in some cases.

[0211]

The weight-average molecular weight (Mw) of the polymer (a1) is preferably in a range of 100000 to 2000000 and more preferably in a range of 300000 to 1500000.

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

[0212]

In a case where the polymer (a1) has at least a portion that is cross-linked by a cross-linking agent, the polymer (a1) does not correspond to any of the above-described monomers which have been described as the monomers constituting the acrylic polymer (a11) and may be cross-linked in a group reacting with a cross-linking agent by polymerization of a monomer containing the group reacting with a cross-linking agent or may be cross-linked in a group reacting with the functional group derived from the energy ray curable compound (a12).

[0213]

The polymer (a1) contained in the protective film-forming composition (IV-1) and the energy ray curable protective film-forming film may be formed of only one or two or more kinds thereof. In a case where the polymer (a1) is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0214]

(Compound (a2) containing energy ray curable group and having molecular weight of 100 to 80000)

Examples of the energy ray curable group contained in a compound (2) containing an energy ray curable group and having a molecular weight of 100 to 80000 include a group having an energy ray curable double bond, and preferred examples thereof include a (meth)acryloyl group and a vinyl group.

[0215]

The compound (a2) is not particularly limited as long as the above-described conditions are satisfied, and examples thereof include a low-molecular-weight compound containing an energy ray curable group, an epoxy resin containing an energy ray curable

group, and a phenol resin containing an energy ray curable group.

[0216]

Among the examples of the compound (a2), as the low-molecular-weight compound containing an energy ray curable group, a polyfunctional monomer or oligomer is an exemplary example, and preferred examples thereof include an acrylate-based compound containing a (meth)acryloyl group.

Examples of the acrylate-based compound include bifunctional (meth)acrylate such as 2-hydroxy-3-(meth)acryloyloxypropyl methacrylate, polyethylene glycol di(meth)acrylate, propoxylated ethoxylated bisphenol A di(meth)acrylate,

- 10 2,2-bis[4-((meth)acryloxypolyethoxy)phenyl]propane, ethoxylated bisphenol A di(meth)acrylate, 2,2-bis[4-((meth)acryoxydiethoxy)phenyl]propane, 9,9-bis[4-(2-(meth)acryloyloxyethoxy)phenyl]fluorene, 2,2-bis[4-((meth)acryloxypolypropoxy)phenyl]propane, tricyclodecanedimethanol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 15 1,9-nonanediol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, polytetramethylene glycol di(meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 2,2-bis[4-((meth)acryloxyethoxy)phenyl]propane, neopentyl glycol di(meth)acrylate, ethoxylated polypropylene glycol di(meth)acrylate, or 20 2-hydroxy-1,3-di(meth)acryloxypropane; polyfunctional (meth)acrylate such as tris(2-(meth)acryloxyethyl)isocyanurate,  $\epsilon$ -caprolactone-modified tris-(2-(meth)acryloxyethyl)isocyanurate, ethoxylated glycerin tri(meth)acrylate, pentaerythritol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, 25 pentaerythritol tetra(meth)acrylate, dipentaerythritol poly(meth)acrylate, or

dipentaerythritol hexa(meth)acrylate; and polyfunctional (meth)acrylate oligomer such as urethane (meth)acrylate oligomer.

[0217]

Among the examples of the compound (a2), those described in paragraph 0043  
5 of “Japanese Unexamined Patent Application, First Application No. 2013-194102” can be used as the epoxy resin containing an energy ray curable group and the phenol resin containing an energy ray curable group. Such a resin also corresponds to the resin constituting a thermosetting component described below, but is handled as the compound (a2) in the present invention.

10 [0218]

The weight-average molecular weight of the compound (a2) is preferably in a range of 100 to 30000 and more preferably in a range of 300 to 10000.

[0219]

The compound (a2) contained in the protective film-forming composition (IV-1)  
15 and the energy ray curable protective film-forming film may be formed of only one or two or more kinds thereof. In a case where the compound (a2) is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

[0220]

[Polymer (b) that does not contain energy ray curable group]

20 In a case where the protective film-forming composition (IV-1) and the energy ray curable protective film-forming film contain the compound (a2) as the energy ray curable component (a), it is preferable that the protective film-forming compound (IV-1) and the energy ray curable protective film-forming film contain a polymer (b) that does not contain an energy ray curable group.

25 The polymer (b) may have at least a portion which is cross-linked by a

cross-linking agent or may not be cross-linked.

[0221]

Examples of the polymer (b) that does not contain an energy ray curable group include an acrylic polymer, a phenoxy resin, a urethane resin, polyester, a rubber-based resin, and an acrylic urethane resin.

Among these, it is preferable that the polymer (b) is an acrylic polymer (hereinafter, also abbreviated as an “acrylic polymer (b-1)”).

[0222]

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

[0223]

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

[0224]

Examples of the (meth)acrylic acid ester include (meth)acrylic acid alkyl ester in which an alkyl group constituting alkyl ester has a chain structure having 1 to 18 carbon atoms such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate,

heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, or octadecyl (meth)acrylate (stearyl (meth)acrylate).

[0225]

Examples of the (meth)acrylic acid ester having a cyclic skeleton include (meth)acrylic acid cycloalkyl ester such as isobornyl (meth)acrylate or dicyclopentanyl (meth)acrylate; (meth)acrylic acid aralkyl ester such as benzyl (meth)acrylate; (meth)acrylic acid cycloalkenyl ester such as (meth)acrylic acid dicyclopentenyl ester; and (meth)acrylic acid cycloalkenyloxy alkyl ester such as (meth)acrylic acid dicyclopentenylloxy ethyl ester.

[0226]

Examples of the glycidyl group-containing (meth)acrylic acid ester include glycidyl (meth)acrylate.

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

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

[0227]

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

[0228]

As the polymer (b) which has at least a portion cross-linked by a cross-linking agent and does not contain the energy ray curable group, a polymer obtained by reacting a reactive functional group in the polymer (b) with a cross-linking agent is an exemplary  
5 example.

The reactive functional group may be appropriately selected according to the kind of cross-linking agent and is not particularly limited. For example, in a case where the cross-linking agent is a polyisocyanate compound, examples of the reactive functional group include a hydroxyl group, a carboxy group, and an amino group.

10 Among these, a hydroxyl group having a high reactivity with an isocyanate group is preferable. Further, in a case where the cross-linking agent is an epoxy-based compound, examples of the reactive functional group include a carboxy group, an amino group, and an amide group. Among these, a carboxy group having a high reactivity with an epoxy group is preferable. Here, from the viewpoint of preventing corrosion of  
15 a circuit such as a semiconductor wafer or a semiconductor chip, a group other than a carboxy group is preferable as the reactive functional group.

[0229]

Examples of the polymer (b) which contains the reactive functional group and does not contain an energy ray curable group include a polymer obtained by  
20 polymerizing a monomer containing at least the reactive functional group. In a case of the acrylic polymer (b-1), monomers containing the reactive functional groups may be used as any one or both of the acrylic monomer and the non-acrylic monomer exemplified by the monomer constituting the acrylic polymer (b-1). For example, a polymer obtained by polymerizing hydroxyl group-containing (meth)acrylic acid ester is  
25 an exemplary example as the polymer (b) containing a hydroxyl group as a reactive

functional group. Other examples thereof include a polymer obtained by polymerizing a monomer formed by one or two or more hydrogen atoms being substituted with the reactive functional groups in the acrylic monomer or the non-acrylic monomer described above.

5 [0230]

In the polymer (b) containing a reactive functional group, the ratio (content) of the amount of the constitutional unit derived from a monomer containing a reactive functional group to the total amount of the constitutional unit constituting the polymer (b) containing a reactive functional group is preferably in a range of 1% to 20% by mass and more preferably in a range of 2% to 10% by mass. In a case where the ratio thereof is in the above-described range, the degree of cross-linking in the polymer (b) is in the more preferable range.

[0231]

From the viewpoint of further improving the film-forming properties of the protective film-forming composition (IV-1), the weight-average molecular weight ( $M_w$ ) of the polymer (b) that does not contain an energy ray curable group is preferably in a range of 10000 to 2000000 and more preferably in a range of 100000 to 1500000. Here, the “weight-average molecular weight” is as described above.

[0232]

20 The polymer (b) which is contained in the protective film-forming composition (IV-1) and the energy ray curable protective film-forming film and does not contain an energy ray curable group may be formed of only one or two or more kinds thereof. In a case where the polymer (b) is formed of two or more kinds thereof, the combination and the ratio of these can be optionally selected.

25 [0233]

Examples of the protective film-forming composition (IV-1) include those containing any one or both of the polymer (a1) and the compound (a2). Further, in a case where the protective film-forming composition contains the compound (a2), it is preferable that the protective film-forming composition (IV-1) further contains the polymer (b) that does not contain an energy ray curable group. In this case, it is also preferable that the protective film-forming composition (IV-1) further contains the polymer (a1). Moreover, the protective film-forming composition (IV-1) may contain the polymer (a1) and the polymer (b) that does not contain an energy ray curable group without containing the compound (a2).

10 [0234]

In a case where the protective film-forming composition (IV-1) contains the polymer (a1), the compound (a2), and the polymer (b) that does not contain an energy ray curable group, the amount of the compound (a2) in the protective film-forming composition (IV-1) is preferably in a range of 10 to 400 parts by mass and more preferably in a range of 30 to 350 parts by mass with respect to 100 parts by mass of the total amount of the polymer (a1) and the polymer (b) that does not contain an energy ray curable group.

[0235]

The ratio of the total amount of the energy ray curable component (a) and the polymer (b) that does not contain an energy ray curable group to the total amount of the components in the protective film-forming composition (IV-1) other than the solvent (in other words, the total amount of the energy ray curable component (a) and the polymer (b) that does not contain an energy ray curable group in the energy ray curable protective film-forming film) is preferably in a range of 5% to 90% by mass, more preferably in a range of 10% to 80% by mass, and particularly preferably in a range of 20% to 70% by

mass. In a case where the content ratio of the energy ray curable component is in the above-described range, the energy ray curability of the energy ray curable protective film-forming film is further improved.

[0236]

5           The protective film-forming composition (IV-1) may contain one or two or more kinds selected from the group consisting of the thermosetting component, the photopolymerization initiator, the filler, the coupling agent, the cross-linking agent, the colorant, and the general-purpose additive other than the energy ray curable component depending on the intended purpose thereof. For example, by using the protective  
10 film-forming composition (IV-1) containing the energy ray curable component and the thermosetting component, the adhesive strength of the energy ray curable protective film-forming film to be formed to the adherend is improved by being heated and the strength of the protective film formed from the energy ray curable protective film-forming film is also improved.

15           [0237]

As the thermosetting component, the photopolymerization initiator, the filler, the coupling agent, the cross-linking agent, the colorant, and the general-purpose additive in the protective film-forming composition (IV-1), the thermosetting component (B), the photopolymerization initiator (H), the filler (D), the coupling agent (E), the cross-linking  
20 agent (F), the colorant (I), and the general-purpose additive (J) in the protective film-forming composition (III-1) are respective exemplary examples.

[0238]

The thermosetting component, the photopolymerization initiator, the filler, the coupling agent, the cross-linking agent, the colorant, and the general-purpose additive in  
25 the protective film-forming composition (IV-1) may be respectively used alone or in

combination of two or more kinds thereof. In a case where a combination of two or more kinds thereof is used, the combination and the ratio of these can be optionally selected.

The amounts of the thermosetting component, the photopolymerization initiator, the filler, the coupling agent, the cross-linking agent, the colorant, and the general-purpose additive in the protective film-forming composition (IV-1) may be appropriately adjusted depending on the intended purpose thereof and are not particularly limited.

[0239]

From the viewpoint of improving the handling properties through dilution, it is preferable that the protective film-forming composition (IV-1) further contains a solvent.

Examples of the solvent contained in the protective film-forming composition (IV-1) are the same as those for the solvent in the protective film-forming composition (III-1).

The solvent contained in the protective film-forming composition (IV-1) may be formed of only one or two or more kinds thereof.

[0240]

<<Method of producing energy ray curable protective film-forming composition>>

The energy ray curable protective film-forming composition such as the protective film-forming composition (IV-1) is obtained by blending respective components for constituting the composition.

The order of each component to be added at the time of blending is not particularly limited, and two or more components may be added at the same time.

In a case of using a solvent, the solvent may be used by being mixed with any of

blending components other than the solvent and diluting the blending components in advance or may be used by being mixed with these blending components without diluting any of blending components other than the solvent in advance.

The method of mixing respective components at the time of blending is not particularly limited and may be appropriately selected from known methods such as a method of mixing components by rotating a stirrer or a stirring blade; a method of mixing components using a mixer; and a method of mixing components by adding ultrasonic waves thereto.

The temperature and the time for the addition and the mixing of respective components are not particularly limited as long as the blending components are not deteriorated and may be appropriately adjusted, but the temperature is preferably in a range of 15°C to 30°C.

[0241]

Coating layer

The coating layer is not particularly limited as long as the surface roughness Ra of the surface of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet is smaller than that of the surface of the support sheet where the coating layer is provided.

As the coating layer, a layer that contains a cured product obtained by being irradiated with energy rays to be cured or a layer obtained by curing a coating composition that is polymerized by irradiation with energy rays and contains an energy ray polymerizable compound is preferable. Further, it is preferable that the energy ray polymerizable compound is (meth)acrylic acid or a derivative thereof.

[0242]

The protective film-forming composite sheet may have a function of forming a

protective film for protecting the rear surface of a semiconductor chip obtained by performing dicing as well as a function of serving as a dicing sheet at the time of dicing a semiconductor wafer. Further, the semiconductor wafer to which the protective film-forming composite sheet adheres is occasionally expanded at the time of dicing the semiconductor wafer. In this case, the protective film-forming composite sheet is required to have moderate flexibility. In order to impart moderate flexibility to the protective film-forming composite sheet, for example, a flexible resin such as propylene is selected as the material constituting the support sheet. Meanwhile, such a flexible resin or the like is deformed by being heated or wrinkled in some cases. Therefore, it is desired that the coating layer can be formed by curing the composition which is a raw material through irradiation with energy rays without curing the composition with heat.

[0243]

The thickness of the coating layer is not particularly limited, but is preferably in a range of 0.1 to 20  $\mu\text{m}$ , more preferably in a range of 0.4 to 15  $\mu\text{m}$ , and particularly preferably in a range of 0.8 to 10  $\mu\text{m}$ . In a case where the thickness of the coating layer is greater than or equal to the above-described lower limit, the surface roughness Ra of the surface of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet can be more easily decreased and the effect of suppressing blocking of the protective film-forming composite sheet is further increased. Further, in a case where the thickness of the coating layer is less than or equal to the above-described upper limit, a clearer inspection image can be obtained when the state of the semiconductor wafer after the protective film-forming composite sheet has adhered thereto is inspected using an infrared camera or the like through the sheet, and the dicing of the semiconductor wafer accompanied by expansion can be more easily performed.

By covering the uneven surface of the support sheet with the coating layer as

described above, the surface where the coating layer is in contact with the support sheet may become an uneven surface. In a portion having a projection in the uneven surface of the coating layer, the thickness of the coating layer can be calculated using the tip of this projection as one starting point.

5 [0244]

The surface roughness Ra of the surface of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet is preferably 0.5  $\mu\text{m}$  or less, more preferably 0.4  $\mu\text{m}$  or less, still more preferably 0.3  $\mu\text{m}$  or less, and particularly preferably 0.2  $\mu\text{m}$  or less. In a case where the surface roughness Ra of the coating layer is less than or equal to the upper limit, clear laser printing can be performed on the protective film.

Further, the lower limit of the surface roughness Ra of the surface of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet is not particularly limited, but can be set to 0.005  $\mu\text{m}$  or the like.

15 In other words, the surface roughness Ra is preferably in a range of 0.005 to 0.5  $\mu\text{m}$ , more preferably in a range of 0.005 to 0.4  $\mu\text{m}$ , still more preferably in a range of 0.005 to 0.3  $\mu\text{m}$ , and particularly preferably in a range of 0.005 to 0.2  $\mu\text{m}$  or less.

The surface roughness Ra of the coating layer can be adjusted according to the surface roughness Ra of the surface of the support sheet on a side where the coating layer is provided, the thickness of the coating layer, the method of applying the coating composition described below which is used for forming the coating layer, or the like.

[0245]

In the coating layer, the value of [thickness ( $\mu\text{m}$ ) of coating layer]/[surface roughness Ra ( $\mu\text{m}$ ) of surface of support sheet on side where coating layer is provided] is

preferably in a range of 0.1 to 30, more preferably in a range of 0.3 to 20, and particularly preferably in a range of 0.5 to 10. In a case where the value is greater than or equal to the above-described lower limit, the surface roughness Ra of the surface of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet is further decreased. Therefore, clearer laser printing can be performed on the protective film and the effect of suppressing blocking of the protective film-forming composite sheet is further increased. In addition, in a case where the value is less than or equal to the above-described upper limit, an excessive increase in thickness of the coating layer is prevented.

10 [0246]

The gloss value of the surface of the coating layer on a side opposite to a side (the support sheet side) where the coating layer is in contact with the support sheet is preferably in a range of 32 to 95, more preferably in a range of 40 to 90, and particularly preferably in a range of 45 to 85. For example, the gloss value thereof may be in a range of 50 to 80. In a case where the gloss value of the coating layer is in the above-described range, clearer laser printing can be performed on the protective film.

Further, in a case where the gloss value of the coating layer is greater than or equal to the above-described lower limit, a clearer inspection image can be obtained when the state of the semiconductor wafer after the protective film-forming composite sheet has adhered thereto is inspected using an infrared camera or the like through the sheet. Further, in a case where the gloss value of the coating layer is less than or equal to the above-described upper limit, similarly, a phenomenon in which the coating layer is lighting is suppressed when the state of the semiconductor wafer is inspected and visual inspection of the inspection image using an infrared camera or the like is more easily

25 performed.

Further, the gloss value indicates a value obtained by measuring the specular glossiness of the surface of the coating layer at 20° from a side of the coating layer opposite to the support sheet side in conformity with JIS K 7105.

[0247]

5           The value of the haze of the protective film-forming composite sheet measured from the coating layer side is preferably 47% or less, more preferably in a range of 1% to 47%, still more preferably in a range of 2% to 40%, and particularly preferably in a range of 3% to 30%. In a case where the haze of the protective film-forming composite sheet is less than or equal to the above-described upper limit, light scattering is suppressed, and  
10   clear laser printing can be performed on the protective film. Further, a clearer inspection image can be obtained when the state of the semiconductor wafer after the protective film-forming composite sheet has adhered thereto is inspected using an infrared camera or the like through the sheet. Here, the measured value of the haze of the protective film-forming composite sheet indicates a value of the haze measured in a  
15   direction of the surface of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet in the protective film-forming composite sheet.

Further, the haze is a value obtained by performing measurement in conformity with JIS K 7136.

[0248]

20           Various characteristics of the coating layer such as the gloss value thereof can be adjusted according to the thickness of the coating layer, the components contained in the coating composition described below which is used for forming the coating layer, and the like.

25           The value of the haze of the protective film-forming composite sheet measured from the coating layer side can be adjusted according to the thickness of each layer such

as the coating layer or the support sheet which constitutes the protective film-forming composite sheet, the components contained in the composition (for example, the coating composition described below) used for forming each of these layers, and the like.

[0249]

5 <<Coating composition>>

It is preferable that the coating composition contains any one or both ( $\alpha$ ) of a silica sol and a silica fine particle to which a radical polymerizable unsaturated group-containing organic compound is bonded (hereinafter, also abbreviated as a “component ( $\alpha$ )”); and one or two or more kinds ( $\beta$ ) selected from the group consisting  
10 of a polyfunctional acrylate-based monomer and an acrylate-based prepolymer (hereinafter, also abbreviated as a “component ( $\beta$ )”).

[0250]

[Component ( $\alpha$ )]

The component ( $\alpha$ ) is a component for decreasing the refractive index of the  
15 coating layer, decreasing curing shrinkage and wet heat shrinkage of the protective film-forming composite sheet, and suppressing occurrence of curling in the protective film-forming composite sheet due to the shrinkage.

[0251]

As the silica sol in the component ( $\alpha$ ), colloidal silica formed by silica fine  
20 particles being suspended in an organic solvent such as alcohol or ether (cellosolve) derived from ethylene glycol in a colloidal state is an exemplary example. The average particle diameter of the silica fine particles being suspended is preferably in a range of 0.001 to 1  $\mu\text{m}$  and more preferably in a range of 0.03 to 0.05  $\mu\text{m}$ .

[0252]

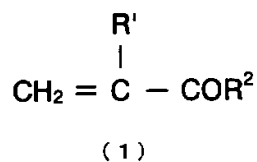
The silica fine particles, to which a radical polymerizable unsaturated group-containing organic compound is bonded, in the component ( $\alpha$ ) are cross-linked and cured by irradiation with energy rays.

Examples of the silica fine particle to which the radical polymerizable unsaturated group-containing organic compound is bonded include particles obtained by reacting a silanol group present on the surface of a silica fine particle with a functional group in a radical polymerizable unsaturated group-containing organic compound, and the average particle diameter of the silica fine particles is preferably in a range of 0.005 to 1  $\mu\text{m}$ . The functional group in a radical polymerizable unsaturated group-containing organic compound is not particularly limited as long as the functional group can react with the silanol group in the silica fine particle.

[0253]

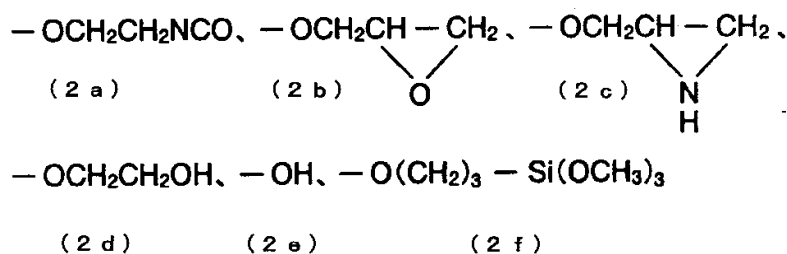
As the radical polymerizable unsaturated group-containing organic compound that contains the functional group, a compound represented by Formula (1) is exemplary example.

[0254]



(In the formula,  $\text{R}^1$  represents a hydrogen atom or a methyl group; and  $\text{R}^2$  represents a halogen atom or a group represented by any of Formulae (2a) to (2f).)

20 [0255]



[0256]

Examples of the halogen atom as  $R^2$  include a chlorine atom, a bromine atom, and an iodine atom.

5 [0257]

Preferred examples of the radical polymerizable unsaturated group-containing organic compound include (meth)acrylic acid, (meth)acrylic acid chloride, 2-isocyanatoethyl (meth)acrylate, glycidyl (meth)acrylate, 2,3-iminopropyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, and

10 (3-(meth)acryloyloxypropyl)trimethoxysilane.

[0258]

In the present invention, the radical polymerizable unsaturated group-containing organic compound may be used alone or in combination of two or more kinds thereof.

[0259]

15 In the component ( $\alpha$ ), the silica sol and the silica fine particle to which the radical polymerizable unsaturated group-containing organic compound is bonded may be respectively formed of only one or two or more kinds thereof.

[0260]

20 As the component ( $\alpha$ ), only the silica sol may be used; only the silica fine particle to which the radical polymerizable unsaturated group-containing organic compound is bonded may be used; or a combination of the silica sol and the silica fine

particle to which the radical polymerizable unsaturated group-containing organic compound is bonded may be used.

[0261]

It is preferable that the amount of the component ( $\alpha$ ) in the coating composition  
5 is selected according to the refractive index of the support sheet. However, typically, it  
is preferable that the content thereof is set to a value such that the amount of the silica  
derived from the component ( $\alpha$ ) of the coating layer is in a range of 20% to 60% by mass.  
In a case where the amount of silica is greater than or equal to the above-described lower  
limit, the effect of decreasing the refractive index of the coating layer and the effect of  
10 suppressing occurrence of curing in the protective film-forming composite sheet are  
further increased. Further, in a case where the amount of silica is less than or equal to  
the above-described upper limit, the coating layer is more easily formed, and the effect of  
suppressing a decrease in hardness of the coating layer is further increased.

From the viewpoints of improving the refractive index of the coating layer,  
15 easily forming the coating layer, improving the hardness thereof, and suppressing  
occurrence of curling in the protective film-forming composite sheet, the amount of silica  
derived from the component ( $\alpha$ ) of the coating layer is more preferably in a range of 20%  
to 45% by mass.

[0262]

20 [Component ( $\beta$ )]

The component ( $\beta$ ) is a main photocurable component that forms the coating  
layer.

[0263]

The polyfunctional acrylate-based monomer in the component ( $\beta$ ) is not

particularly limited as long as the polyfunctional acrylate-based monomer is a (meth)acrylic acid derivative containing two or more (meth)acryloyl groups in one molecule.

Preferred examples of the polyfunctional acrylate-based monomer include

5 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, hydroxypivalic acid neopentyl glycol di(meth)acrylate, dicyclopentanyl di(meth)acrylate, caprolactone-modified dicyclopentenyl di(meth)acrylate, ethylene oxide-modified phosphoric acid di(meth)acrylate, allylated cyclohexyl di(meth)acrylate, isocyanurate di(meth)acrylate,

10 trimethylolpropane tri(meth)acrylate, dipentaerythritol tri(meth)acrylate, propionic acid-modified dipentaerythritol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, propylene oxide-modified trimethylolpropane tri(meth)acrylate, tris(acryloxyethyl)isocyanurate, dipentaerythritol penta(meth)acrylate, propionic acid-modified dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate,

15 and caprolactone-modified dipentaerythritol hexa(meth)acrylate.

[0264]

The acrylate-based prepolymer in the component ( $\beta$ ) is not particularly limited as long as the acrylate-based prepolymer is (meth)acrylic acid ester and also a polymer or an oligomer having photocurability.

20 Preferred examples of the acrylate-based prepolymer include a polyester acrylate-based prepolymer, an epoxy acrylate-based prepolymer, a urethane acrylate-based prepolymer, and a polyol acrylate-based prepolymer.

[0265]

Examples of the polyester acrylate-based prepolymer include a prepolymer

25 obtained by esterifying hydroxyl groups in a polyester oligomer containing hydroxyl

groups in both terminals of a molecule, obtained by a condensation reaction between polyvalent carboxylic acid and polyhydric alcohol, using (meth)acrylic acid; and a prepolymer obtained by esterifying a hydroxyl group in the terminal of an oligomer, obtained by adding alkylene oxide to polyvalent carboxylic acid to cause a reaction,  
 5 using (meth)acrylic acid.

Examples of the epoxy acrylate-based prepolymer include a prepolymer obtained by reacting (meth)acrylic acid with an oxirane ring of a bisphenol type epoxy resin or a novolak type epoxy resin having a relatively low molecular weight and esterifying the reactant.

10 Examples of the urethane acrylate-based prepolymer include a prepolymer obtained by esterifying a polyurethane oligomer, obtained by reacting a polyether polyol or a polyester polyol with polyisocyanate, using (meth)acrylic acid.

Examples of the polyol acrylate-based prepolymer include a prepolymer obtained by esterifying a hydroxyl group in a polyether polyol using (meth)acrylic acid.

15 [0266]

The polyfunctional acrylate-based monomer and the acrylate-based prepolymer in the component ( $\beta$ ) may be formed of only one or two or more kinds thereof.

[0267]

As the component ( $\beta$ ), only the polyfunctional acrylate-based monomer may be  
 20 used; only the acrylate-based prepolymer may be used; or a combination of the polyfunctional acrylate-based monomer with the acrylate-based prepolymer may be used.

[0268]

[Solvent]

It is preferable that the coating composition further contains a solvent other than  
 25 the component ( $\alpha$ ) and the component ( $\beta$ ). In a case where the coating composition

contains a solvent, a coating film for forming the coating layer can be more easily formed by applying and drying the coating composition as described below.

The solvent may be used alone or in combination of two or more kinds thereof.

[0269]

5           Examples of the solvent include an aliphatic hydrocarbon such as hexane, heptane, or cyclohexane; an aromatic hydrocarbon such as toluene or xylene; a halogenated hydrocarbon such as methylene chloride or ethylene chloride; an alcohol such as methanol, ethanol, propanol, butanol, or 1-methoxy-2-propanol; a ketone such as acetone, methyl ethyl ketone, 2-pentanone, isophorone, or cyclohexanone; an ester such  
10 as ethyl acetate or butyl acetate; and a cellosolve such as 2-ethoxyethanol (ethyl cellosolve).

[0270]

[Optional components]

The coating composition may contain various optional components such as a  
15 monofunctional acrylate-based monomer, a photopolymerization initiator, a photosensitizer, a polymerization inhibitor, a cross-linking agent, an antioxidant, an ultraviolet absorbing agent, a light stabilizer, a leveling agent, and an antifoaming agent in addition to the component ( $\alpha$ ) and the component ( $\beta$ ) within the range not damaging the effects of the present invention.

20           The optional components may be used alone or in combination of two or more kind thereof.

[0271]

(Monofunctional acrylate-based monomer)

The monofunctional acrylate-based monomer as an optional component is not  
25 particularly limited as long as the monofunctional acrylate-based monomer is a

photocurable component and also a (meth)acrylic acid derivative containing only one (meth)acryloyl group in one molecule.

Preferred examples of the monofunctional acrylate-based monomer include cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, dodecyl (meth)acrylate (lauryl (meth)acrylate), octadecyl (meth)acrylate (stearyl (meth)acrylate), and isobornyl (meth)acrylate.

[0272]

(Photopolymerization initiator)

As the photopolymerization initiator as an optional component, known components of the related art which have been used for radical polymerization are exemplary examples.

Preferred examples of the photopolymerization initiator include an aryl ketone-based photopolymerization initiator such as an acetophenone-based compound, a benzophenone-based compound, an alkylaminobenzophenone-based compound, a benzyl-based compound, a benzoin-based compound, a benzoin ether-based compound, a benzyl dimethyl acetal-based compound, a benzoyl benzoate-based compound, or an  $\alpha$ -acyloxime ester-based compound; a sulfur-containing photopolymerization initiator such as a sulfide-based compound or a thioxanthone-based compound; an acylphosphine oxide-based compound such as acyl diaryl phosphine oxide; and an anthraquinone-based compound.

Further, in a case where the coating composition is cured by irradiation with electron beams, a photopolymerization initiator is not necessary.

[0273]

The amount of the photopolymerization initiator in the coating composition is preferably in a range of 0.2 to 10 parts by mass and more preferably in a range of 0.5 to 7

parts by mass with respect to 100 parts by mass of the total amount of the photocurable components.

[0274]

(Photosensitizer)

5        Examples of the photosensitizer include tertiary amines, p-dimethylaminobenzoic acid ester, and a thiol-based sensitizer.

The amount of the photosensitizer in the coating composition is preferably in a range of 1 to 20 parts by mass and more preferably in a range of 2 to 10 parts by mass with respect to 100 parts by mass of the total amount of the photocurable components.

10       [0275]

(Antioxidant, ultraviolet absorbing agent, and light stabilizer)

The antioxidant, the ultraviolet absorbing agent, and the light stabilizer may be known, but a reactive antioxidant, a reactive ultraviolet absorbing agent, and a reactive light stabilizer containing a (meth)acryloyl group or the like in a molecule are preferable.

15       Since these antioxidant, ultraviolet absorbing agent, and light stabilizer are bonded to a polymer chain formed by irradiation with energy rays, dissipation from a cured layer with time is suppressed and the functions of these components are exhibited for a long period of time.

[0276]

20       It is preferable that the coating composition contains a silica sol as the component ( $\alpha$ ) and more preferable that the coating composition contains a silica sol having silica fine particles, suspended in a colloidal state, with an average particle diameter of 0.03 to 0.05  $\mu\text{m}$ .

In a case where the coating layer contains such a silica sol, the effect of  
25       suppressing blocking of the protective film-forming composite sheet is further increased.

In addition, a larger amount of such a silica sol is present and unevenly distributed in the surface of the coating layer on a side opposite to the support sheet side and a region in the vicinity of the coating layer than other regions, the effect of suppressing blocking of the protective film-forming composite sheet is further increased. In order to unevenly  
 5 distribute components contained in the coating composition such as a silica sol in the coating layer, the conditions for applying the coating composition may be adjusted.

[0277]

<<Method of producing coating composition>>

The coating composition is obtained by blending respective components for  
 10 constituting the coating composition, for example, the energy ray polymerizable compounds such as the component ( $\alpha$ ) and the component ( $\beta$ ) and other components as necessary. The coating composition is obtained according to the same method as the method for the above-described pressure sensitive adhesive composition except that the blending components for the coating composition are different from those for the  
 15 pressure sensitive adhesive composition.

In a case of using a solvent, the solvent may be used by being mixed with any of blending components other than the solvent and diluting the blending components in advance or may be used by being mixed with these blending components without diluting any of blending components other than the solvent in advance.

20 The components in the coating composition other than the solvent may be dissolved or may be dispersed without being dissolved. Further, the concentration or the viscosity of each component in the coating composition is not particularly limited as long as the coating composition can be applied.

[0278]

25 Method of producing protective film-forming composite sheet

The protective film-forming composite sheet according to the present invention can be produced by forming a protective film-forming film using the protective film-forming composition, forming a coating layer using the coating composition, and laminating the coating layer, the support sheet, and the protective film-forming film in this order. In a case where the support sheet is formed of a plurality of layers, the support sheet may be prepared by laminating a plurality of these layers on one another. For example, in a case where the support sheet is formed by laminating the base material and the pressure sensitive adhesive layer, the pressure sensitive adhesive layer may be formed using the pressure sensitive adhesive composition.

10 [0279]

The order of forming respective layers (the coating layer, the support sheet, and the protective film-forming film) constituting the protective film-forming composite sheet is not particularly limited. Further, the formation of each of these layers from the compositions thereof may be performed directly on the surface of the adjacent layer in the state of the protective film-forming composite sheet or the formation may be performed on the surface of a release film using a separate release film (release sheet) and then the formed layer may be allowed to adhere to the surface of the adjacent layer in the state of the protective film-forming composite sheet. Here, it is preferable that the coating layer is formed by directly coating the uneven surface of the support sheet with the coating composition in order to suppress generation of a gap portion between the coating layer and the uneven surface (rear surface) of the support sheet.

20 Hereinafter, a preferred example of a method of producing the protective film-forming composite sheet will be described.

[0280]

25 It is preferable that the coating layer is formed by coating the uneven surface (in

FIGS. 1 and 2, the rear surface 10b of the support sheet 10, that is, the rear surface 11b of the base material 11) of the support sheet with the coating composition, drying the surface, and curing the formed coating film as necessary.

[0281]

5           The application of the coating composition to the target surface may be performed according to a known method, and examples thereof include methods using various 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 Meyer bar coater, and a kiss coater.

10           [0282]

          In a case where the uneven surface of the support sheet is coated with the coating composition, it is preferable that generation of a gap portion between the coating layer and the uneven surface of the support sheet is suppressed. By suppressing generation of the gap portion, irregular reflection of light at the boundary between the coating layer and the uneven surface of the support sheet and clearer laser printing can be performed on the protective film.

          In order to suppress generation of the gap portion, it is preferable to use a coating composition having a low viscosity. In addition, the coating composition containing an energy ray polymerizable compound is usually suitable for suppressing generation of the gap portion.

[0283]

          The conditions for drying the coating composition are not particularly limited, but it is preferable that the coating composition is heated and dried. In this case, it is preferable that the coating composition is dried under a temperature condition of 70°C to 130°C for 0.5 to 5 minutes.

[0284]

The conditions for curing the coating film formed from the coating composition are not particularly limited, and the coating film may be cured according to a known method.

5           In a case where the coating film is cured by irradiation with energy rays and, for example, irradiated with ultraviolet rays, the irradiation may be performed by setting the irradiation dose to be preferably in a range of 100 to 500 mJ/cm<sup>2</sup> using a high pressure mercury lamp, a fusion H lamp, a xenon lamp, a black light, or an LED lamp as an ultraviolet ray source. Further, in a case where the coating film is irradiated with  
10   electron beams, the irradiation may be performed by generating electron beams using an electron beam accelerator or the like and setting the irradiation dose to be preferably in a range of 150 to 350 kV. Among these, it is preferable that the coating layer is formed by irradiation with ultraviolet rays.

[0285]

15           In a case where the support sheet is formed by laminating the base material and the pressure sensitive adhesive layer, the pressure sensitive adhesive layer can be formed by directly coating the surface (the surface 11a of the base material 11 in FIGS. 1 and 2) of the base material in contact with the coating layer with the pressure sensitive adhesive composition. However, it is usually preferable to employ a method of coating the  
20   surface of the release sheet, to which a release treatment has been applied, with the pressure sensitive adhesive composition, drying the surface, adhering the formed pressure sensitive adhesive layer to the surface of the base material, removing the release sheet to separately form a pressure sensitive adhesive layer, and adhering the pressure sensitive adhesive layer to the surface of the base material.

25           [0286]

The target surface can be coated with the pressure sensitive adhesive composition according to the same method as in the case of the coating composition.

[0287]

The applied pressure sensitive adhesive composition may be cross-linked by being heated and the cross-linking by heating the composition may be performed while drying. The composition can be heated under conditions of a temperature of 100°C to 130°C for 1 to 5 minutes, but the heating conditions are not limited to these.

[0288]

In both of a case where the support sheet is formed of only one layer (single layer) such as a base material and a case where the support sheet is formed of a plurality of layers by, for example, the base material and the pressure sensitive adhesive layer being laminated on each other, the surface (in FIGS. 1 and 2, the surface 10a of the support sheet 10, that is, the surface 12a of the pressure sensitive adhesive layer 12) of the support sheet in contact with the coating layer can be directly coated with the protective film-forming composition to form a protective film-forming film. However, it is usually preferable to employ a method of coating the surface of the release sheet, to which a release treatment has been applied, with the protective film-forming composition, drying the surface, adhering the formed protective film-forming film to the surface of the support sheet, removing the release sheet as necessary to separately form a pressure sensitive adhesive layer, and adhering the protective film-forming film to the surface of the support sheet.

[0289]

The target surface can be coated with the protective film-forming composition according to the same method as in the case of the coating composition.

The conditions for drying the protective film-forming composition are not

particularly limited, but the protective film-forming composition can be dried according to the same method as in the case of the coating composition.

[0290]

In a case where the support sheet is formed by laminating the base material and  
5 the pressure sensitive adhesive layer, the protective film-forming composite sheet  
according to the present invention can also be produced using a method other than the  
above-described method. For example, the protective film-forming composite sheet can  
also be produced by forming a pressure sensitive adhesive layer using the pressure  
sensitive adhesive composition, forming a protective film-forming film using the  
10 protective film-forming composition to obtain a laminate formed by laminating the  
pressure sensitive adhesive layer and the protective film-forming film, and adhering the  
surface of the base material (the surface 11a of the base material 11 in FIGS. 1 and 2) on  
which the coating layer is provided to the surface (the surface which is not provided with  
the protective film-forming film of the pressure sensitive adhesive layer) of the pressure  
15 sensitive adhesive layer in this laminate.

The conditions for forming the pressure sensitive adhesive layer and the  
protective film-forming film in this case are the same as in the case of the  
above-described method.

[0291]

20 For example, when the protective film-forming composite sheet is seen from the  
above in a plan view as shown in FIG. 1, in a case of producing a protective film-forming  
composite sheet that includes a protective film-forming film having a surface area  
smaller than that of the pressure sensitive adhesive layer, the protective film-forming film  
cut into have a predetermined size and a predetermined shape in advance may be  
25 provided on the pressure sensitive adhesive layer according to the above-described

production method.

[0292]

Method of using protective film-forming composite sheet

For example, a method of using the protective film-forming composite sheet  
5 according to the present invention is as described below.

First, a method of using the protective film-forming composite sheet in a case  
where the protective film-forming film is thermosetting will be described.

In this case, first, the rear surface of the semiconductor wafer is allowed to  
adhere to the protective film-forming film of the protective film-forming composite sheet,  
10 and the protective film-forming composite sheet is fixed to a dicing device.

Next, the protective film-forming film is heated and cured to obtain a protective  
film. In a case where back grinding tape adheres to the surface (the surface on which an  
electrode is formed) of the semiconductor wafer, a protective film is typically formed  
after the back grinding tape is removed from the semiconductor wafer.

15 [0293]

Next, a semiconductor chip is obtained by dicing the semiconductor wafer.  
During the period from the formation of the protective film to the dicing, printing can be  
performed on the surface of the protective film by irradiating the protective film with  
laser light from the coating layer side of the protective film-forming composite sheet.

20 In this case, as described above, the surface roughness Ra of the surface (rear surface) of  
the coating layer on a side opposite to a side where the coating layer is in contact with the  
support sheet is sufficiently small, and the rear surface of the coating layer is a smooth  
surface or a surface with a degree of suppressed unevenness. Accordingly, when laser  
light is applied, irregular reflection of the laser light on the rear surface of the coating  
25 layer is suppressed and clear laser printing can be performed on the protective film.

[0294]

Further, the state of the semiconductor wafer before dicing is performed or the semiconductor chip obtained by performing dicing is occasionally inspected by observing the semiconductor wafer or the semiconductor chip from the rear surface (the surface to which the protective film-forming composite sheet adheres) thereof using a semiconductor camera or the like. For example, the presence of damage such as chipping or cracking is occasionally inspected in a case of the semiconductor chip.

In the semiconductor chip provided with a protective film according to the present invention, as described above, the surface roughness Ra of the surface (rear surface) of the coating layer on a side opposite to a side where the coating layer is in contact with the support sheet is sufficiently small, and occurrence of a gap portion between the coating layer and the uneven surface (rear surface) of the support sheet is suppressed. Accordingly, since a clear inspection image can be obtained when the semiconductor wafer or the semiconductor chip is observed through the protective film-forming composite sheet from the coating layer side using an infrared camera or the like, inspection can be performed with high precision.

[0295]

Next, the semiconductor chip and the protective film adhering to the rear surface thereof are peeled off and picked up from the support sheet, thereby obtaining a semiconductor chip provided with a protective film. For example, in a case where the support sheet is formed by laminating the base material and the pressure sensitive adhesive layer and the pressure sensitive adhesive layer is energy ray curable, the semiconductor chip provided with a protective film is easily obtained by curing the pressure sensitive adhesive layer through irradiation with energy rays and picking up the semiconductor chip and the protective film adhering the rear surface thereof from the

cured pressure sensitive adhesive layer.

[0296]

For example, in a case of using the protective film-forming composite sheet 1 shown in FIG. 1, the rear surface of the semiconductor wafer is allowed to adhere to the protective film-forming film 13 of the protective film-forming composite sheet 1, the exposed support sheet 10 (pressure sensitive adhesive layer 12) is allowed to adhere to a dicing jig (not shown) such as a ring frame, and the protective film-forming composite sheet 1 is fixed to a dicing device. Next, the protective film-forming film 13 is cured to obtain a protective film, the protective film is laser-printed and then diced, a region of the pressure sensitive adhesive layer 12 other than the side where the pressure sensitive adhesive layer 12 adheres to the jig is cured by irradiation with energy rays as necessary, and the semiconductor chip provided with a protective film may be picked up. As described above, in a case where the protective film-forming composite sheet 1 including the pressure sensitive adhesive layer 12 which is energy ray curable is used, adjustment is required such that a specific region of the pressure sensitive adhesive layer 12 is not cured in order for the protective film-forming composite sheet 1 not to be peeled off from the jig. In the case of using the protective film-forming composite sheet 1, it is not necessary to separately provide a configuration for adhering the protective film-forming composite sheet 1 to the jig.

[0297]

Meanwhile, in a case of using the protective film-forming composite sheet 2 shown in FIG. 2, the rear surface of the semiconductor wafer is allowed to adhere to the protective film-forming film 23 of the protective film-forming composite sheet 2, the adhesive layer 16 for a jig is allowed to adhere to a dicing jig (not shown) such as a ring frame, and the protective film-forming composite sheet 2 is fixed to a dicing device.

Next, the protective film-forming film 23 is cured to obtain a protective film, the protective film is laser-printed and then diced, the pressure sensitive adhesive layer 12 is cured by irradiation with energy rays as necessary, and the semiconductor chip provided with a protective film may be picked up. As described above, a case where the

5 protective film-forming composite sheet 2 including the pressure sensitive adhesive layer 12 which is energy ray curable is used is different from the case where the protective film-forming composite sheet 1 is used, it is not necessary to perform adjustment such that the specific region of the pressure sensitive adhesive layer 12 is not cured.

However, it is necessary to provide the adhesive layer 16 for a jig for the protective

10 film-forming composite sheet 2, which is different from the case of the protective film-forming composite sheet 1. By providing the adhesive layer 16 for a jig, a composition for forming the pressure sensitive adhesive layer 12 can be selected from various kinds of compositions depending on the intended purpose thereof.

[0298]

15 Next, a method of using the protective film-forming composite sheet in a case where the protective film-forming film is energy ray curable will be described.

In this case, first, the rear surface of the semiconductor wafer is allowed to adhere to the protective film-forming film of the protective film-forming composite sheet, and the protective film-forming composite sheet is fixed to a dicing device similar to the  
20 above-described case where the protective film-forming film is thermosetting.

Next, the protective film-forming film is cured by irradiation with energy rays to obtain a protective film. In a case where back grinding tape adheres to the surface (the surface on which an electrode is formed) of the semiconductor wafer, a protective film is typically formed after the back grinding tape is removed from the semiconductor wafer.

25 [0299]

Next, a semiconductor chip is obtained by dicing the semiconductor wafer.

During the period from the formation of the protective film to the dicing, printing can be performed on the surface of the protective film by irradiating the protective film with laser light from the coating layer side of the protective film-forming composite sheet.

- 5 The process from the printing to the dicing can be performed in the same manner as in the above-described case where the protective film-forming film is thermosetting.

Similar to this case, clear laser printing can be performed on the protective film and the inspection can be performed using an infrared camera or the like with high precision.

[0300]

- 10 Next, a semiconductor chip provided with a protective film is obtained by peeling and picking up the semiconductor chip together with the protective film adhering to the rear surface of the semiconductor chip from the support sheet.

- This method is particularly suitable for a case where the support sheet of the protective film-forming composite sheet is formed by laminating the base material and the pressure sensitive adhesive layer and the pressure sensitive adhesive layer is non-energy ray curable. Here, the case where the protective film-forming film is cured by irradiation with energy rays, the semiconductor wafer is diced, and the semiconductor chip provided with a protective film is picked up has been described. However, in the case where the pressure sensitive adhesive layer is non-energy ray curable, the curing of the protective film-forming film by irradiation with energy rays can be performed at any stage up to the picking up of the semiconductor chip.

[0301]

- For example, in a case of using the protective film-forming composite sheet in which the support sheet is formed by laminating the base material and the pressure sensitive adhesive layer and the pressure sensitive adhesive layer is energy ray curable, a

method described below is preferable.

In other words, first, the rear surface of the semiconductor wafer is allowed to adhere to the protective film-forming film of the protective film-forming composite sheet, and the protective film-forming composite sheet is fixed to a dicing device similar to the  
5 above-described case where the protective film-forming film is thermosetting.

Next, the protective film is irradiated with laser light from the coating layer side of the protective film-forming composite sheet, printing is performed on the surface of the protective film, and the semiconductor wafer is diced to obtain a semiconductor chip.

The process from the printing to the dicing can be performed in the same manner as in

10 the above-described case where the protective film-forming film is thermosetting.

Similar to this case, clear laser printing can be performed on the protective film and the inspection can be performed using an infrared camera or the like with high precision.

[0302]

Next, the protective film-forming film is cured by being irradiated with energy  
15 rays to obtain a protective film, the pressure sensitive adhesive layer is cured, and the semiconductor chip and the protective film adhering the rear surface thereof are picked up from the cured pressure sensitive adhesive layer, thereby obtaining a semiconductor chip provided with a protective film.

[0303]

20 Meanwhile, in a case where a long protective film-forming composite sheet is wound, a protective film-forming composite sheet in a state in which the release film (the release film 15 in FIGS. 1 and 2) is laminated on the exposed surface of the protective film-forming film is typically used. In all configurations (for example, both of the protective film-forming composite sheet 1 shown in FIG. 1 and the protective  
25 film-forming composite sheet 2 shown in FIG. 2) of the protective film-forming

composite sheet according to the present invention, as the protective film-forming composite sheet is wound in a roll shape, a laminate unit formed by laminating the coating layer, the support sheet, the protective film-forming film, and the release film in this order is sequentially stacked in the radial direction of the roll. As a result, between

5 laminate units in contact with each other in the radial direction of the roll, the surface (the surface on a side opposite to a side where the protective film-forming film is provided) of the release film in one laminate unit and the rear surface (the surface on a side opposite to a side where the coating layer is in contact with the base material) of the coating layer in another laminate unit are in a state of being in contact with each other and being pressed

10 against each other, and thus the roll of the protective film-forming composite sheet is stored in this state. However, since the coating layer is provided, adhesion between the release film and the coating layer is suppressed between the laminate units, and thus blocking is suppressed in the protective film-forming composite sheet according to the present invention.

15 [0304]

The protective film-forming composite sheet of the present invention which has a width of 50 mm and a length of 100 mm in a state in which the release film is provided on the protective film-forming film is formed into a laminate whose one outermost layer is the coating layer and the other outermost layer is the release film by overlapping a

20 plurality of the protective film-forming composite sheets such that all the coating layers are directed to the same direction and the total thickness of the coating layers is in a range of 10 to 60  $\mu\text{m}$ , the laminate is allowed to stand at 40°C for 3 days in a lamination direction of the protective film-forming composite sheet while a force (external force) of 980.665 mN (that is, 100 gf) is applied thereto, and the peeling force when the release

25 film closest to the coating layer which is the outermost layer in the lamination direction is

peeled off from the coating layer (the coating layer closest to the coating layer as the outermost layer in the lamination direction) adjacent to the release film under conditions of a peeling rate of 300 mm/min and a peeling angle of 180° is preferably 10 mN/50 mm or less, more preferably 7.5 mN/50 mm or less, and particularly preferably 5 mN/50 mm or less. Here, all of the plurality of sheets of the protective film-forming composite sheet are considered to have the same configuration. Further, the number of sheets of the protective film-forming composite sheet to be stacked is preferably 10. It can be confirmed that the effect of suppressing blocking (blocking resistance) of the protective film-forming composite sheet according to the present invention is excellent based on the peeling force of the release film.

#### Examples

[0305]

Hereinafter, the present invention will be described in more detail with reference to the specific examples. However, the present invention is not limited to the following examples.

[0306]

<Production of protective film-forming composite sheet>

[Example 1]

The protective film-forming composite sheet shown in FIG. 1 was produced. FIG. 3 is a plan view of this protective film-forming composite sheet. More specifically, the production was performed as follows.

[0307]

[Production of first laminate]

(Preparation of thermosetting protective film-forming composition)

The following components with the following amounts (solid contents) were

blended, and methyl ethyl ketone was blended with the mixture, thereby obtaining a protective film-forming composition (III-1) having a solid content concentration of 51% by mass.

[0308]

5 (Polymer component (A))

(A)-1: 150 parts by mass of acrylic resin (weight-average molecular weight of 400000, glass transition temperature of -1°C) formed by copolymerizing 10 parts by mass of n-butyl acrylate, 70 parts by mass of methyl acrylate, 5 parts by mass of glycidyl methacrylate, and 15 parts by mass of 2-hydroxyethyl acrylate

10 (Thermosetting component (B))

Epoxy resin (B1)

(B1)-1: 60 parts by mass of bisphenol A type epoxy resin (“JER828” manufactured by Mitsubishi Chemical Corporation, epoxy equivalent of 183 to 194 g/eq, molecular weight of 370)

15 (B1)-2: 10 parts by mass of bisphenol A type epoxy resin (“JER1055” manufactured by Mitsubishi Chemical Corporation, epoxy equivalent of 800 to 900 g/eq, molecular weight of 1600)

(B1)-3: 30 parts by mass of dicyclopentadiene type epoxy resin (“EPICLON HP-7200HH” manufactured by DIC Corporation, epoxy equivalent of 274 to 286 g/eq)

20 Thermosetting agent (B2)

(B2)-1: 2 parts by mass of dicyandiamide (solid dispersion type latent curing agent, “ADEKA HARDENER EH-3636AS” manufactured by ADAKA CORPORATION, active hydrogen amount of 21 g/eq)

(Curing accelerator (C))

25 (C)-1: 2 parts by mass of 2-phenyl-4,5-dihydroxymethylimidazole (“CUAZOL

2PHZ”, manufactured by SHIKOKU CHEMICALS CORPORATION)

(Filler (D))

(D)-1: 320 parts by mass of silica filler (“SC2050MA” manufactured by Admatechs Co., Ltd., surface was modified with epoxy-based compound, average

5 particle diameter of 0.5  $\mu\text{m}$ )

(Coupling agent (E))

(E)-1: 0.4 parts by mass of  $\gamma$ -glycidoxypolytrimethoxysilane (silane coupling agent, “KBM403” manufactured by Shin-Etsu Chemical Co., Ltd., methoxy equivalent of 12.7 mmol/g, molecular weight of 236.3)

10 (Colorant (I))

(I)-1: 1.2 parts by mass of carbon black (pigment, “MA600B” manufactured by Mitsubishi Chemical Corporation, average particle diameter of 28 nm)

[0309]

(Formation of protective film-forming film and production of first laminate)

15 The surface of a first release film (“SP-P502010\*” manufactured by LINTEC Corporation, thickness of 50  $\mu\text{m}$ ), on which a release treatment was performed, was coated with the protective film-forming composition (III-1) obtained in the above-described manner using a knife coater and dried at 120°C for 2 minutes, thereby forming a protective film-forming film (thickness of 25  $\mu\text{m}$ ).

20 Next, the surface of a second release film (“SP-PET381031C” manufactured by LINTEC Corporation, thickness of 38  $\mu\text{m}$ ), on which a release treatment was performed, was allowed to adhere to the surface of the protective film-forming film on a side opposite to the surface on which the first release film was provided, and a long laminate formed by laminating the first release film, the protective film-forming film, and the

second release film in this order was obtained. Next, this long laminate was wound to be formed into a roll, and only a portion having a size of 300 mm in the width direction (the direction of the width indicated by the reference numeral w1 of the protective film-forming composite sheet 1 shown in FIG. 3) was cut from this laminate.

5 [0310]

Further, this cut laminate was subjected to half cutting, in the central portion in the width direction, for making a notch in the second release film and the protective film-forming film from the second release film side so as to draw a circle having a diameter of 220 mm in a plan view. Further, the “plan view” of the laminate in the  
10 present specification means that the laminate is seen from the above in the lamination direction thereof. In addition, by removing the second release film and the protective film-forming film from the laminate such that only the circular portion formed by the half cutting remained, a first laminate formed by laminating the protective film-forming film and the second release film, respectively having a circular shape in a plan view in  
15 this order, on the surface of the first release film on which a release treatment was performed was obtained. The circular protective film-forming film in the first laminate corresponds to the circular protective film-forming film 13 having a diameter d1 of 220 mm in the protective film-forming composite sheet 1 shown in FIG. 3.

[0311]

20 (Preparation of coating composition)

100 parts by mass of a hard coating agent formed of urethane acrylate and a polyfunctional acrylate monomer (“BEAM SET 575CB” manufactured by Arakawa Chemical Industries, Ltd., solid content concentration of 100% by mass, containing photopolymerization initiator) was blended with 150 parts by mass of a dispersion liquid  
25 (“OSCAL1632” manufactured by JGC C&C, silica sol having particle diameter of 30 to

50 nm, solid content concentration of 30% by mass) formed by a silica sol being dispersed in 2-ethoxyethanol (ethyl cellosolve), thereby obtaining a coating composition (solid content concentration of 30% by mass).

[0312]

5 (Formation of coating layer)

Next, an uneven surface of a polypropylene base material (thickness of 100  $\mu\text{m}$ , melting point of 140°C to 160°C) having an uneven surface with a surface roughness Ra of 0.4  $\mu\text{m}$  and a surface, on the opposite side of the uneven surface, with a surface roughness Ra of 0.02  $\mu\text{m}$  was coated with the coating composition obtained in the  
10 above-described manner using a Meyer bar coater, dried at 80°C for 1 minute, and irradiated with ultraviolet rays at a light dose of approximately 230  $\text{mJ}/\text{cm}^2$  so that the dried coating film was cured, thereby forming a coating layer (thickness of 3  $\mu\text{m}$ ).

[0313]

(Preparation of pressure sensitive adhesive composition)

15 100 parts by mass of a (meth)acrylic acid alkyl ester copolymer and 10 parts by mass (solid content) of an aromatic polyisocyanate compound (cross-linking agent, “TAKENATE D110N” manufactured by Mitsui Chemicals, Inc.) were blended with each other, and methyl ethyl ketone was blended with the resulting mixture, thereby obtaining a pressure sensitive adhesive composition (iii) having a solid content concentration of  
20 30% by mass.

The (meth)acrylic acid alkyl ester copolymer is an acrylic resin having a weight-average molecular weight of 600000 which is formed by copolymerizing 40 parts by mass of n-butyl acrylate, 55 parts by mass of 2-ethylhexyl acrylate, and 5 parts by mass of 2-hydroxyethyl acrylate.

[0314]

(Formation of pressure sensitive adhesive layer (support sheet) and production of second laminate)

A surface of a third release film ("SP-PET381031C" manufactured by LINTEC Corporation), having a surface on which a release treatment was performed by forming a silicone-based release agent layer thereon, formed of a polyethylene terephthalate film having a thickness of 38  $\mu\text{m}$  was coated with the pressure sensitive adhesive composition (iii) obtained in the above-described manner using a knife coater and dried, thereby forming a pressure sensitive adhesive layer (thickness of 5  $\mu\text{m}$ ).

Next, the surface of the above-described base material, on which the coating layer was formed, on a side opposite to the uneven surface was subjected to a corona treatment, the above-described pressure sensitive adhesive layer was allowed to adhere to the surface on which the corona treatment was performed, and the coating layer, the base material, the pressure sensitive adhesive layer, and the third release film were laminated on one another in this order, thereby obtaining a long second laminate including a support sheet.

Thereafter, this long second laminate was wound to be formed into a roll, and only a portion having a size of 300 mm in the width direction (the direction of the width indicated by the reference numeral w1 of the protective film-forming composite sheet 1 shown in FIG. 3) was cut from this second laminate.

[0315]

(Production of protective film-forming composite sheet)

The second release film was removed from the first laminate obtained in the above-described manner so that the circular protective film-forming film was exposed.

Further, the third release film was removed from the second laminate obtained in the

above-described manner so that the pressure sensitive adhesive layer was exposed. In addition, the exposed surface of the above-described protective film-forming film was allowed to adhere to the exposed surface of the pressure sensitive adhesive layer, thereby obtaining a third laminate corresponding to the protective film-forming composite sheet formed by laminating the coating layer, the base material, the pressure sensitive adhesive layer, the protective film-forming film, and the first release film in this order.

[0316]

The third laminate obtained in the above-described manner was subjected to half cutting for making a notch in all of the coating layer, the base material, and the pressure sensitive adhesive layer from the coating layer side so as to draw a circle having a diameter of 270 mm in a plan view. In this half cutting, a notch was made in all of the coating layer, the base material, and the pressure sensitive adhesive layer such that the circle having a diameter of 270 mm was concentric with the circle having a diameter of 220 mm, on which the protective film-forming film was formed, in a plan view.

Next, the third laminate was subjected to half cutting for making a notch in all of the coating layer, the base material, and the pressure sensitive adhesive layer from the coating layer side so as to draw a pair of arcs, facing each other in the width direction (the direction of the width indicated by the reference numeral w1 of the protective film-forming composite sheet 1 shown in FIG. 3) of the third laminate, at a position separated from the circle having a diameter of 270 mm by a distance of 20 mm outward in the radial direction of this circle in a plan view.

This notch corresponding to the pair of arcs forms a curved peripheral portion on the pressure sensitive adhesive layer indicated by the reference numeral 121 in the protective film-forming composite sheet 1 shown in FIG. 3. Further, the distance (20 mm) between the circle having a diameter of 270 mm and the arcs corresponds to the

reference numeral w2 in the protective film-forming composite sheet 1 shown in FIG. 3.

[0317]

The above-described half cutting for drawing two concentric circles and a pair of arcs was performed at a plurality of sites of the third laminate in the longitudinal direction (the direction orthogonal to the direction of the width indicated by the reference numeral w1 of the protective film-forming composite sheet 1 shown in FIG. 3), and half cutting for making a notch in all of the coating layer, the base material, and the pressure sensitive adhesive layer was performed from the coating layer side such that two straight lines connecting arcs at sites adjacent to each other in the longitudinal direction in a plan view were drawn. The notch corresponding to two straight lines forms a planar peripheral portion on the pressure sensitive adhesive layer indicated by the reference numeral 122 in the protective film-forming composite sheet 1 shown in FIG. 3.

Next, the protective film-forming composite sheet shown in FIGS. 1 and 3 was obtained by removing the coating layer, the base material, and the pressure sensitive adhesive layer from the portion between the circle having a diameter of 270 mm and the pair of arcs and the portion interposed between two straight lines connecting the arcs in a plan view. The circular pressure sensitive adhesive layer (support sheet) in the protective film-forming composite sheet corresponds to the circular pressure sensitive adhesive layer 12 (support sheet 10) having a diameter d2 of 270 mm in FIG. 3. In addition, the first release film in the protective film-forming composite sheet corresponds to the release film 15 in FIG. 3.

[0318]

[Example 2]

A protective film-forming composite sheet was obtained according to the same method as in Example 1 except that a base material having an uneven surface with a

surface roughness Ra of 1  $\mu\text{m}$  was used in place of the base material having an uneven surface with a surface roughness Ra of 0.4  $\mu\text{m}$ , as listed in Table 1.

[0319]

[Example 3]

5           A protective film-forming composite sheet was obtained according to the same method as in Example 1 except that a base material having an uneven surface with a surface roughness Ra of 1  $\mu\text{m}$  was used in place of the base material having an uneven surface with a surface roughness Ra of 0.4  $\mu\text{m}$  and the thickness of the coating layer was set to 1  $\mu\text{m}$  in place of 3  $\mu\text{m}$ , as listed in Table 1.

10           [0320]

[Example 4]

A protective film-forming composite sheet was obtained according to the same method as in Example 1 except that the thickness of the coating layer was set to 1  $\mu\text{m}$  in place of 3  $\mu\text{m}$ , as listed in Table 1.

15           [0321]

[Example 5]

A protective film-forming composite sheet was obtained according to the same method as in Example 1 except that a base material having an uneven surface with a surface roughness Ra of 1  $\mu\text{m}$  was used in place of the base material having an uneven surface with a surface roughness Ra of 0.4  $\mu\text{m}$  and the thickness of the coating layer was set to 6  $\mu\text{m}$  in place of 3  $\mu\text{m}$ , as listed in Table 1.

[0322]

[Example 6]

A protective film-forming composite sheet was obtained according to the same

method as in Example 1 except that a base material having an uneven surface with a surface roughness Ra of 3  $\mu\text{m}$  was used in place of the base material having an uneven surface with a surface roughness Ra of 0.4  $\mu\text{m}$  and the thickness of the coating layer was set to 6  $\mu\text{m}$  in place of 3  $\mu\text{m}$ , as listed in Table 1.

5 [0323]

[Comparative Example 1]

A protective film-forming composite sheet was obtained according to the same method as in Example 1 except that a base material having an uneven surface with a surface roughness Ra of 1  $\mu\text{m}$  was used in place of the base material having an uneven surface with a surface roughness Ra of 0.4  $\mu\text{m}$  and the coating layer was not formed, as listed in Table 1.

[0324]

[Comparative Example 2]

A protective film-forming composite sheet was obtained according to the same method as in Example 1 except that the base material was disposed such that the uneven surface was directed to the opposite side, in other words, the pressure sensitive adhesive layer side (inside) and the coating layer was not formed (in other words, the configuration of the related art shown in FIG. 5 was employed), as listed in Table 1.

[0325]

20 [Comparative Example 3]

A protective film-forming composite sheet was obtained according to the same method as in Example 1 except that a base material having an uneven surface with a surface roughness Ra of 1  $\mu\text{m}$  was used in place of the base material having an uneven surface with a surface roughness Ra of 0.4  $\mu\text{m}$ , the base material was disposed such that

the uneven surface was directed to the opposite side, in other words, the pressure sensitive adhesive layer side (inside), and the coating layer was not formed (in other words, the configuration of the related art shown in FIG. 5 was employed), as listed in Table 1.

5 [0326]

[Comparative Example 4]

A coating composition was prepared according to the same method as in Example 1 except that spherical silica ("SC2050MA" manufactured by Admatechs Co., Ltd., average particle diameter of 0.5  $\mu\text{m}$ ) which had the same solid content as silica sol  
10 and was surface-modified with an epoxy group was used in place of a dispersion liquid in which the silica sol was dispersed in 2-ethoxyethanol.

Further, a protective film-forming composite sheet was obtained according to the same method as in Example 1 except that this coating composition was used.

In the obtained protective film-forming composite sheet, the surface roughness  
15 Ra of the outermost surface on the base material side was 0.8  $\mu\text{m}$  as listed in Table 1.

[0327]

<Evaluation of protective film-forming composite sheet>

[Laser printability]

In each of the obtained protective film-forming composite sheets of each  
20 example and each comparative example, the first release film was removed, the pressure sensitive adhesive layer was allowed to adhere to a stainless steel ring frame using an adhering device ("RAD-2700F/12", manufactured by LINTEC Corporation), and the protective film-forming film was allowed to adhere to the rear surface of a silicon wafer (outer diameter of 8 inches, thickness of 100  $\mu\text{m}$ ) heated to 70°C.

25 Next, the protective film-forming film was thermally cured by performing a heat

treatment on the protective film-forming film at 130°C for 2 hours, thereby forming a protective film.

Next, the protective film was irradiated with laser light having a wavelength of 532 nm from the base material side under conditions of an output of 0.6 W, a frequency of 40 kHz, and a scanning speed of 100 mm/sec using a printing device (“VK9700” manufactured by KEYENCE CORPORATION), and laser printing was performed on the protective film in the following two patterns (the pattern 1 and the pattern 2).

(Pattern)

Pattern 1: character size of 0.4 mm × 0.5 mm, character spacing of 0.3 mm,  
number of characters: 20

Pattern 2: character size of 0.2 mm × 0.5 mm, character spacing of 0.3 mm,  
number of characters: 20

[0328]

Next, the visibility (laser printability) of the characters, from the base material side, formed on the protective film by performing the laser printing was evaluated based on the following criteria. The results are listed in Table 1.

(Evaluation criteria)

A: All the characters in the patterns 1 and 2 were clear and the characters in the patterns 1 and 2 were able to be read without problem.

B: At least some characters in the pattern 2 were unclear, but all characters in the pattern 1 were clear and the characters in the pattern 1 were able to be read without problem.

C: At least some characters in both patterns 1 and 2 were unclear.

[0329]

[Blocking resistance (1)]

Each of the obtained protective film-forming composite sheets of each example and each comparative example was wound around a core, made of an ABS resin with a diameter of 3 inches, to have a length of 10 m and allowed to stand in this state at room temperature for 3 days.

5           Next, in the protective film-forming composite sheets of Examples 1 to 6 and Comparative Example 4, ten laminate units formed by laminating the coating layer, the base material, the pressure sensitive adhesive layer, the protective film-forming film, and the first release film in this order were sent out. Further, in the protective film-forming composite sheets of Comparative Examples 1 to 3, since the coating layer was not  
10   present, ten laminate units formed by laminating the base material, the pressure sensitive adhesive layer, the protective film-forming film, and the first release film in this order were sent out. At this time, the presence of adhesion between contact portions of the protective film-forming composite sheet which were in contact with each other at the time of winding and the degree of adhesion in a case where adhesion occurred were  
15   evaluated based on the following criteria. The results are listed in Table 1.

(Evaluation criteria)

A: Adhesion between the contact portions was not found at all.

B: A low degree of adhesion between the contact portions was found, but the protective film-forming composite sheet was able to be sent out without problem.

20           C: The contact portions partially adhered to each other completely and the first release film was peeled off from the pressure sensitive adhesive layer when the protective film-forming composite sheet was sent out.

[0330]

[Blocking resistance (2)]

25           Each of the obtained protective film-forming composite sheets of each example

and each comparative example was cut into tape having a width of 50 mm and a length of 100 mm. Further, during the cutting, the length direction of the tape was made to coincide with the application direction of the pressure sensitive adhesive composition.

10 sheets of tape obtained in the above-described manner were prepared to  
5 obtain a test piece by laminating these sheets of tape. At this time, in all cases of Examples 1 to 6 and Comparative Example 4, these sheets of tape were laminated such that the coating layer faced upward. Further, in all cases of Comparative Examples 1 to 3, since the coating layer was not present, these sheets of tape were laminated such that the base material faced upward. Next, this test piece was interposed between two glass  
10 plates (width of 75 mm, length of 15 mm, and thickness of 5 mm), the entire laminate formed of these glass plates and the test piece was placed on a predetermined site using one glass plate as the bottom layer, and the test piece was pressed by placing a weight on the other glass plate used as the top layer. The force applied to the test piece in the lamination direction of the tape at this time was 980.665 mN (in other words, 100 gf).  
15 The entire laminate formed of the glass plates and the test piece was stored in a moist heat promoter (manufactured by ESPEC Corp.) at 40°C for 3 days in this state, and a heating and pressing promotion test was performed on the test piece.

[0331]

Next, the test piece was taken out from the moist heat promoter, the first release  
20 film as the bottom layer (the first release film in contact with the glass plate as the bottom layer) and the protective film-forming film adjacent to the first release film were removed, the exposed pressure sensitive adhesive layer was allowed to adhere to the support plate through double-sided adhesive tape, and the test piece, after the heating and pressing promotion test was performed, from which only the first release film as the  
25 bottom layer and the protective film-forming film adjacent to the first release film were

removed was fixed to the support plate.

Next, in the above-described fixed test piece in the cases of Examples 1 to 6 and Comparative Example 4, the laminate formed of the coating layer as the top layer furthest from the support plate, the base material, the pressure sensitive adhesive layer, and the protective film-forming film was removed, the peeling force when the exposed first release film was peeled off from the coating layer adjacent to the first release film using a tensile testing machine under conditions of a peeling rate of 300 mm/min and a peeling angle of 180° was measured. In the above-described fixed test piece in the cases of Comparative Examples 1 to 3, the laminate formed of the base material as the top layer furthest from the support plate, the pressure sensitive adhesive layer, and the protective film-forming film was removed, the peeling force when the exposed first release film was peeled off from the base material adjacent to the first release film using a tensile testing machine under conditions of a peeling rate of 300 mm/min and a peeling angle of 180° was measured. The measured value of the peeling force of the first release film obtained in the above-described manner was set as an index of the blocking resistance of the protective film-forming composite sheet.

Further, in a case where the peeling force of the first release film to be measured was sufficiently small, the first release film which was the measurement target of the peeling force was peeled off from the layer (the coating layer in the cases of Examples 1 to 6 and Comparative Example 4 and the base material in the cases of Comparative Examples 1 to 3) adjacent to the first release film first when the protective film-forming film adjacent to the first release film as the bottom layer (the first release film in contact with the glass plate as the bottom layer) as described above was intended to be removed from the test piece taken out from the moist heat promoter. In this case, the first release film as the bottom layer was removed from the test piece taken out from the moist heat

promoter, the protective film-forming film was allowed to adhere to the support plate through double-sided adhesive tape without removing this protective film-forming film adjacent to the first release film, the test piece from which only the first release film as the bottom layer was removed was fixed to the support plate, and the peeling force of the first release film was measured with respect to this fixed test piece.

The results are listed in Table 1.

[0332]

[Surface roughness Ra of outermost surface on base material side]

In each of the obtained protective film-forming composite sheets of Examples 1 to 6 and Comparative Example 4, the surface roughness Ra of the outermost surface on the base material side, in other words, the surface of the coating layer on a side opposite to the base material side was measured using a contact type surface roughness meter (“SURFTEST SV-3000”, manufactured by Mitutoyo Corporation) by setting a cutoff value  $\lambda_c$  to 0.8 mm and an evaluation length  $L_n$  to 4 mm in conformity with JIS B 0601:2001. The results are listed in Table 1. In the protective film-forming composite sheets of Comparative Examples 1 to 3, the surface roughness Ra of the surface of the base material on a side opposite to the pressure sensitive adhesive layer side was listed as the surface roughness Ra of the outermost surface of the base material side, in Table 1.

[0333]

[Gloss value of surface of coating layer]

In each of the obtained protective film-forming composite sheets of Examples 1 to 6 and Comparative Example 4, the specular glossiness of the surface of the coating layer at 20° was measured from the coating layer side opposite to the base material side using a gloss meter (gloss meter “VG 2000”, manufactured by Nippon Denshoku Industries Co., Ltd.) in conformity with JIS K 7105, and the measured value was set as

the gloss value of the surface of the coating layer. The results are listed in Table 1.

[0334]

[Value of haze measured from coating layer side]

In each of the obtained protective film-forming composite sheets of Examples 1  
5 to 6 and Comparative Example 4, the haze was measured from the coating layer side  
using a haze meter (“NDH-2000” manufactured by Nippon Denshoku Industries Co.,  
Ltd.) in conformity with JIS K 7136. The results are listed in Table 1.

[0335]

[Table 1]

|                                                          |                                                                                                  | Example     |             |             |             |             |             | Comparative Example |        |        |             |
|----------------------------------------------------------|--------------------------------------------------------------------------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|---------------------|--------|--------|-------------|
|                                                          |                                                                                                  | 1           | 2           | 3           | 4           | 5           | 6           | 1                   | 2      | 3      | 4           |
| Configuration of protective film-forming composite sheet | Coating layer (thickness (μm))                                                                   | Present (3) | Present (3) | Present (1) | Present (1) | Present (6) | Present (6) | Absent              | Absent | Absent | Present (3) |
|                                                          | Orientation of uneven surface of base material                                                   | Outside     | Outside     | Outside     | Outside     | Outside     | Outside     | Outside             | Inside | Inside | Outside     |
|                                                          | Surface roughness Ra of uneven surface of base material (μm)                                     | 0.4         | 1           | 1           | 0.4         | 1           | 3           | 1                   | 0.4    | 1      | 0.4         |
|                                                          | Surface roughness Ra of surface of base material on side opposite to uneven surface (μm)         | 0.02        | 0.02        | 0.02        | 0.02        | 0.02        | 0.02        | 0.02                | 0.02   | 0.02   | 0.02        |
|                                                          | Surface roughness Ra of outermost surface of base material side (μm)                             | 0.02        | 0.02        | 0.1         | 0.02        | 0.02        | 0.05        | 1                   | 0.02   | 0.02   | 0.8         |
|                                                          | [Thickness (μm) of coating layer]/[Surface roughness Ra (μm) of uneven surface of base material] | 7.5         | 3.0         | 1.0         | 2.5         | 6.0         | 2.0         | -                   | -      | -      | 7.5         |
|                                                          | Thickness of pressure sensitive adhesive layer (μm)                                              | 5           | 5           | 5           | 5           | 5           | 5           | 5                   | 5      | 5      | 5           |
|                                                          | Haze of coating layer side (%)                                                                   | 9           | 13          | 29          | 9           | 9           | 15          | -                   | -      | -      | 48          |
|                                                          | Gloss value of surface of coating layer                                                          | 74          | 66          | 52          | 68          | 73          | 63          | -                   | -      | -      | 31          |
| Evaluation results                                       | Laser printability                                                                               | A           | A           | B           | A           | A           | B           | C                   | B      | C      | C           |
|                                                          | Blocking resistance (1)                                                                          | A           | A           | A           | A           | B           | B           | A                   | C      | C      | A           |
|                                                          | Blocking resistance (2) (peeling force (mN/50 mm) of first release film)                         | <5          | <5          | <5          | <5          | 5           | 5           | <5                  | 22     | 27     | <5          |

[0336]

Since each of the protective film-forming composite sheets of Examples 1 to 6 includes the coating layer on the outermost layer on the base material side, both of the laser printability and the blocking resistance were excellent.

5            Particularly, each of the protective film-forming composite sheets of Examples 1, 2, 4, and 5 has excellent laser printability compared to each of the protective film-forming composite sheets of Examples 3 and 6, and the reason for this was assumed that, in each of the protective film-forming composite sheets of Examples 1, 2, 4, and 5, the value of “[thickness (μm) of coating layer]/[surface roughness Ra (μm) of uneven  
10 surface of base material]” is greater and the relative thickness of the coating layer with respect to the surface roughness Ra of the uneven surface of the base material is larger so that the surface roughness Ra (μm) of the outermost surface (surface of the coating layer on a side opposite to the base material side) on the base material side is smaller.

            Further, each of the protective film-forming composite sheets of Examples 1 to 4  
15 has excellent blocking resistance compared to each of the protective film-forming composite sheets of Examples 5 and 6, and the reason for this was assumed that the thickness of the coating layer in each of the protective film-forming composite sheets of Examples 1 to 4 was smaller.

            Moreover, in each of the protective film-forming composite sheets of Examples  
20 1 to 6, a gap portion between the base material and the pressure sensitive adhesive layer was not found.

[0337]

            Meanwhile, the protective film-forming composite sheet of Comparative  
Example 1 had excellent blocking resistance, but the laser printability thereof was  
25 degraded because the surface (rear surface) of the base material on a side opposite to the

surface (front surface) where the pressure sensitive adhesive layer was provided was uneven surface and the coating layer was not present, similar to the sheet shown in FIG.

4.

[0338]

5           Similar to the sheet shown in FIG. 5, the protective film-forming composite sheet of Comparative Example 2 had excellent laser printability, but the blocking resistance thereof was degraded because the surface (rear surface) of the base material on a side opposite to the surface (front surface) where the pressure sensitive adhesive layer was provided was a smooth surface and the coating layer was not present. The

10   protective film-forming composite sheet of Comparative Example 3 had poor blocking resistance and laser printability even though the protective film-forming composite sheet of Comparative Example 3 had the same configuration as the protective film-forming composite sheet of Comparative Example 2. The reason for this was assumed that the surface (front surface) of the base material on a side where the pressure sensitive

15   adhesive layer was provided was an uneven surface and the surface roughness Ra thereof was larger than that of the protective film-forming composite sheet of Comparative Example 2. In Comparative Example 3, it was assumed that the shape of the uneven surface was reflected on the surface of the protective film because the surface roughness Ra of the uneven surface was large, and the degree of unevenness in the surface of the

20   protective film was higher than the case of Comparative Example 2 and thus irregular reflection of light was further increased and the laser printability was further degraded. Further, in both protective film-forming composite sheets of Comparative Examples 2 and 3, a gap portion was found between the uneven surface of the base material and the pressure sensitive adhesive layer, and the gap portion in Comparative Example 3 was

25   larger than the gap portion of Comparative Example 2 since the surface roughness Ra of

the uneven surface was larger than that of comparative Example 2. Therefore, it was assumed that irregular reflection of light was further increased and the laser printability was further degraded in the case of Comparative Example 3 compared to the case of Comparative Example 2.

5 [0339]

Similar to the protective film-forming composite sheet of Example 1, the protective film-forming composite sheet of Comparative Example 4 had excellent blocking resistance, but the laser printability was degraded because the surface (rear surface) of the base material on a side opposite to the surface (front surface) where the pressure sensitive adhesive layer was provided was an uneven surface and the coating layer was also present. The reason for this was assumed that the surface roughness Ra ( $\mu\text{m}$ ) of the outermost surface (surface of the coating layer on a side opposite to the base material side) on the base material side was larger than that of the surface (rear surface) of the base material on a side opposite to the surface (front surface) where the pressure sensitive adhesive layer is provided in the case of the protective film-forming composite sheet of Comparative Example 4.

10  
15

#### Industrial Applicability

[0340]

20 The present invention can be used for manufacturing a semiconductor chip or the like whose rear surface is protected by a protective film.

#### Reference Signs List

[0341]

25 1, 2: protective film-forming composite sheet

- 10: support sheet
- 10a: surface of support sheet
- 10b: rear surface of support sheet
- 11: base material
- 5 11a: surface of base material
- 11b: rear surface of base material
- 12: pressure sensitive adhesive layer
- 12a: surface of pressure sensitive adhesive layer
- 13, 23: protective film-forming film
- 10 13a, 23a: surface of protective film-forming film
- 14: coating layer
- 14a: surface of coating layer
- 14b: rear surface of coating layer
- 15: release film
- 15 15a: surface of release film
- 16: adhesive layer for jig
- 16a: surface of adhesive layer for jig

## CLAIMS

What is claimed is:

1. A protective film-forming composite sheet, comprising:

a support sheet;

5 a protective film-forming film provided on one surface of the support sheet; and

a coating layer provided on a surface of the support sheet on a side opposite to the side on which the protective film-forming film is provided,

wherein the coating layer contains a cured product of a coating composition containing a photopolymerization initiator, and

10 a surface roughness Ra of a surface of the coating layer on a side opposite to a side on which the coating layer is in contact with the support sheet is smaller than that of the surface of the support sheet on a side on which the coating layer is provided.

2. A protective film-forming composite sheet, comprising:

15 a support sheet;

a protective film-forming film provided on one surface of the support sheet; and

a coating layer provided on a surface of the support sheet on a side opposite to the side on which the protective film-forming film is provided,

wherein the coating layer is obtained by curing a coating composition containing  
20 an energetic radiation-polymerizable compound polymerized through irradiation with energetic radiation and a photopolymerization initiator and the energetic radiation-polymerizable compound is (meth)acrylic acid or derivatives thereof, and

a surface roughness Ra of a surface of the coating layer on a side opposite to the side on which the coating layer is in contact with the support sheet is smaller than that of  
25 the surface of the support sheet on the side on which the coating layer is provided.

3. A protective film-forming composite sheet, comprising:

a support sheet;

a protective film-forming film provided on one surface of the support sheet; and

5 a coating layer provided on a surface of the support sheet on a side opposite to the side on which the protective film-forming film is provided,

wherein a surface roughness Ra of a surface of the coating layer on the side opposite to a side on which the coating layer is in contact with the support sheet is smaller than that of the surface of the support sheet on the side on which the coating layer  
10 is provided, and

a value of [a thickness ( $\mu\text{m}$ ) of the coating layer]/[a surface roughness Ra ( $\mu\text{m}$ ) of the surface of the support sheet on the side on which the coating layer is provided] is 0.5 to 10.

15 4. The protective film-forming composite sheet according to any one of claims 1 to 3,

wherein a peeling force of a release film measured according to the following method using the protective film-forming composite sheet which further includes the release film on the protective film-forming film is 10 mN/50 mm or less;

20 (method of measuring peeling force of release film)

the protective film-forming composite sheet having a width of 50 mm and a length of 100 mm which includes the protective film-forming film on which the release film is provided is formed into a laminate whose outermost layer is the coating layer and the other outermost layer is the release film using a plurality of the protective

25 film-forming composite sheets which overlap each other so that all of the coating layers

are directed in the same direction and a total thickness of the coating layers is within a range of 10 to 60  $\mu\text{m}$ ,

the laminate is allowed to stand at 40 °C for 3 days in a lamination direction of the protective film-forming composite sheet while being subjected to a force of 980.665 mN, and then the peeling force when the release film closest to the coating layer which is the outermost layer in the lamination direction is peeled off from the coating layer adjacent to the release film under conditions that are a peeling rate of 300 mm/min and a peeling angle of 180° is measured.

- 10 5. The protective film-forming composite sheet according to any one of claims 1 to 4,

wherein the support sheet includes a base material and a pressure sensitive adhesive layer which are laminated on each other, and

- 15 the protective film-forming composite sheet is formed by laminating the coating layer, the base material, the pressure sensitive adhesive layer, and the protective film-forming film in this order.

6. The protective film-forming composite sheet according to claim 5,  
wherein the pressure sensitive adhesive layer is energetic radiation curable or  
20 non-energetic radiation curable.

7. The protective film-forming composite sheet according to any one of claims 1 to 6,  
wherein the protective film-forming film is thermosetting or energetic radiation  
25 curable.