

DESCRIPTION

PROTECTIVE FILM FORMATION SHEET, MANUFACTURING METHOD FOR PROTECTIVE FILM FORMATION SHEET, AND MANUFACTURING METHOD FOR SEMICONDUCTOR DEVICE

TECHNICAL FIELD

[0001]

The present invention relates to a protective film formation sheet, a manufacturing method for forming a protective film formation sheet, and a manufacturing method for a semiconductor device.

Priority is claimed on Japanese Patent Application No. 2016-031343, filed on February 22, 2016, the content of which is incorporated herein by reference.

BACKGROUND ART

[0002]

In recent years, many semiconductor devices have been produced using a mounting method known as the so-called face down method. In the face down method, a semiconductor chip having electrodes such as bumps on the circuit surface is used, and these electrodes are bonded to a circuit board. As a result, the back surface of the chip on the opposite side from the circuit surface sometimes remains exposed.

[0003]

A resin film formed from an organic material is sometimes formed as a protective film on this exposed back surface of the chip, with the resulting chip incorporated in a semiconductor device as a semiconductor chip with a protective film. The protective

film is used for preventing cracks from developing in the chip following the dicing step and packaging.

[0004]

A protective film formation sheet containing a protective film formation layer provided on a support sheet is used for formation of this type of protective film. Resin substrates, or laminated structures of a substrate and an adhesive layer or the like, are typically used as the support sheet, and the surface of the substrate to which the protective film formation layer or the adhesive layer or the like is laminated is sometimes subjected to a surface treatment. In the protective film formation sheet, the protective film formation layer has a protective film formation ability, whereas the support sheet can function as a dicing sheet, meaning the protective film formation sheet can be used as an integrated combination of a protective film formation layer and a dicing sheet.

[0005]

Prior to processing, the substrate used in the support sheet typically has uneven shapes on either one or both surfaces. This is because if the substrate lacks these types of uneven shapes, then when the substrate is wound into a roll for storage, blocking tends to occur in which the contact surfaces of the substrate stick to each other, making it impossible to feed the substrate from the roll at the time of use. If at least one of the contact surfaces of the substrate has uneven shapes thereon, then blocking is suppressed as a result of the reduction in the contact surface area, enabling feeding of the substrate to be performed favorably.

[0006]

A conventional protective film formation sheet that uses a substrate having this type of uneven surface typically has the type of structure illustrated in FIG. 10. FIG. 10 is a cross-sectional view that schematically illustrates one example of a conventional

protective film formation sheet. In the drawings used in the following description, specific portions may be drawn larger as appropriate to facilitate comprehension of the features of the protective film formation sheet, and the dimensional ratios and the like between the constituent elements may not necessarily represent the actual values.

[0007]

The conventional protective film formation sheet 9 illustrated in FIG. 10 has a protective film formation layer 13 provided on a support sheet 90, the support sheet 90 is composed of a laminated structure of a substrate 91 and an adhesive layer 12, and the protective film formation layer 13 is provided on top of the adhesive layer 12. The protective film formation layer 13 becomes a protective film upon curing. The conventional protective film formation sheet 9 also has a release film 15 provided on top of the protective film formation layer 13, and this release film 15 is removed when the protective film formation sheet 9 is used. In the protective film formation sheet 9, the surface (back surface) 90b of the support sheet 90 on the opposite side from the surface (upper surface) 90a on which the protective film formation layer 13 is provided, in other words, the surface (back surface) 91b of the substrate 91 on the opposite side from the surface (upper surface) 91a on which the adhesive layer 12 is provided, has an uneven surface. In the protective film formation sheet 9, because the back surface 91b of the substrate 91 has this type of uneven surface, when the sheet is wound into a roll, sticking of the back surface 91b of the substrate 91 to the exposed surface (upper surface) 15a of the release film 15, namely blocking, can be suppressed.

[0008]

On the other hand, the protective film formation sheet is bonded via the protective film formation layer to the back surface of a semiconductor wafer on the opposite side from the circuit surface, and the protective film formation layer is then cured, thereby

forming a protective film on the back surface of the semiconductor wafer. This type of laminated body having the support sheet, the protective film and the semiconductor wafer laminated in this order is then subjected to dicing, thereby dividing the laminated body into individual laminated bodies having the support sheet, the protective film and a semiconductor chip laminated in that order. Following dicing, the semiconductor chips with the protective film and the like still provided thereon are examined for the existence of damage such as cracking or chipping. This type of examination is typically performed using an infrared camera from the back surface side of the semiconductor chip, through the support sheet and the protective film, and therefore the support sheet and the protective film must exhibit infrared transmittance. At this time, in the case where the protective film formation sheet 9 is used, the infrared rays are irradiated onto the semiconductor chip from the side of the back surface 91b of the substrate 91, but because the back surface 91b of the substrate 91 is an uneven surface, a problem arises in that the infrared rays are scattered at this surface, making examination of the semiconductor chip impossible.

[0009]

An example of a known protective film formation sheet capable of preventing this type of infrared ray scattering is a protective film formation sheet 8 having the type of structure illustrated in FIG. 11 (for example, see Patent Document 1). FIG. 11 is a cross-sectional view that schematically illustrates another example of a conventional protective film formation sheet.

[0010]

In a similar manner to the conventional protective film formation sheet 9, the conventional protective film formation sheet 8 illustrated in FIG. 11 has a protective film formation layer 13 provided on a support sheet 80, the support sheet 80 is composed of a

laminated structure of a substrate 81 and an adhesive layer 12, and the protective film formation layer 13 is provided on top of the adhesive layer 12. However, in the support sheet 80, the positioning of the uneven surface in the substrate 81 is opposite that of the substrate 91 in the support sheet 90. In other words, in the protective film formation sheet 8, a surface (upper surface) 81a of the substrate 81 on which the adhesive layer 12 is provided is an uneven surface, whereas a surface (back surface) 81b of the substrate 81 on the opposite side from the surface 81a is a smooth surface. The substrate 81 in the support sheet 80, the protective film formation layer 13 and the release film 15 are the same as the substrate 91 in the support sheet 90, the protective film formation layer 13 and the release film 15 respectively.

[0011]

However, in the case of the protective film formation sheet 8, the back surface 81b of the substrate 81, namely the surface (back surface) 80b of the support sheet 80 on the opposite side from the surface (upper surface) 80a on which the adhesive layer 12 is provided, is a smooth surface, and therefore when the protective film formation sheet 8 is wound into a roll, sticking of the back surface 81b of the substrate 81 to the exposed surface (upper surface) 15a of the release film 15, namely blocking, cannot be suppressed. As a result, the protective film formation sheet 8 cannot be fed from the roll during use, or even if able to be fed, suffers from the release film 15 peeling from the protective film formation layer 13.

PRIOR ART LITERATURE

Patent Documents

[0012]

Patent Document 1: Japanese Patent (Granted) Publication No. 5432853

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0013]

In this manner, there is no protective film formation sheet conventionally available that enables both feeding from the roll and infrared examination of the chips to be performed without hindrance.

The present invention has been developed in light of the above circumstances, and has an object of providing a protective film formation sheet used for forming a protective film on the back surface of a semiconductor chip, wherein feeding of the sheet from a roll and infrared inspection of the semiconductor chip can both be performed favorably.

Means for Solving the Problems

[0014]

In order to achieve the above object, the present invention provides a protective film formation sheet having a protective film formation layer provided on a support sheet and a release film provided on the protective film formation layer, wherein the surface roughness of a surface of the support sheet on the opposite side from the side on which the protective film formation layer is provided is not more than $0.5\ \mu\text{m}$, and the static friction force, measured in accordance with JIS K7125, between the aforementioned surface of the support sheet and a surface of the release film on the opposite side from the side on which the protective film formation layer is provided is not more than 29 N.

In the protective film formation sheet of the present invention, it is preferable that the support sheet has a substrate, and that the surface of the substrate has been subjected to a roughening treatment using a sand blasting treatment.

In the protective film formation sheet of the present invention, the support sheet preferably has an adhesive layer laminated onto a substrate.

In the protective film formation sheet of the present invention, the thickness of the adhesive layer is preferably from 1 to 100 μm .

[0015]

Further, the present invention also provides a manufacturing method for the aforementioned protective film formation sheet, the method including:

a step of forming a laminated structure of the support sheet and the protective film formation layer so that the surface roughness of the surface of the support sheet on the opposite side from the side on which the protective film formation layer is provided is not more than 0.5 μm ,

and a step of forming a laminated structure of the protective film formation layer and the release film so that the static friction force, measured in accordance with JIS K7125, between the surface of the support sheet on the opposite side from the side on which the protective film formation layer is provided and a surface of the release film on the opposite side from the side on which the protective film formation layer is provided is not more than 29 N.

Furthermore, the present invention also provides a manufacturing method for a semiconductor device using the protective film formation sheet, the method having:

a step of removing the release film from the protective film formation sheet, and then affixing the protective film formation layer to the back surface of a semiconductor wafer on the opposite side from the surface on which a circuit is provided, a step of

curing the protective film formation layer following affixing to the semiconductor wafer to form a protective film, a step of dicing the semiconductor wafer to form semiconductor chips, a step of examining the semiconductor chips by irradiating infrared rays onto the semiconductor chips from the support sheet side of the protective film formation sheet, a step of obtaining semiconductor chips with a protective film by detaching each semiconductor chip, together with the protective film affixed to the back surface of the chip, from the support sheet, and a step of performing flip-chip connection of the semiconductor chip of the semiconductor chip with a protective film to the circuit surface of a circuit board.

[0016]

In other words, the present invention includes the following aspects.

[1] A protective film formation sheet having a protective film formation layer provided on a support sheet, and a release film provided on the protective film formation layer, wherein

the surface roughness of a surface of the support sheet on the opposite side from the side on which the protective film formation layer is provided is not more than 0.5 μm , and

the static friction force, measured in accordance with JIS K7125, between the aforementioned surface of the support sheet and a surface of the release film on the opposite side from the side on which the protective film formation layer is provided is not more than 29 N.

[2] The protective film formation sheet according to [1], wherein the support sheet has a substrate, and the surface of the substrate has been subjected to a roughening treatment using a sand blasting treatment.

[3] The protective film formation sheet according to [1], wherein the support sheet has an adhesive layer laminated onto a substrate.

[4] The protective film formation sheet according to [2], wherein the support sheet has an adhesive layer laminated onto the substrate.

[5] The protective film formation sheet according to [3] or [4], wherein the thickness of the adhesive layer is from 1 to 100 μm .

[6] A manufacturing method for a protective film formation sheet, wherein the protective film formation sheet is the protective film formation sheet according to any one of [1] to 5], and

the method includes:

a step of forming a laminated structure of the support sheet and the protective film formation layer so that the surface roughness of the surface of the support sheet on the opposite side from the side on which the protective film formation layer is provided is not more than 0.5 μm , and

a step of forming a laminated structure of the protective film formation layer and the release film so that the static friction force, measured in accordance with JIS K7125, between the surface of the support sheet on the opposite side from the side on which the protective film formation layer is provided and a surface of the release film on the opposite side from the side on which the protective film formation layer is provided is not more than 29 N.

[6] A manufacturing method for a semiconductor device, the method including:

a step of removing the release film from the protective film formation sheet according to any one of [1] to [5], and then affixing the protective film formation layer to the back surface of a semiconductor wafer on the opposite side from the surface on which a circuit is provided,

a step of curing the protective film formation layer following affixing to the semiconductor wafer to form a protective film,

a step of dicing the semiconductor wafer with the protective film formation sheet formed thereon to form semiconductor chips,

a step of examining the semiconductor chips by irradiating infrared rays onto the semiconductor chips from the support sheet side of the protective film formation sheet,

a step of obtaining semiconductor chips with a protective film by detaching each semiconductor chip, together with the protective film affixed to the back surface of the chip, from the support sheet, and

a step of performing flip-chip connection of the semiconductor chip of the semiconductor chip with a protective film to the circuit surface of a circuit board.

Effects of the Invention

[0017]

The present invention provides a protective film formation sheet used for forming a protective film on the back surface of a semiconductor chip, wherein feeding of the sheet from a roll and infrared inspection of the semiconductor chip can both be performed favorably.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

FIG. 1 is a cross-sectional view schematically illustrating one embodiment of the protective film formation sheet according to the present invention.

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

FIG. 3 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

FIG. 4 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

FIG. 5 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

FIG. 6 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

FIG. 7 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

FIG. 8 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

FIG. 9 is a cross-sectional view for describing one example of a manufacturing method for the protective film formation sheet illustrated in FIG. 2.

FIG. 10 is a cross-sectional view schematically illustrating one example of a conventional protective film formation sheet.

FIG. 11 is a cross-sectional view schematically illustrating another example of a conventional protective film formation sheet.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0019]

>> Protective Film Formation Sheet

The protective film formation sheet according to the present invention has a protective film formation layer provided on a support sheet, and a release film provided on the protective film formation layer, wherein the surface roughness of a surface of the

support sheet on the opposite side from the side on which the protective film formation layer is provided is not more than $0.5\text{ }\mu\text{m}$, and the static friction force, measured in accordance with JIS K7125, between the aforementioned surface of the support sheet and a surface of the release film on the opposite side from the side on which the protective film formation layer is provided is not more than 29 N.

Following removal of the release film, the protective film formation sheet according to the present invention is affixed, via the protective film formation layer, to the surface (back surface) of a semiconductor wafer on the opposite side from the surface on which a circuit is provided. Subsequently, the protective film formation layer is cured at some stage to form a protective film. The resulting laminated body having the support sheet, the protective film or the protective film formation layer, and the semiconductor wafer laminated in this order is then subjected to dicing, thereby dividing the laminated body into individual laminated bodies having the support sheet, the protective film or the protective film formation layer, and a semiconductor chip laminated in that order. Finally, each semiconductor chip is picked up from the support sheet with the protective film affixed to the back surface of the chip. In this manner, the protective film formation sheet according to the present invention is used for forming a protective film on the back surface of semiconductor chips.

[0020]

On the other hand, the laminated body having the support sheet, the protective film or the protective film formation layer, and the semiconductor chip laminated in this order is examined, in this state, for the existence of damage such as cracking or chipping of the semiconductor chip. This type of examination is typically performed by irradiating infrared rays from the opposite side (the back surface side) of the support sheet from the side on which the protective film or protective film formation layer is

provided (in other words, from the support sheet side of the protective film formation sheet), and using an infrared camera to perform an examination from the back surface side of the semiconductor chip, through the support sheet and the protective film or protective film formation layer. At this time, in those cases where the protective film formation sheet according to the present invention is used, the surface roughness of the surface (back surface) of the support sheet on the opposite side from the side on which the protective film formation layer is provided is not more than $0.5\ \mu\text{m}$, meaning the surface (back surface) is either a smooth surface, or is a surface having low levels of unevenness. Accordingly, scattering of the infrared rays at this surface (back surface) of the support sheet is suppressed, meaning the infrared examination described above can be performed favorably.

In this description, unless specifically stated otherwise, the "surface roughness" means the so-called arithmetical mean roughness (Ra) measured in accordance with JIS B0601:2001.

[0021]

Furthermore, by ensuring that the protective film formation sheet has a static friction force between the aforementioned surface (back surface) of the support sheet and the surface of the release film on the opposite side from the side on which the protective film formation layer is provided that is not more than 29 N, blocking is suppressed when the protective film formation sheet is wound into a roll. Accordingly, when the protective film formation sheet according to the present invention is fed from the roll, no abnormalities such as peeling of the release film are observed, and the sheet can be fed favorably. The static friction force is dependent upon the coefficient of static friction determined between the aforementioned surface of the support sheet and the surface of

the release film on the opposite side from the side on which the protective film formation layer is provided.

In the present invention, unless specifically stated otherwise, the static friction force means the value measured in accordance with JIS K7125.

[0022]

In this description, in the protective film formation sheet, the protective film obtained by curing the protective film formation layer by heating or irradiation with energy rays is also termed a protective film formation sheet, provided the laminated structure of the support sheet and the protective film is maintained. Further, in the protective film formation sheet, in those cases where, for example, the support sheet has an adhesive layer, a structure in which this adhesive layer has been cured is also termed a protective film formation sheet, provided the laminated structure of the cured product of the adhesive layer and the protective film formation layer or protective film or the like is maintained.

[0023]

Examples of the support sheet include those provided with a substrate, and examples of such support sheets include sheets composed solely of the substrate, and sheets having another layer such as an adhesive layer, an intermediate layer or a coating layer provided on the substrate. The sheet may have only one of these other layers (single layer), or may have a plurality of two or more other layers, and in the case of a plurality of layers, the plurality of layers may be the same or different, and the combination of the plurality of layers is not particularly limited.

In this description, the expression that "the plurality of layers may be the same or different" means that "all of the layers may be the same, all of the layers may be mutually different, or only a portion of the layers may be the same", and this definition applies not

only in the case of the other layers described above. Moreover, the expression that "the plurality of layers are mutually different" means that "at least one of the material or the thickness of each layer is different from the other layers".

[0024]

In this manner, in the present invention, sheets of various configurations may be used as the support sheet. In the protective film formation sheet according to the present invention, the "surface of the support sheet on the opposite side from the side on which the protective film formation layer is provided" for which the surface roughness is prescribed as being not more than $0.5\ \mu\text{m}$ means the surface of the support sheet that is exposed as the outermost layer onto which the infrared rays are irradiated directly during the infrared examination described above.

[0025]

On the other hand, in the protective film formation sheet according to the present invention, the "surface of the release film on the opposite side from the side on which the protective film formation layer is provided", for which the static friction force relative to the surface of the support sheet having the above type of surface roughness (not more than $0.5\ \mu\text{m}$) is prescribed as being not more than 29 N, means the exposed surface of the release film that makes direct contact with the adjacent outermost layer of the support sheet when the protective film formation sheet is wound into a roll in the manner described above. Usually, this exposed surface is a surface that has not undergone release treatment.

Descriptions of the protective film formation sheet according to the present invention are provided below for each of the various types of support sheet.

[0026]

FIG. 1 is a cross-sectional view schematically illustrating one embodiment of the protective film formation sheet according to the present invention.

The drawings used in the following description may be drawn with specific portions enlarged as appropriate to facilitate comprehension of the features of the present invention, and the dimensional ratios and the like between the constituent elements may differ from the actual values.

[0027]

The protective film formation sheet 1A illustrated in FIG. 1 has an adhesive layer 12 provided on a substrate 11, and a protective film formation layer 13 provided on the adhesive layer 12. The support sheet 10 is a laminated body composed of the substrate 11 and the adhesive layer 12, and the protective film formation sheet 1A has a structure in which the protective film formation layer 13 is laminated to one surface 10a of the support sheet 10. Further, the protective film formation sheet 1A also includes a release film 15 on top of the protective film formation layer 13.

[0028]

In the protective film formation sheet 1A, the adhesive layer 12 is laminated to one surface 11a of the substrate 11, the protective film formation layer 13 is laminated across the entire surface of a surface 12a of the adhesive layer 12 (namely, the surface of the adhesive layer 12 on the opposite side from the surface that contacts the substrate 11), a jig adhesive layer 16 is laminated to a portion of a surface 13a of the protective film formation layer 13 (namely, the surface of the protective film formation layer 13 on the opposite side from the surface that contacts the adhesive layer 12), and the release film 15 is laminated to the portion of the surface 13a of the protective film formation layer 13 on which the jig adhesive layer 16 has not been formed, and on a surface 16a of the jig adhesive layer 16 (namely, the surface of the jig adhesive layer 16 on the opposite side

from the surface that contacts the protective film formation layer 13, and the side surface of the jig adhesive layer 16).

[0029]

The jig adhesive layer 16 may be a single-layer structure containing an adhesive component, or may be a multilayer structure having layers containing an adhesive component laminated to both surfaces of a sheet that acts as a core material.

[0030]

In the protective film formation sheet 1A, the surface 10b of the support sheet 10 on the opposite side from the side of the surface 10a on which the protective film formation layer 13 is provided (hereafter also referred to as the back surface of the support sheet), or in other words, the surface 11b of the substrate 11 on the opposite side from the side of the surface 11a on which the adhesive layer 12 is provided (hereafter also referred to as the back surface of the substrate), has a surface roughness of not more than 0.5 μm .

Further, in the protective film formation sheet 1A, the static friction force between the back surface 10b of the support sheet 10 and a surface 15a of the release film 15 on the opposite side from the side on which the protective film formation layer 13 is provided (hereafter also referred to as the back surface of the release film) is not more than 29 N.

[0031]

The protective film formation sheet 1A illustrated in FIG. 1 is used in a state where the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to the surface 13a of the protective film formation layer 13, and affixing the upper surface of the surface 16a of the jig adhesive layer 16 to a jig such as a ring frame.

[0032]

FIG. 2 is a cross-sectional view schematically illustrating another embodiment of the protective film formation sheet according to the present invention. In FIG. 2, those structural elements that are the same as those illustrated in FIG. 1 are labeled with the same symbols as those used in FIG. 1, and detailed descriptions of those elements are omitted. This also applies in FIG. 3 and subsequent figures.

[0033]

With the exception of not having the jig adhesive layer 16, the protective film formation sheet 1B illustrated in FIG. 2 is the same as the protective film formation sheet 1A illustrated in FIG. 1. In other words, in the protective film formation sheet 1B, the adhesive layer 12 is laminated to one surface 11a of the substrate 11, the protective film formation layer 13 is laminated across the entire surface of the surface 12a of the adhesive layer 12 (namely, the surface of the adhesive layer 12 on the opposite side from the surface that contacts the substrate 11), and the release film 15 is laminated across the entire surface of the surface 13a of the protective film formation layer 13 (namely, the surface of the protective film formation layer 13 on the opposite side from the surface that contacts the adhesive layer 12).

[0034]

In the protective film formation sheet 1B, the back surface 10b of the support sheet 10 (the surface of the support sheet 10 on the opposite side from the surface that contacts the protective film formation layer 13), or in other words, the back surface 11b of the substrate 11 (the surface of the substrate 11 on the opposite side from the surface that contacts the adhesive layer 12), has a surface roughness of not more than 0.5 μm .

Further, in the protective film formation sheet 1B, the static friction force between the back surface 10b of the support sheet 10 and the surface 15a of the release film 15 is not more than 29 N.

[0035]

The protective film formation sheet 1B illustrated in FIG. 2 is used in a state where the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to a region in the central portion of the surface 13a of the protective film formation layer 13, and affixing a region near the periphery of the protective film formation layer 13 that surrounds the semiconductor wafer to a jig such as a ring frame.

[0036]

FIG. 3 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet formation according to the present invention.

With the exception of not having the adhesive layer 12, the protective film formation sheet 1C illustrated in FIG. 3 is the same as the protective film formation sheet 1A illustrated in FIG. 1. In other words, in the protective film formation sheet 1C, the support sheet 10 is composed of only the substrate 11. The protective film formation layer 13 is laminated to one surface 11a of the substrate 11, the jig adhesive layer 16 is laminated to a portion of the surface 13a of the protective film formation layer 13 (namely, the surface of the protective film formation layer 13 on the opposite side from the surface that contacts the substrate), and the release film 15 is laminated to the portion of the surface 13a of the protective film formation layer 13 to which the jig adhesive layer 16 has not been laminated, and to the surface 16a of the jig adhesive layer 16 (the

upper surface, namely the surface of the jig adhesive layer 16 on the opposite side from the surface that contacts the protective film formation layer 13, and the side surface).

[0037]

In the protective film formation sheet 1C, the back surface 10b of the support sheet 10 (the surface of the support sheet 10 on the opposite side from the surface that contacts the protective film formation layer 13), or in other words, the back surface 11b of the substrate 11 (the surface of the substrate 11 on the opposite side from the surface that contacts the protective film formation layer 13), has a surface roughness of not more than 0.5 μm .

Further, in the protective film formation sheet 1C, the static friction force between the back surface 10b of the support sheet 10 and the surface 15a of the release film 15 is not more than 29 N.

[0038]

The protective film formation sheet 1C illustrated in FIG. 3 is used in a similar manner to the protective film formation sheet 1A illustrated in FIG. 1, in a state where the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to the surface 13a of the protective film formation layer 13, and affixing the upper surface of the surface 16a of the jig adhesive layer 16 to a jig such as a ring frame.

[0039]

FIG. 4 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

With the exception of not having the jig adhesive layer 16, the protective film formation sheet 1D illustrated in FIG. 4 is the same as the protective film formation sheet 1C illustrated in FIG. 3. In other words, in the protective film formation sheet 1D, the

protective film formation layer 13 is laminated to one surface 11a of the substrate 11, and the release film 15 is laminated across the entire surface of the surface 13a of the protective film formation layer 13 (namely, the surface of the protective film formation layer 13 on the opposite side from the surface that contacts the substrate 11).

[0040]

In the protective film formation sheet 1D, the back surface 10b of the support sheet 10 (the surface of the support sheet 10 on the opposite side from the surface that contacts the protective film formation layer 13), or in other words, the back surface 11b of the substrate 11 (the surface of the substrate 11 on the opposite side from the surface that contacts the protective film formation layer 13), has a surface roughness of not more than 0.5 μm .

Further, in the protective film formation sheet 1D, the static friction force between the back surface 10b of the support sheet 10 and the surface 15a of the release film 15 is not more than 29 N.

[0041]

The protective film formation sheet 1D illustrated in FIG. 4 is used in a similar manner to the protective film formation sheet 1B illustrated in FIG. 2, in a state where the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to a region in the central portion of the surface 13a of the protective film formation layer 13, and affixing a region near the periphery of the protective film formation layer 13 that surrounds the semiconductor wafer to a jig such as a ring frame.

[0042]

FIG. 5 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

With the exception that a coating layer 14 is provided on the surface 11b of the substrate 11 on the opposite side from the side on which the adhesive layer 12 is provided (hereafter also referred to as the back surface of the substrate), the protective film formation sheet 1E illustrated in FIG. 5 is the same as the protective film formation sheet 1A illustrated in FIG. 1.

In other words, in the protective film formation sheet 1E, the support sheet 10 is a laminated body composed of the coating layer 14, the substrate 11 and the adhesive layer 12 laminated in that order, and the protective film formation sheet 1E has a structure in which the protective film formation layer 13 is laminated to one surface 10a of the support sheet 10. Further, the adhesive layer 12 is laminated to one surface 11a of the substrate 11, the protective film formation layer 13 is laminated across the entire surface of the surface 12a of the adhesive layer 12 (namely, the surface of the adhesive layer 12 on the opposite side from the surface that contacts the substrate 11), a jig adhesive layer 16 is laminated to a portion of the surface 13a of the protective film formation layer 13 (namely, the surface of the protective film formation layer 13 on the opposite side from the surface that contacts the adhesive layer 12), and the release film 15 is laminated to the portion of the surface 13a of the protective film formation layer 13 to which the jig adhesive layer 16 has not been laminated, and on a surface 16a of the jig adhesive layer 16 (the upper surface, namely the surface of the jig adhesive layer 16 on the opposite side from the surface that contacts the protective film formation layer 13, and the side surface).

[0043]

Furthermore, a surface 11b of the substrate 11 (hereafter also referred to as the back surface of the substrate) on the opposite side from the surface 11a on which the adhesive layer 12 is provided (hereafter also referred to as the upper surface of the

substrate) is an uneven surface. The coating layer 14 is provided covering this uneven surface, and a surface 14b of the coating layer 14 (hereafter also referred to as the back surface of the coating layer 14) on the opposite side from the surface 14a that contacts the substrate 11 (hereafter also referred to as the upper surface of the coating layer) has a surface roughness Ra that is smaller than that of the back surface 11b of the substrate 11. The back surface 14b of the coating layer 14, or in other words, the back surface 10b of the support sheet 10 (the surface of the support sheet 10 on the opposite side from the surface that contacts the protective film formation layer 13) has a surface roughness of not more than 0.5 μm . The coating layer 14 functions as a layer that improves the degree of smoothness of the back surface (namely, the exposed surface) of the support sheet 10.

Further, in the protective film formation sheet 1E, the static friction force between the back surface 10b of the support sheet 10 and the surface 15a of the release film 15 (namely, the surface of the release film 15 on the opposite side from the surface that contacts the protective film formation layer 13) is not more than 29 N.

[0044]

The protective film formation sheet 1E illustrated in FIG. 5 is used in a similar manner to the protective film formation sheet 1A illustrated in FIG. 1, in a state where the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to the surface 13a of the protective film formation layer 13, and affixing the upper surface of the surface 16a of the jig adhesive layer 16 to a jig such as a ring frame.

[0045]

FIG. 6 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

With the exception of not having the jig adhesive layer 16, the protective film formation sheet 1F illustrated here is the same as the protective film formation sheet 1E illustrated in FIG. 5. In other words, in the protective film formation sheet 1F, the adhesive layer 12 is laminated to one surface 11a of the substrate 11, the protective film formation layer 13 is laminated across the entire surface of a surface 12a of the adhesive layer 12 (the surface of the adhesive layer 12 on the opposite side from the surface that contacts the substrate 11), and the release film 15 is laminated across the entire surface of the surface 13a of the protective film formation layer 13 (the surface of the protective film formation layer on the opposite side from the surface that contacts the adhesive layer 12). Further, the back surface 11b of the substrate 11 (the surface of the substrate 11 on the opposite side from the surface that contacts the adhesive layer 12) is the same as that of the protective film formation sheet 1E illustrated in FIG. 5, and is laminated with the coating layer 14.

The back surface 14b of the coating layer 14 (the surface of the coating layer on the opposite side from the surface that contacts the substrate 11), or in other words, the back surface 10b of the support sheet 10 (the surface of the support sheet on the opposite side from the surface that contacts the protective film formation layer 13), has a surface roughness of not more than $0.5\ \mu\text{m}$.

Further, in the protective film formation sheet 1F, the static friction force between the back surface 10b of the support sheet 10 and the surface 15a of the release film 15 (the surface of the release film 15 on the opposite side from the surface that contacts the protective film formation layer 13) is not more than 29 N.

[0046]

The protective film formation sheet 1F illustrated in FIG. 6 is used in a similar manner to the protective film formation sheet 1B illustrated in FIG. 2, in a state where

the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to a region in the central portion of the surface 13a of the protective film formation layer 13, and affixing a region near the periphery of the protective film formation layer 13 that surrounds the semiconductor wafer to a jig such as a ring frame.

[0047]

FIG. 7 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

With the exception that the shape of the protective film formation layer differs, the protective film formation sheet 1G illustrated here is the same as the protective film formation sheet 1A illustrated in FIG. 1. In other words, the protective film formation sheet 1G has the adhesive layer 12 provided on the substrate 11, and a protective film formation layer 23 provided on the adhesive layer 12. The support sheet 10 is a laminated body composed of the substrate 11 and the adhesive layer 12, and the protective film formation sheet 1G has a structure in which the protective film formation layer 23 is laminated to one surface 10a of the support sheet 10. Further, the protective film formation sheet 1G also has a release film 15 provided on top of the protective film formation layer 23. With the exception of having a different shape, the protective film formation layer 23 is the same as the protective film formation layer 13.

[0048]

When the protective film formation sheet 1G is viewed from above in plan view, the protective film formation layer 23 has a smaller surface area than the adhesive layer 12, and may, for example, have a circular shape.

[0049]

In the protective film formation sheet 1G, the adhesive layer 12 is laminated to one surface 11a of the substrate 11, and the protective film formation layer 23 is laminated to a portion of the surface 12a of the adhesive layer 12 (the surface of the adhesive layer 12 on the opposite side from the surface that contacts the substrate 11). The release film 15 is laminated to the portion of the surface 12a of the adhesive layer 12 to which the protective film formation layer 23 has not been laminated, and to a surface 23a of the protective film formation layer 23 (the upper surface, namely the surface of the protective film formation layer 23 on the opposite side from the surface that contacts the adhesive layer 12, and the side surface).

[0050]

In the protective film formation sheet 1G, the back surface 10b of the support sheet 10 (the surface of the support sheet 10 on the opposite side from the surface that contacts the protective film formation layer 23), or in other words, the back surface 11b of the substrate 11 (the surface of the substrate 11 on the opposite side from the surface that contacts the adhesive layer 12), has a surface roughness of not more than 0.5 μm .

Further, in the protective film formation sheet 1G, the static friction force between the back surface 10b of the support sheet 10 and the surface 15a of the release film 15 (the surface of the release film 15 on the opposite side from the surface that contacts the protective film formation layer 23 and the adhesive layer 12) is not more than 29 N.

[0051]

The protective film formation sheet 1G illustrated in FIG. 7 is used in a state where the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to the surface 23a of the protective film formation layer 23, and affixing the portion of the surface 12a of the adhesive layer 12 to

which the protective film formation layer 23 has not been laminated to a jig such as a ring frame.

[0052]

FIG. 8 is a cross-sectional view schematically illustrating yet another embodiment of the protective film formation sheet according to the present invention.

With the exception of not having the adhesive layer 12, the protective film formation sheet 1H illustrated here is the same as the protective film formation sheet 1G illustrated in FIG. 7. In other words, in the protective film formation sheet 1H, the support sheet is composed of only the substrate 11. The protective film formation layer 23 is laminated to a portion of one surface 11a of the substrate 11, and the release film 15 is laminated to the portion of the surface 11a of the substrate 11 to which the protective film formation layer 23 has not been laminated, and to a surface 23a of the protective film formation layer 23 (the upper surface, namely the surface of the protective film formation layer 23 on the opposite side from the surface that contacts the substrate 11, and the side surface).

[0053]

In the protective film formation sheet 1H, the back surface 10b of the support sheet 10 (the surface of the support sheet 10 on the opposite side from the surface that contacts the protective film formation layer 23), or in other words, the back surface 11b of the substrate 11 (the surface of the substrate 11 on the opposite side from the surface that contacts the protective film formation layer 23 and the release film 15), has a surface roughness of not more than 0.5 μm .

Further, in the protective film formation sheet 1H, the static friction force between the back surface 10b of the support sheet 10 and the surface 15a of the release film 15 (namely, the surface of the release film 15 on the opposite side from the surface

that contacts the protective film formation layer 23 and the substrate 11) is not more than 29 N.

[0054]

The protective film formation sheet 1H illustrated in FIG. 8 is used in a state where the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to the surface 23a of the protective film formation layer 23, and affixing the portion of the surface 11a of the substrate 11 to which the protective film formation layer 23 has not been laminated to a jig such as a ring frame using a jig adhesive layer (not shown in the figure). A layer similar to the jig adhesive layer 16 illustrated in FIG. 1 and the like can be used as the jig adhesive layer.

Regardless of the structure of the support sheet, the protective film formation sheet can be affixed to a jig such as a ring frame using a jig adhesive layer.

[0055]

The protective film formation sheet according to the present invention is not limited to the structures illustrated in FIGS. 1 to 8, and structures in which a portion of one of the structures illustrated in one of FIGS. 1 to 8 has been altered or eliminated, and structures having an additional structure to those described above, may also be used, provided they do not impair the effects of the present invention.

[0056]

For example, in FIG. 5 and FIG. 6, protective film formation sheets were described in which the support sheet has a laminated structure composed of a coating layer and a substrate, the back surface of the substrate (the surface that contacts the coating layer) is an uneven surface, and the back surface of the coating layer (the surface that does not contact the substrate) has a surface roughness Ra that is smaller than that of the back surface of the substrate. However, in the protective film formation sheet

according to the present invention, within the laminated structure of the coating layer and the substrate, the back surface of the substrate (the surface that contacts the coating layer) need not necessarily be an uneven surface, and may be a smooth surface. In other words, the coating layer may have a function other than improving the degree of smoothness of the back surface (the exposed surface) of the support sheet 10.

[0057]

Further, in FIG. 1 to FIG. 8, protective film formation sheets were described in which the back surface of the support sheet, namely the back surface of the substrate in those cases where the support sheet is either composed solely of the substrate or is a laminated body composed of a substrate and an adhesive layer, or the back surface of the coating layer in those cases where the support sheet has a coating layer, is a smooth surface. However, in the protective film formation sheet according to the present invention, the back surface of the support sheet may be an uneven surface, provided the surface roughness is not more than 0.5 μm .

[0058]

Furthermore, in FIG. 1 to FIG. 8, protective film formation sheets were described in which the back surface of the support sheet is uniform, but in the protective film formation sheet according to the present invention, the back surface of the support sheet may have two or more regions having different degrees of smoothness (degrees of unevenness), and for example, may have a region that is a smooth surface and a region that is an uneven surface.

[0059]

Further, in FIG. 1, FIG. 2, FIG. 5, FIG. 6 and FIG. 7, protective film formation sheets were described in which an adhesive layer is provided in direct contact with the substrate, but the protective film formation sheet according to the present invention may

have an intermediate layer provided between the substrate and the adhesive layer. In other words, in the protective film formation sheet according to the present invention, the support sheet may have a laminated structure composed of a substrate, an intermediate layer and an adhesive layer laminated in this order.

Moreover, in FIG. 3, FIG. 4 and FIG. 8, protective film formation sheets were described in which the protective film formation layer was provided in direct contact with the substrate, but the protective film formation sheet according to the present invention may have an intermediate layer provided between the substrate and the protective film formation layer.

Any arbitrary layer may be selected as this intermediate layer in accordance with the intended purpose, but examples of preferred intermediate layer include layers that improve the adhesion between the two adjacent layers.

[0060]

Furthermore, the protective film formation sheet according to the present invention may also include a layer other than the above intermediate layer in any arbitrary location.

[0061]

Next is a more detailed description of each of the constituent members of the protective film formation sheet according to the present invention.

[0062]

> Support Sheet

There are no particular limitations on the support sheet, provided the protective film formation layer can be provided thereon, and the support sheet satisfies both the aforementioned surface roughness condition (not more than 0.5 μm) and the static friction force condition (not more than 29 N). As described above, examples of preferred

support sheets include support sheets typically used in the field of process sheets for semiconductor wafers, including those composed solely of a substrate, those having an adhesive layer laminated to a substrate, those having a coating layer laminated to a substrate, and those having a coating layer, a substrate and an adhesive layer laminated together in that order. Further examples of preferred support sheets include sheets having an intermediate layer provided between two adjacent layers in one of the laminated structures exemplified above, such as sheets composed of a substrate, an intermediate layer and an adhesive layer laminated together.

[0063]

The support sheet may be composed of one layer (a single layer), or may be composed of a plurality of two or more layers. In those cases where the support sheet is composed of a plurality of layers, these layers may be the same or different, and there are no particular limitations on the combination of the plurality of layers.

[0064]

The thickness of the support sheet may be selected in accordance with the intended purpose, but in terms of being able to impart adequate flexibility to the protective film formation sheet, and achieving good fixability to a semiconductor wafer, the thickness is preferably from 10 to 500 μm , more preferably from 20 to 350 μm and particularly preferably from 30 to 200 μm .

Here, the "thickness of the support sheet" means the total thickness of all the layers that constitute the support sheet, and for example, in the case of a support sheet containing an adhesive layer laminated to a substrate, means the total of the thickness of the substrate and the thickness of the adhesive layer.

In those cases where at least one surface of the support sheet is an uneven surface, the thickness of this type of support sheet may be measured in a region that includes a

protrusion in the uneven surface, using the tip of that protrusion as one measurement point.

In this description, the "thickness" means the value representing the average of five thickness values measured at five random locations using a contact thickness meter.

[0065]

As mentioned above, the surface roughness of the surface of the support sheet on the opposite side from the side on which the protective film formation layer is provided (hereafter also referred to as the exposed surface) is not more than 0.5 μm , and is preferably not more than 0.45, more preferably not more than 0.4, and particularly preferred 0.35 μm or less. By ensuring that the surface roughness of the support sheet is not more than the above upper limit, the aforementioned infrared examination of the semiconductor chips can be performed more favorably. There are no particular limitations on the lower limit for the surface roughness of the support sheet, which may, for example, be 0 μm or 0.01 μm or the like.

In other words, the surface roughness of the support sheet is from 0 to 0.5 μm , preferably from 0 to 0.45 μm , more preferably from 0.01 to 0.4 μm , even more preferably from 0.01 to 0.35 μm , and particularly preferably from 0.03 to 0.3 μm .

The surface roughness of the support sheet can be adjusted, for example, by altering the formation conditions or surface treatment conditions or the like to achieve a layer that satisfies this surface roughness condition.

[0066]

- Substrate

The material for the substrate is preferably any of various resins, and specific examples include polyethylene (including low-density polyethylene (sometimes abbreviated as LDPE), linear low-density polyethylene (sometimes abbreviated as

LLDPE) and high-density polyethylene (sometimes abbreviated as HDPE)), polypropylene, ethylene/propylene copolymers, polybutene, polybutadiene, polymethylpentene, polyvinyl chloride, vinyl chloride copolymers, polyethylene terephthalate, polyethylene naphthalate, polybutylene terephthalate, polyurethane, polyurethane acrylate, polyimide, ethylene/vinyl acetate copolymers, ionomer resins, ethylene/(meth)acrylic acid copolymers, ethylene/(meth)acrylate ester copolymers, polystyrene, polycarbonate, fluororesins, and hydrogenated products, modified products, crosslinked products and copolymers of any of these resins.

[0067]

In this description, the term "(meth)acrylic acid" is deemed to include both "acrylic acid" and "methacrylic acid". Terms similar to (meth)acrylic acid are also similarly defined, and for example, "(meth)acrylate" is deemed to include both "acrylate" and "methacrylate", and "(meth)acryloyl group" is deemed to include both "acryloyl group" and "methacryloyl group".

[0068]

The thickness of the substrate may be selected in accordance with the intended purpose.

In those cases where the support sheet is composed of the substrate laminated to another layer such as an adhesive layer, the thickness of the substrate is preferably from 15 to 300 μm , and more preferably from 20 to 200 μm . By ensuring that the thickness of the substrate falls within this type of range, the flexibility of the protective film formation sheet and the fixability to a semiconductor wafer or semiconductor chip can be improved.

[0069]

The substrate may be composed of one layer (a single layer), or may be composed of a plurality of two or more layers. In those cases where the substrate is

composed of a plurality of layers, these layers may be the same or different, and there are no particular limitations on the combination of the plurality of layers.

When the substrate is composed of a plurality of layers, the total thickness of all of the layers preferably satisfies the preferred substrate thickness described above.

[0070]

In order to improve the adhesion with other layers such as the adhesive layer, protective film formation layer or coating layer provided on top of the substrate, the surface of the substrate may be subjected to a roughening treatment (matte treatment) such as a sandblasting treatment, solvent treatment or embossing treatment, or to an oxidation treatment such as a corona discharge treatment, electron beam irradiation treatment, plasma treatment, ozone/ultraviolet irradiation treatment, flame treatment, chromic acid treatment or hot air treatment. Further, the surface of the substrate may also be subjected to a primer treatment.

[0071]

- Adhesive Layer

The adhesive layer may be formed as appropriate using a conventional material.

The adhesive layer can be formed using an adhesive composition containing the various components such as an adhesive that constitute the adhesive layer. The ratio between the amounts of those components within the adhesive composition that do not volatilize at normal temperature is typically the same as the ratio between the amounts of those components in the adhesive layer. In this description, "normal temperature" means a temperature at which no particular cooling or heating is performed, namely ordinary room temperature, and for example, is typically a temperature of 15 to 25°C.

[0072]

The thickness of the adhesive layer may be selected in accordance with the intended purpose, but is preferably from 1 to 100 μm , more preferably from 2 to 80 μm , and even more preferably from 3 to 50 μm .

[0073]

The adhesive layer may be composed of one layer (a single layer), or may be composed of a plurality of two or more layers. In those cases where the adhesive layer is composed of a plurality of layers, these layers may be the same or different, and there are no particular limitations on the combination of the plurality of layers.

When the adhesive layer is composed of a plurality of layers, the total thickness of all of the layers preferably satisfies the preferred adhesive layer thickness described above.

[0074]

Examples of the above adhesive include adhesive resins such as acrylic-based resins, urethane-based resins, rubber-based resins, silicone-based resins and vinyl ether-based resins, and in terms of the functionality of those resins, examples include energy ray-curable resins and the like.

In this description, the term "energy rays" means rays among electromagnetic waves and charged particle beams that have an energy quantum, and specific examples include ultraviolet rays and electron beams. Ultraviolet rays can be irradiated, for example, using a high-pressure mercury lamp, a fusion H lamp, or a xenon lamp or the like as an ultraviolet source. Electron beams can be generated and irradiated from an electron beam accelerator or the like.

[0075]

Examples of the energy ray-curable resins include resins having a polymerizable group such as a (meth)acryloyl group or a vinyl group.

The adhesive resin is preferably an acrylic-based resin, and is more preferably a (meth)acrylate ester copolymer containing a structural unit derived from a (meth)acrylate ester.

Here, "derived from" means that the chemical structure changes in order to undergo polymerization.

[0076]

In those cases where the adhesive layer contains a component that polymerizes upon irradiation with energy rays, such as an energy ray-curable resin, the adhesive layer becomes energy ray-curable, and by reducing the adhesiveness by irradiation with energy rays, pickup of the semiconductor chips with a protective film described below becomes a simple process. This type of adhesive layer can be formed, for example, from various adhesive compositions containing a component that polymerizes upon irradiation with energy rays.

[0077]

<<Adhesive Composition>>

Examples of preferred adhesive compositions include those containing a component that polymerizes upon irradiation with energy rays, and specific examples of this type of adhesive composition include compositions containing an acrylic-based resin and an energy ray-polymerizable compound (hereafter also referred to as an "adhesive composition (i)"), and compositions containing an acrylic-based resin having a hydroxyl group and also having a polymerizable group on a side chain (for example, an acrylic-based resin having a hydroxyl group, and having a polymerizable group bonded via a urethane linkage on a side chain), and also containing an isocyanate crosslinking agent (hereafter also referred to as an "adhesive composition (ii)").

[0078]

[Adhesive Composition (i)]

The adhesive composition (i) contains an acrylic-based resin and an energy ray-polymerizable compound as essential components.

Each of these components is described below.

[0079]

(Acrylic-Based Resin)

Examples of preferred acrylic-based resins for use in the adhesive composition (i) include (meth)acrylate ester copolymers obtained by polymerizing a (meth)acrylate ester as a monomer, and where necessary another monomer besides the (meth)acrylate ester.

[0080]

Examples of the (meth)acrylate ester include alkyl (meth)acrylate esters in which the alkyl group that constitutes the alkyl ester is a chain-like structure of 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 (also called lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (also called myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (also called palmityl (meth)acrylate), heptadecyl (meth)acrylate, octadecyl (meth)acrylate (also called stearyl (meth)acrylate), and isooctadecyl (meth)acrylate (also called isostearyl (meth)acrylate);

cycloalkyl (meth)acrylate esters such as isobornyl (meth)acrylate and dicyclopentanyl (meth)acrylate;

aralkyl (meth)acrylate esters such as benzyl (meth)acrylate;

cycloalkenyl (meth)acrylate esters such as dicyclopentenyl (meth)acrylate;

cycloalkenyloxyalkyl (meth)acrylate esters such as dicyclopentenloxyethyl (meth)acrylate;

(meth)acrylimides;

glycidyl group-containing (meth)acrylate esters such as glycidyl (meth)acrylate; and

hydroxyl group-containing (meth)acrylate esters such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, and 4-hydroxybutyl (meth)acrylate.

Among the above compounds, methyl methacrylate, 2-ethylhexyl acrylate, and 2-hydroxyethyl acrylate are preferred.

[0081]

Examples of the aforementioned other monomer besides the (meth)acrylate ester include (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene, and N-methylolacrylamide.

[0082]

Each of the monomers that constitute the acrylic-based resin such as the above (meth)acrylate ester and the other monomer besides the (meth)acrylate ester may be a single monomer or two or more monomers.

[0083]

The acrylic-based resin contained in the adhesive composition (i) may be a single resin or two or more resins.

[0084]

The amount of the acrylic-based resin of the adhesive composition (i), relative to the total mass of all of the components besides the solvent in the adhesive composition (i), is preferably from 40 to 99% by mass, and more preferably from 50 to 91% by mass.

[0085]

(Energy Ray-Polymerizable Compound)

The aforementioned energy ray-polymerizable compound is a compound that polymerizes and cures upon irradiation with energy rays, and examples include compounds having an energy ray-polymerizable group such as an energy ray-curable double bond within the molecule.

[0086]

Examples of the energy ray-polymerizable compound include low-molecular weight compounds (monofunctional or polyfunctional monomers and oligomers) having an energy ray-polymerizable group, and specific examples include (meth)acrylates such as trimethylolpropane tri(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol monohydroxy penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, 1,4-butylene glycol di(meth)acrylate, and 1,6-hexanediol di(meth)acrylate;

cyclic aliphatic skeleton-containing (meth)acrylates such as dicyclopentadiene dimethoxy di(meth)acrylate; and

(meth)acrylate-based compounds such as polyethylene glycol di(meth)acrylates, oligoester (meth)acrylates, urethane (meth)acrylate oligomers, epoxy-modified (meth)acrylates, polyether (meth)acrylates, and itaconic acid oligomers.

[0087]

The energy ray-polymerizable compound has a molecular weight that is preferably from 100 to 30,000, and more preferably from 300 to 10,000.

[0088]

The energy ray-polymerizable compound contained in the adhesive composition (i) may be a single compound or two or more compounds.

[0089]

The amount of the energy ray-polymerizable compound in the adhesive composition (i) is preferably from 1 to 125 parts by mass, and more preferably from 10 to 125 parts by mass, per 100 parts by mass of the acrylic-based resin.

[0090]

(Photopolymerization Initiator)

In addition to the acrylic-based resin and the energy ray-polymerizable compound described above, the adhesive composition (i) may also include a photopolymerization initiator.

[0091]

The photopolymerization initiator may be a conventional initiator, and specific examples include:

α -ketol-based compounds such as 4-(2-hydroxyethoxy)phenyl (2-hydroxy-2-propyl) ketone, α -hydroxy- α,α' -dimethylacetophenone, 2-methyl-2-hydroxypropiophenone, 1-hydroxycyclohexyl phenyl ketone, and 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]phenyl}-2-methyl-propan-1-one;

acetophenone-based compounds such as acetophenone, dimethylaminoacetophenone, methoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxyacetophenone, 2,2-diethoxy-2-phenylacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1;

benzoin ether-based compounds such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin n-butyl ether, benzoin isobutyl ether, and anisoin methyl ether;

ketal-based compounds such as benzyl dimethyl ketal and acetophenone dimethyl ketal;

aromatic sulfonyl chloride-based compounds such as 2-naphthalenesulfonyl chloride;

optically active oxime-based compounds such as 1-phenone-1,1-propanedione-2-(o-ethoxycarbonyl)oxime, and ethanone,1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-,1-(O-acetyloxime);

benzophenone-based compounds such as benzophenone, p-phenylbenzophenone, benzoyl benzoate, dichlorobenzophenone, 4,4'-diethylaminobenzophenone, and 3,3'-dimethyl-4-methoxybenzophenone;

anthraquinone-based compounds such as 2-methylantraquinone, 2-ethylantraquinone, 2-tert-butylantraquinone, and 2-aminoanthraquinone;

thioxanthone-based compounds such as thioxanthone, 2-chlorothioxanthone, 2-methylthioxanthone, 2-ethylthioxanthone, isopropylthioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2,4-dichlorothioxanthone, and 2,4-diisopropylthioxanthone; and

p-dimethylaminobenzoate esters, camphorquinone, halogenated ketones, acyl phosphine oxides such as diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, acyl phosphonates, and oligo[2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone].
[0092]

The photopolymerization initiator contained in the adhesive composition (i) may be a single initiator or two or more initiators.

[0093]

When a photopolymerization initiator is used, the amount of the photopolymerization initiator in the adhesive composition (i) is preferably from 0.1 to 10 parts by mass, and more preferably from 1 to 5 parts by mass, per 100 parts by mass of the energy ray-polymerizable compound. Ensuring that the amount of the photopolymerization initiator is at least as large as the above lower limit enables the effect of using the photopolymerization initiator to be achieved satisfactorily. Further, ensuring that the amount of the photopolymerization initiator is not more than the above upper limit suppresses the generation of by-products caused by excess photopolymerization initiator, and enables the curing of the adhesive layer to proceed favorably.

[0094]

(Crosslinking Agent)

In addition to the acrylic-based resin and the energy ray-polymerizable compound, the adhesive composition (i) may also include a crosslinking agent.

Examples of the crosslinking agent include organic polyvalent isocyanate compounds and organic polyvalent imine compounds.

[0095]

Examples of the organic polyvalent isocyanate compounds include aromatic polyvalent isocyanate compounds, aliphatic polyvalent isocyanate compounds, alicyclic polyvalent isocyanate compounds, as well as trimers, isocyanurates and adducts of these compounds, and isocyanate-terminated urethane prepolymers obtained by reacting one of these aromatic polyvalent isocyanate compounds, aliphatic polyvalent isocyanate compounds or alicyclic polyvalent isocyanate compounds with a polyol compound. The aforementioned adducts mean reaction products of the aromatic polyvalent isocyanate

compound, aliphatic polyvalent isocyanate compound or alicyclic polyvalent isocyanate compound with a low-molecular weight active hydrogen-containing compound such as ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane or castor oil.

[0096]

Specific examples of the organic polyvalent isocyanate compounds include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, 3-methyldiphenylmethane diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, dicyclohexylmethane-2,4'-diisocyanate, compounds in which one or both of tolylene diisocyanate and hexamethylene diisocyanate have been added to some or all of the hydroxyl groups of a polyol such as trimethylolpropane, and lysine diisocyanate.

[0097]

Examples of the organic polyvalent imine compound include N,N'-diphenylmethane-4,4'-bis(1-aziridinecarboxamide), trimethylolpropane-tri- β -aziridinypropionate, tetramethylolmethane-tri- β -aziridinypropionate, and N,N'-toluene-2,4-bis(1-aziridinecarboxamide)triethylenemelamine.

[0098]

When an isocyanate compound is used as the crosslinking agent, a hydroxyl group-containing polymer is preferably used as the acrylic-based resin. When the crosslinking agent has isocyanate groups and the acrylic-based resin has hydroxyl groups, reaction between the isocyanate groups and the hydroxyl groups enables crosslinked structures to be easily introduced into the adhesive layer.

[0099]

The crosslinking agent contained in the adhesive composition (i) may be a single compound or two or more compounds.

[0100]

When a crosslinking agent is used, the amount of the crosslinking agent in the adhesive composition (i) is preferably from 0.01 to 20 parts by mass, and more preferably from 0.1 to 16 parts by mass, per 100 parts by mass of the acrylic-based resin.

[0101]

(Solvent)

In addition to the acrylic-based resin and the energy ray-polymerizable compound, the adhesive composition (i) preferably also contains a solvent.

There are no particular limitations on the solvent contained, but examples of preferred solvents include hydrocarbons such as toluene and xylene; alcohols such as methanol, ethanol, 2-propanol, isobutyl alcohol (also called 2-methylpropan-1-ol) and 1-butanol; esters such as ethyl acetate; ketones such as acetone and methyl ethyl ketone; ethers such as tetrahydrofuran; and amides (namely, compounds having an amide linkage) such as dimethylformamide and N-methylpyrrolidone.

The solvent contained in the composition (i) may be a single solvent or two or more solvents.

[0102]

The amount of the solvent in those cases where the adhesive composition (i) contains a solvent is preferably from 40 to 90% by mass, and more preferably from 50 to 80% by mass, relative to the total mass of the adhesive composition.

[0103]

(Other Components)

In addition to the acrylic-based resin and the energy ray-polymerizable compound, the adhesive composition (i) may also contain other components that do not correspond with any of the aforementioned photopolymerization initiator, crosslinking agent or solvent, provided the effects of the present invention are not impaired.

These other components may be conventional components, which may be selected as required in accordance with the intended purpose, and although there are no particular limitations, examples of preferred components include various additives such as colorants (dyes and pigments), age resistors, antistatic agents, flame retardants, silicone compounds, and chain transfer agents.

These other components contained in the adhesive composition (i) may include a single component or two or more components.

[0104]

[Adhesive Composition (ii)]

The adhesive composition (ii) contains an acrylic-based resin having a hydroxyl group and also having a polymerizable group on a side chain (for example, an acrylic-based resin having a hydroxyl group, and having a polymerizable group bonded via a urethane linkage on a side chain) and an isocyanate crosslinking agent as essential components.

In those cases where the adhesive composition (ii) is used, because the acrylic-based resin has a polymerizable group on a side chain, the improvement in releasability from the adherend due to the reduction in adhesiveness following the polymerization reaction (curing) is superior to that obtained when the polymerization reaction uses an energy ray-polymerizable compound and is performed by irradiation with energy rays, such as the case of the adhesive composition (i), meaning the pickup characteristics of the semiconductor chips with a protective film also improve.

In this description, unless specifically stated otherwise, references to an "acrylic-based resin" in the adhesive composition (ii) mean an "acrylic-based resin having a polymerizable group on a side chain".

[0105]

(Acrylic-Based Resin)

Examples of the aforementioned acrylic-based resin having a polymerizable group on a side chain include resins obtained by copolymerizing monomers including a non-hydroxyl group-containing (meth)acrylate ester having no hydroxyl group and a hydroxyl group-containing compound such as a hydroxyl group-containing (meth)acrylate ester having a hydroxyl group, and then reacting the hydroxyl groups of the obtained hydroxyl group-containing copolymer with the isocyanate group of a compound having an isocyanate group and a polymerizable group, thus forming urethane linkages.

[0106]

Examples of the non-hydroxyl group-containing (meth)acrylate ester include those (meth)acrylate esters mentioned in relation to the adhesive composition (i) other than the hydroxyl group-containing (meth)acrylate esters.

Further, examples of the above hydroxyl group-containing compound include the same compounds as the hydroxyl group-containing (meth)acrylate esters included in the adhesive composition (i).

The non-hydroxyl group-containing (meth)acrylate ester and the hydroxyl group-containing compound that constitute the acrylic-based resin may each include a single compound or two or more compounds.

[0107]

Examples of the compound having an isocyanate group and a polymerizable group include isocyanate group-containing (meth)acrylate esters such as 2-(meth)acryloyloxyethyl isocyanate.

This compound having an isocyanate group and a polymerizable group that forms the acrylic-based resin may be a single compound or two or more compounds.

[0108]

The acrylic-based resin contained in the adhesive composition (ii) may be a single resin or two or more resins.

[0109]

The amount of the acrylic-based resin in the adhesive composition (ii), relative to the total mass of all of the components besides the solvent within the adhesive composition (ii), is preferably from 80 to 99% by mass, and more preferably from 90 to 97% by mass.

[0110]

(Isocyanate-Based Crosslinking Agent)

Examples of the isocyanate-based crosslinking agent include the same compounds as the organic polyvalent isocyanate compounds used as a crosslinking agent in the adhesive composition (i).

[0111]

The isocyanate-based crosslinking agent contained in the adhesive composition (ii) may be a single compound or two or more compounds.

[0112]

The number of moles of isocyanate groups within the isocyanate-based crosslinking agent in the adhesive composition (ii) is preferably 0.2 to 3 times the number of moles of hydroxyl groups within the acrylic-based resin in the adhesive

composition (ii). Ensuring that the number of moles of isocyanate groups is at least as large as the above lower limit improves the releasability of the adhesive layer from the adherend due to the reduction in adhesiveness of the adhesive layer following curing, thus improving the pickup characteristics of the semiconductor chips with a protective film. Further, ensuring that the number of moles of isocyanate groups is not more than the above upper limit enables better suppression of the generation of by-products formed by reaction between molecules of the isocyanate-based crosslinking agent.

[0113]

The amount of the isocyanate-based crosslinking agent in the adhesive composition (ii) may be adjusted as appropriate so that the number of moles of isocyanate groups falls within the above range, but provided this condition is satisfied, the amount of the isocyanate-based crosslinking agent is preferably from 0.01 to 20 parts by mass, more preferably from 0.1 to 15 parts by mass, and particularly preferably from 0.3 to 12 parts by mass, per 100 parts by mass of the acrylic-based resin.

[0114]

(Photopolymerization Initiator)

In addition to the acrylic-based resin and the isocyanate-based crosslinking agent described above, the adhesive composition (ii) may also include a photopolymerization initiator.

Examples of the photopolymerization initiator include the same compounds as those mentioned above for the case of the adhesive composition (i).

The photopolymerization initiator contained in the adhesive composition (ii) may be a single initiator or two or more initiators.

[0115]

When a photopolymerization initiator is used, the amount of the photopolymerization initiator in the adhesive composition (ii) is preferably from 0.05 to 20 parts by mass per 100 parts by mass of the acrylic-based resin.

Ensuring that the amount of the photopolymerization initiator is at least as large as the above lower limit enables the effect of using the photopolymerization initiator to be achieved satisfactorily. Further, ensuring that the amount of the photopolymerization initiator is not more than the above upper limit suppresses the generation of by-products caused by excess photopolymerization initiator, and enables the curing of the adhesive layer to proceed favorably.

[0116]

(Solvent)

In addition to the acrylic-based resin and the isocyanate-based crosslinking agent described above, the adhesive composition (ii) preferably also includes a solvent.

Examples of the solvent include the same solvents as those mentioned above for the case of the adhesive composition (i).

The solvent contained in the adhesive composition (ii) may include a single solvent or two or more solvents.

[0117]

The amount of the solvent in those cases where the adhesive composition (ii) contains a solvent is preferably from 40 to 90% by mass, and more preferably from 50 to 80% by mass, relative to the total mass of the adhesive composition (ii).

[0118]

(Other Components)

In addition to the acrylic-based resin and the isocyanate-based crosslinking agent, the adhesive composition (ii) may also contain other components that do not correspond

with the aforementioned photopolymerization initiator or solvent, provided the effects of the present invention are not impaired.

Examples of these other components include the same components as those mentioned above for the case of the adhesive composition (i).

These other components contained in the adhesive composition (ii) may include a single component or two or more components.

[0119]

The description until this point has focused on adhesive compositions containing a component that polymerizes upon irradiation with energy rays, but an adhesive composition that does not contain a component that polymerizes upon irradiation with energy rays may also be used in the formation of the adhesive layer. In other words, the adhesive layer may be a non-energy ray-curable adhesive composition.

Examples of preferred non-energy ray-curable adhesive compositions include compositions containing an acrylic-based resin and a crosslinking agent (hereafter also referred to as an "adhesive composition (iii)"), and these compositions may also contain a solvent and other optional components that are not classified as solvents.

[0120]

[Adhesive Composition (iii)]

The acrylic-based resin, crosslinking agent, solvent and other components contained in the adhesive composition (iii) may each be the same as the corresponding component in the adhesive composition (i).

[0121]

The amount of the acrylic-based resin in the adhesive composition (iii), relative to the total mass of all of the components besides the solvent in the adhesive composition

(iii), is preferably from 40 to 99% by mass, and more preferably from 50 to 97% by mass.

[0122]

The amount of the crosslinking agent in the adhesive composition (iii) is preferably from 2 to 30 parts by mass, and more preferably from 4 to 25 parts by mass, per 100 parts by mass of the acrylic-based resin.

[0123]

With the exception of the points described above, the adhesive composition (iii) is the same as the adhesive composition (i).

[0124]

<<Manufacturing Method for Adhesive Composition>>

The adhesive compositions such as the adhesive compositions (i) to (iii) can be obtained by blending the various components that constitute the adhesive composition, such as the adhesive and those components besides the adhesive that are added as required.

There are no particular limitations on the order in which the components are added during blending, and two or more components may be added simultaneously.

There are no particular limitations on the method used for mixing the components during blending, and a method may be selected from among conventional methods such as methods in which mixing is performed by rotation with a stirring bar or stirring blade, methods in which mixing is performed using a mixer, and methods in which mixing is performed by application of ultrasound.

The temperature and time during addition and mixing of each component are not particularly limited and may be set as appropriate provided the blended component does not degrade, but the temperature is preferably from 15 to 30°C.

[0125]

- Coating Layer

In the aforementioned coating layer, the surface of the coating layer on the opposite side from the side that contacts the substrate preferably has a smaller surface roughness Ra than the surface of the substrate on the side on which the coating layer is provided.

The coating layer preferably contains a cured product that is obtained by curing by irradiation with energy rays, and is preferably a layer obtained by curing a coating composition containing an energy ray-polymerizable compound that polymerizes upon irradiation with energy rays. This energy ray-polymerizable compound is preferably (meth)acrylic acid or a derivative thereof.

In this description, a "derivative" means a compound in which at least one hydrogen atom of the original compound has been substituted with a group (substituent) other than a hydrogen atom.

[0126]

The protective film formation sheet described above may have not only the function of forming a protective film for protecting the back surface of the semiconductor chips obtained upon dicing, but may also combine the function of a dicing sheet when the semiconductor wafer undergoes dicing. During dicing of the semiconductor wafer, the semiconductor wafer with the affixed protective film formation sheet may be subjected to expansion, and in such cases, the protective film formation sheet is required to have appropriate flexibility. In order to impart the protective film formation sheet with appropriate flexibility, a flexible resin such as a polypropylene may sometimes be selected as a material for forming the support sheet. On the other hand, this type of flexible resin can sometimes deform or suffer from wrinkling upon heating.

Accordingly, it can be stated that the coating layer is preferably formed from a raw material composition that does not undergo heat curing, but rather cures upon irradiation with energy rays.

[0127]

Although there are no particular limitations on the thickness of the coating layer, the thickness is preferably from 0.1 to 20 μm , more preferably from 0.4 to 15 μm , and particularly preferably from 0.8 to 10 μm . Ensuring that the thickness of the coating layer is at least as large as the above lower limit facilitates a reduction in the surface roughness R_a of the surface of the coating layer on the opposite side from the side that contacts the substrate, and enhances the suppression effect on blocking of the protective film formation sheet. Further, ensuring that the thickness of the coating layer is not more than the above upper limit means that when the semiconductor chip having the affixed protective film formation sheet undergoes an aforementioned examination through the sheet using an infrared camera or the like, a clearer examination image can be acquired, and also enables dicing of the semiconductor wafer including expansion to be performed more easily.

By covering the uneven surface of the substrate in the manner described above, the surface of the coating layer that contacts the substrate can develop an uneven surface, but the thickness of the coating layer may be measured in a region that includes a protrusion in this uneven surface of the coating layer, using the tip of that protrusion as one measurement point.

[0128]

In the protective film formation sheet, in those cases where the coating layer becomes the outermost layer on the opposite side from the release film side, the surface roughness R_a of the surface of the coating layer on the opposite side from the side that

contacts the substrate (namely, the exposed surface) is at least 0 μm but not more than 0.5 μm .

The surface roughness R_a of the coating layer can be adjusted, for example, by altering factors such as the surface roughness R_a of the surface of the substrate on which the coating layer is provided, the thickness of the coating layer, or the coating method used for the coating composition described below that is used for forming the coating layer.

[0129]

<<Coating Composition>>

The above coating composition preferably contains (α) one or both of a silica sol and silica microparticles having a bound radical-polymerizable unsaturated group-containing organic compound (hereafter sometimes abbreviated as "the component (α)"), and (β) at least one compound selected from the group consisting of polyfunctional acrylate-based monomers and acrylate-based prepolymers (hereafter sometimes abbreviated as "the component (β)").

[0130]

[Component (α)]

The component (α) lowers the refractive index of the coating layer, reduces the curing shrinkage and heat and moisture shrinkage of the protective film formation sheet, thereby suppressing the occurrence of curling of the protective film formation sheet caused by these types of shrinkage.

[0131]

Examples of the silica sol in the component (α) include colloidal silicas obtained by suspending silica microparticles in a colloidal state in an organic solvent such as an alcohol or an ether derived from ethylene glycol (such as cellosolve), wherein the

average particle size of the suspended silica microparticles is preferably from 0.001 to 1 μm , and more preferably from 0.03 to 0.05 μm .

[0132]

In the component (α), the silica microparticles having a bound radical-polymerizable unsaturated group-containing organic compound are microparticles that undergo crosslinking and curing upon irradiation with energy rays.

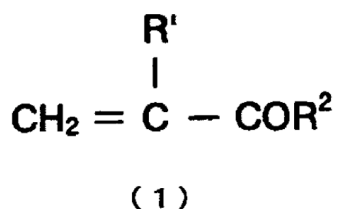
Examples of the silica microparticles having a bound radical-polymerizable unsaturated group-containing organic compound include materials obtained by reacting the silanol groups that exist on the surface of silica microparticles with a functional group in the radical-polymerizable unsaturated group-containing organic compound, and the average particle size of these silica microparticles is preferably from 0.005 to 1 μm . There are no particular limitations on the aforementioned functional group in the radical-polymerizable unsaturated group-containing organic compound, provided the functional group is capable of reacting with the silanol groups in the silica microparticles.

[0133]

Examples of the radical-polymerizable unsaturated group-containing organic compound having a functional group include compounds represented by general formula (1) shown below.

[0134]

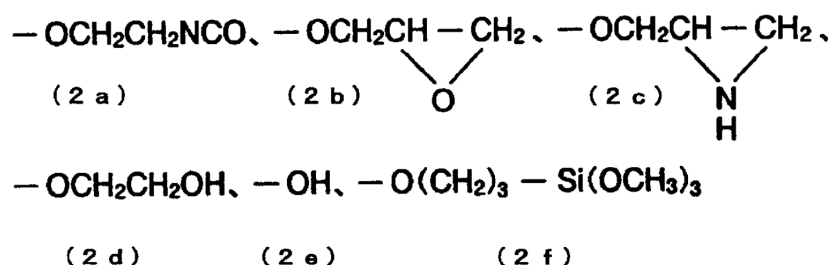
[Chemical formula 1]



(In the formula, R^1 represents a hydrogen atom or a methyl group, and R^2 represents a halogen atom or a group represented by any of formulas (2a) to (2f) shown below.)

[0135]

[Chemical formula 2]



[0136]

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

[0137]

Examples of preferred radical-polymerizable unsaturated group-containing organic compounds include (meth)acrylic acid, (meth)acryloyl chloride, 2-isocyanatoethyl (meth)acrylate, glycidyl (meth)acrylate, 2,3-iminopropyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, and (3-(meth)acryloyloxypropyl)trimethoxysilane.

[0138]

In the present invention, the radical-polymerizable unsaturated group-containing organic compound may be a single compound or a combination of two or more compounds.

[0139]

In the component (α), the silica sol and the silica microparticles having a bound radical-polymerizable unsaturated group-containing organic compound may each include a single material or two or more materials.

[0140]

For the component (α), a silica sol may be used alone, silica microparticles having a bound radical-polymerizable unsaturated group-containing organic compound may be used alone, or a combination of a silica sol and silica microparticles having a bound radical-polymerizable unsaturated group-containing organic compound may be used.

[0141]

The amount of the component (α) in the coating composition is preferably selected in accordance with the refractive index of each of the layers of the support sheet other than the coating layer, and typically, is preferably selected so that the amount of silica derived from the component (α) is from 20 to 60% by mass relative to the total mass of the coating composition. Ensuring that the amount of silica is at least as large as the above lower limit enhances the reduction effect on the refractive index of the coating layer and the suppression effect on the occurrence of curling in the protective film formation sheet. Further, ensuring that the amount of silica is not more than the above upper limit makes formation of the coating layer easier, and enhances the suppression effect on any decrease in the hardness of the coating layer.

In order to achieve a superior refractive index, ease of formation and hardness for the coating layer, and also achieve better suppression of curling in the protective film formation sheet, the amount of silica derived from the component (α) in the coating layer is more preferably from 20 to 45% by mass relative to the total mass of the coating composition.

[0142]

[Component (β)]

The component (β) is the main photocurable component for forming the coating layer described above.

[0143]

There are no particular limitations on the polyfunctional acrylate-based monomer in the component (β), provided the monomer is a (meth)acrylic acid derivative containing at least two (meth)acryloyl groups in a single molecule.

Examples of preferred polyfunctional acrylate-based monomers include 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, neopentyl glycol hydroxypivalate 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, 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, and caprolactone-modified dipentaerythritol hexa(meth)acrylate.

[0144]

There are no particular limitations on the acrylate-based prepolymer in the component (β), provided the prepolymer is a (meth)acrylate ester, and is a polymer or oligomer having photocurability.

Examples of preferred acrylate-based prepolymers include polyester acrylate-based prepolymers, epoxy acrylate-based prepolymers, urethane acrylate-based prepolymers, and polyol acrylate-based prepolymers.

[0145]

Examples of the above polyester acrylate-based prepolymers include compounds obtained by using (meth)acrylic acid to esterify the hydroxyl groups of a polyester oligomer having hydroxyl groups at both terminals of the molecule, obtained by a condensation reaction between a polyvalent carboxylic acid and a polyhydric alcohol; and compounds obtained by using (meth)acrylic acid to esterify the terminal hydroxyl groups of an oligomer obtained by an addition reaction of an alkylene oxide to a polyvalent carboxylic acid.

Examples of the epoxy acrylate-based prepolymers include compounds obtained by using a reaction with (meth)acrylic acid to esterify the oxirane ring of a bisphenol epoxy resin or novolac epoxy resin of comparatively low molecular weight.

Examples of the urethane acrylate-based prepolymers include compounds obtained by using (meth)acrylic acid to esterify a polyurethane oligomer obtained by a reaction between a polyether polyol or polyester polyol and a polyisocyanate.

Examples of the polyol acrylate-based prepolymers include compounds obtained by using (meth)acrylic acid to esterify the hydroxyl groups of a polyether polyol.

[0146]

In the component (β), the polyfunctional acrylate-based monomer and the acrylate-based prepolymer may each include a single compound or two or more compounds.

[0147]

For the component (β), a polyfunctional acrylate-based monomer may be used alone, an acrylate-based prepolymer may be used alone, or a combination of a polyfunctional acrylate-based monomer and an acrylate-based prepolymer may be used.

[0148]

In addition to the component (α) and the component (β), the coating composition preferably also contains a solvent. By including a solvent in the coating composition, a coating film can be formed more easily by applying and drying the coating composition to form a coating layer.

A single solvent may be used alone, or a combination of two or more solvents may be used.

[0149]

Examples of the solvent include aliphatic hydrocarbons such as hexane, heptane and cyclohexane; aromatic hydrocarbons such as toluene and xylene; halogenated hydrocarbons such as methylene chloride and ethylene chloride; alcohols such as methanol, ethanol, propanol, butanol, and 1-methoxy-2-propanol; ketones such as acetone, methyl ethyl ketone, 2-pentanone, isophorone, and cyclohexanone; esters such as ethyl acetate and butyl acetate; and cellosolves such as 2-ethoxyethanol (also known as ethyl cellosolve).

[0150]

In addition to the component (α) and the component (β), the coating composition may also contain various optional components such as monofunctional acrylate-based monomers, photopolymerization initiators, photosensitizers, polymerization inhibitors, crosslinking agents, antioxidants, ultraviolet absorbers, photostabilizers, leveling agents and antifoaming agents, provided the effects of the present invention are not impaired.

A single optional component may be used alone, or a combination of two or more components may be used.

[0151]

There are no particular limitations on the monofunctional acrylate-based monomers that may be used as optional components, provided they are photocurable components, and are (meth)acrylic acid derivatives having only one (meth)acryloyl group in a single molecule.

Examples of preferred monofunctional acrylate-based monomers include cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, dodecyl (meth)acrylate (also called lauryl (meth)acrylate), octadecyl (meth)acrylate (also called stearyl (meth)acrylate), and isobornyl (meth)acrylate.

[0152]

Examples of the photopolymerization initiators that may be used as optional components include known materials conventionally used in radical polymerization.

Examples of preferred photopolymerization initiators include aryl ketone-based photopolymerization initiators such as acetophenone-based compounds, benzophenone-based compounds, alkylaminobenzophenone-based compounds, benzil-based compounds, benzoin-based compounds, benzoin ether-based compounds, benzyl dimethyl acetal-based compounds, benzoyl benzoate-based compounds, and α -acyloxime ester-based compounds; sulfur-containing photopolymerization initiators such as sulfide-based compounds and thioxanthone-based compounds; acylphosphine oxide-based compounds such as acyldiarylphosphine oxides; and anthraquinone-based compounds.

In those cases where the coating composition is cured by irradiation with an electron beam, a photopolymerization initiator is unnecessary.

[0153]

In the coating composition, the amount of the photopolymerization initiator is preferably from 0.2 to 10 parts by mass, and more preferably from 0.5 to 7 parts by mass, per 100 parts by mass of the total amount of photocurable components.

[0154]

Examples of the aforementioned photosensitizers include tertiary amines, p-dimethylaminobenzoate esters, and thiol-based sensitizers.

In the coating composition, the amount of the photosensitizer is preferably from 1 to 20 parts by mass, and more preferably from 2 to 10 parts by mass, per 100 parts by mass of the total amount of photocurable components.

[0155]

The antioxidants, ultraviolet absorbers and photostabilizers may be conventional materials, but reactive antioxidants, ultraviolet absorbers and photostabilizers having a (meth)acryloyl group or the like in the molecule are preferred. These antioxidants, ultraviolet absorbers and photostabilizers bind to the polymer chains formed upon irradiation of the energy rays, and therefore dissipation of the components from the cured layer over time is suppressed, meaning the function of the components can manifest over a long period of time.

[0156]

The coating composition preferably contains a silica sol as the component (α), and more preferably contains a silica sol in which the average particle size of the silica microparticles suspended in a colloidal state is from 0.03 to 0.05 μm .

By including this type of silica sol in the coating layer, the suppression effect on blocking of the protective film formation sheet is enhanced. Further, in the coating layer, because this type of silica sol is distributed unevenly, with the sol existing in greater amounts at the surface on the opposite side from the substrate side and in regions near

that surface rather than other regions, the suppression effect on blocking of the protective film formation sheet is enhanced even further. An uneven distribution of components such as the silica sol in the coating layer can be achieved by appropriate adjustment of the coating conditions for the coating composition.

[0157]

<<Manufacturing Method for Coating Composition>>

The coating composition can be obtained by blending the components used for forming the coating composition, such as the energy ray-polymerizable compounds such as the component (α) and the component (β), and any other components that may be added as necessary. With the exception of having different blend components, the coating composition can be obtained using the same method as that described above for the adhesive composition.

In those cases where a solvent is used, the solvent may first be mixed with one of the other components besides the solvent to dilute the other component, or the solvent may simply be mixed with the other blend components without being used to first dilute one of the other components.

The components besides the solvent in the coating composition may be dissolved, or may be dispersed without being dissolved. There are no particular limitations on the concentration of each component or the viscosity of the coating composition, provided the coating composition can be applied favorably.

Application of the coating composition may be performed using a conventional method, and examples include methods that use any of various coaters such as an air knife coater, blade coater, bar coater, gravure coater, roll coater, roll knife coater, curtain coater, die coater, knife coater, screen coater, Meyer bar coater or kiss coater.

[0158]

> Protective Film Formation Layer

The protective film formation layer may be either heat-curable or energy ray-curable. The protective film formation layer undergoes curing to finally become a protective film having superior impact resistance. This protective film prevents the occurrence of cracking in the semiconductor chips in steps from the dicing step onward.

The protective film formation layer can be formed using a heat-curable protective film formation layer composition or an energy ray-curable protective film formation layer composition described below (and hereafter jointly referred to as the "protective film formation layer composition").

[0159]

The protective film formation layer may be composed of only one layer (a single layer), or may have a plurality of two or more layers, and in the case of a plurality of layers, the plurality of layers may be the same or different, and the combination of the plurality of layers is not particularly limited.

[0160]

Although there are no particular limitations on the thickness of the protective film formation layer, the thickness is preferably from 1 to 100 μm , more preferably from 5 to 75 μm , and particularly preferably from 5 to 50 μm . Ensuring that the thickness of the protective film formation layer is at least as large as the above lower limit means that when laser printing is performed by irradiating a laser onto the protective film or the protective film formation layer, the effect of the layer in preventing damage to the semiconductor wafer as a result of laser penetration can be enhanced. Further, the protective action of the protective film also improves. On the other hand, by ensuring that the thickness of the protective film formation layer is not more than the above upper limit, the degree of shrinkage of the film during curing is reduced, and the reduction

effect on warping of the semiconductor chips with a protective film is enhanced. Further, when a temperature cycling test is performed, stress generation caused by the difference in the coefficients of linear expansion of the protective film and the semiconductor wafer is suppressed, thus enhancing the suppression effect on detachment of the protective film from the semiconductor wafer.

Here, the "thickness of the protective film formation layer" means the thickness of the entire protective film formation layer, so that the thickness of a protective film formation layer composed of a plurality of layers means the total thickness of all of the layers that constitute the protective film formation layer.

[0161]

- Heat-Curable Protective Film Formation Layer

An example of a preferred heat-curable protective film formation layer is a layer containing a polymer component (A) and a heat-curable component (B). The polymer component (A) is a component that is considered to have been formed by a polymerization reaction of a polymerizable compound. Further, the heat-curable component (B) is a component that can undergo a curing (polymerization) reaction with heat acting as the reaction trigger. In the present invention, polymerization reactions are deemed to include polycondensation reactions.

[0162]

<<Heat-Curable Protective Film Formation Layer Composition>>

The heat-curable protective film formation layer can be formed from a heat-curable protective film formation layer composition containing the constituent materials for the layer. For example, by applying the heat-curable protective film formation layer composition to a formation target surface for the heat-curable protective film formation layer, and then performing drying as necessary, the heat-curable protective film

formation layer can be formed in the targeted region. The ratio between the amounts of those components within the heat-curable protective film formation layer composition that do not volatilize at normal temperature is typically the same as the ratio between the amounts of those components in the heat-curable protective film formation layer.

Here, "normal temperature" is as defined above.

[0163]

Application of the heat-curable protective film formation layer composition may be performed using a conventional method, and examples include methods that use any of various coaters such as an air knife coater, blade coater, bar coater, gravure coater, roll coater, roll knife coater, curtain coater, die coater, knife coater, screen coater, Meyer bar coater or kiss coater.

[0164]

There are no particular limitations on the drying conditions for the heat-curable protective film formation layer composition, but in those cases where the heat-curable protective film formation layer composition contains a solvent described below, drying under heat is preferably performed, and in such cases, drying is preferably performed, for example, under conditions of 70 to 130°C for 10 seconds to 5 minutes.

[0165]

<Protective Film Formation Layer Composition (III-1)>

An example of the heat-curable protective film formation layer composition is a heat-curable protective film formation layer composition (III-1) (in this description, also abbreviated as "the protective film formation layer composition (III-1)") containing a polymer component (A) and a heat-curable component (B).

[0166]

[Polymer Component (A)]

The polymer component (A) is a polymer compound used for imparting the heat-curable protective film formation layer with film forming characteristics and flexibility and the like.

The polymer component (A) contained in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may be a single polymer or two or more polymers, and in the case of two or more polymers, the combination and ratio between those polymers may be selected as desired.

[0167]

Examples of the polymer component (A) include acrylic-based resins (for example, resins having (meth)acryloyl groups), polyesters, urethane-based resins (for example, resins having urethane linkages), acrylic urethane resins, silicone-based resins (for example, resins having siloxane linkages), rubber-based resins (for example, resins having rubber structures), phenoxy resins and heat-curable polyimides, and acrylic-based resins are preferred.

[0168]

Examples of the acrylic-based resin for the polymer component (A) include conventional acrylic polymers.

The weight average molecular weight (M_w) of the acrylic-based resin is preferably from 10,000 to 2,000,000, and more preferably from 100,000 to 1,500,000. Provided the weight average molecular weight of the acrylic-based resin is at least as large as the above lower limit, the shape stability (the stability over time upon storage) of the heat-curable protective film formation layer improves. Further, provided the weight average molecular weight of the acrylic-based resin is not more than the above upper limit, the heat-curable protective film formation layer can more easily conform to any

uneven surfaces on the adherend, thus suppressing the occurrence of voids or the like between the adherend and the heat-curable protective film formation layer.

[0169]

The glass transition temperature (T_g) of the acrylic-based resin is preferably from -60 to 70°C, and more preferably from -30 to 50°C. By ensuring that the T_g of the acrylic-based resin is at least as large as the above lower limit, the adhesive strength between the protective film and the support sheet is suppressed, thus improving the releasability of the support sheet. Further, by ensuring that the T_g of the acrylic-based resin is not more than the above upper limit, the adhesive strength between the heat-curable protective film formation layer and the protective film adherend can be increased.

In this description, the "glass transition temperature" is obtained by measuring a DSC curve for a sample using a differential scanning calorimeter, and represents the temperature at the inflection point in the obtained DSC curve.

[0170]

Examples of the acrylic-based resin include polymers of one or two or more (meth)acrylate esters; and copolymers of at least two monomers selected from among (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene and N-methylolacrylamide.

[0171]

Examples of the monomer that constitutes the acrylic-based resin include alkyl (meth)acrylate esters in which the alkyl group that constitutes the alkyl ester is a chain-like structure of 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 (also called lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (also called myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (also called palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (also called stearyl (meth)acrylate);

cycloalkyl (meth)acrylate esters such as isobornyl (meth)acrylate and dicyclopentanyl (meth)acrylate;

aralkyl (meth)acrylate esters such as benzyl (meth)acrylate;

cycloalkenyl (meth)acrylate esters such as dicyclopentenyl (meth)acrylate;

cycloalkenyloxyalkyl (meth)acrylate esters such as dicyclopentenylloxyethyl (meth)acrylate;

(meth)acrylimides;

glycidyl group-containing (meth)acrylate esters such as glycidyl (meth)acrylate;

hydroxyl group-containing (meth)acrylate esters such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, and 4-hydroxybutyl (meth)acrylate; and

substituted amino group-containing (meth)acrylate esters such as N-methylaminoethyl (meth)acrylate. Here, a "substituted amino group" means a group in which one or two hydrogen atoms of an amino group have each been substituted with a group other than a hydrogen atom.

Among the above compounds, n-butyl acrylate, methyl acrylate, glycidyl methacrylate, and 2-hydroxyethyl acrylate and the like are preferred.

[0172]

The acrylic-based resin may also be a resin obtained by copolymerizing one or two or more monomers selected from among (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene and N-methylolacrylamide in addition to the (meth)acrylate ester described above.

[0173]

The monomer for forming the acrylic-based resin may be composed of a single monomer or two or more monomers, and in the case of two or more monomers, the combination and ratio between those monomers may be selected as desired.

[0174]

The acrylic-based resin may have a functional group that can bond to other compounds, such as a vinyl group, (meth)acryloyl group, amino group, hydroxyl group, carboxyl group or isocyanate group. This functional group of the acrylic-based resin may be bonded to another compound via a crosslinking agent (F) described below, or may be bonded directly to the other compound without requiring the crosslinking agent (F). Bonding the acrylic-based resin to another compound via the above functional group tends to improve the reliability of a package obtained using the protective film formation sheet.

[0175]

In the present invention, a thermoplastic resin other than an acrylic-based resin (hereafter sometimes abbreviated as simply "the thermoplastic resin") may be used in combination with an acrylic-based resin as the polymer component (A).

Using the thermoplastic resin can improve the releasability of the protective film from the support sheet and make the heat-curable protective film formation layer conform more easily to uneven surfaces on the adherend, thus better suppressing the occurrence of voids and the like between the adherend and the heat-curable protective film formation layer.

[0176]

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

[0177]

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

[0178]

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

[0179]

The thermoplastic resin contained in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may be a single resin or two or more resins, and in the case of two or more thermoplastic resins, the combination and ratio between those resins may be selected as desired.

[0180]

The amount of the polymer component (A), regardless of the type of polymer component (A), is preferably from 5 to 50% by mass, more preferably from 10 to 40% by mass, and particularly preferably from 15 to 35% by mass, relative to the total mass of all of the components besides the solvent that constitute the protective film formation layer

composition (III-1) (namely, relative to the total mass of the heat-curable protective film formation layer).

[0181]

The polymer component (A) may sometimes also correspond with the heat-curable component (B). In the present invention, in those cases where the protective film formation layer composition (III-1) contains this type of component that corresponds with both the polymer component (A) and the heat-curable component (B), the protective film formation layer composition (III-1) is deemed to include both the polymer component (A) and the heat-curable component (B).

[0182]

[Heat-Curable Component (B)]

The heat-curable component (B) is the component used for curing the heat-curable protective film formation layer to form a hard protective film.

The heat-curable component (B) contained in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may be a single component or two or more components, and in the case of two or more components, the combination and ratio between those components may be selected as desired.

[0183]

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

[0184]

(Epoxy-Based Heat-Curable Resin)

An epoxy-based heat-curable resin is composed of an epoxy resin (B1) and a heat curing agent (B2).

The epoxy-based heat-curable resin contained in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may be a single resin or two or more resins, and in the case of two or more resins, the combination and ratio between those resins may be selected as desired.

[0185]

- Epoxy Resin (B1)

Examples of the epoxy resin (B1) include conventional resins such as polyfunctional epoxy resins, biphenyl compounds, bisphenol A glycidyl ether and hydrogenated products thereof, ortho-cresol novolac epoxy resins, dicyclopentadiene epoxy resins, biphenyl epoxy resins, bisphenol A epoxy resins, bisphenol F epoxy resins, phenylene backbone epoxy resins, and difunctional or higher epoxy compounds.

Among the above resins, bisphenol A epoxy resins and dicyclopentadiene epoxy resins and the like are preferred.

[0186]

An epoxy resin having an unsaturated hydrocarbon group may also be used as the epoxy resin (B1). Epoxy resins having an unsaturated hydrocarbon group exhibit better compatibility with acrylic-based resins than epoxy resins that do not have an unsaturated hydrocarbon group. Accordingly, by using an epoxy resin having an unsaturated hydrocarbon group, the reliability of a package obtained using the protective film formation sheet can be improved.

[0187]

Examples of the epoxy resin having an unsaturated hydrocarbon group include compounds in which a portion of the epoxy groups of a polyfunctional epoxy resin have each been substituted with a group containing an unsaturated hydrocarbon group.

Examples of this type of compound include compounds obtained by performing an addition reaction of (meth)acrylic acid or a derivative thereof to an epoxy resin.

Further, other examples of epoxy resins having an unsaturated hydrocarbon group include compounds in which a group having an unsaturated hydrocarbon group is bonded directly to the aromatic ring or the like that constitutes the epoxy resin.

The unsaturated hydrocarbon group is an unsaturated group that has polymerizability, and specific examples include an ethenyl group (vinyl group), 2-propenyl group (allyl group), (meth)acryloyl group and (meth)acrylamide group, and an acryloyl group is preferred.

[0188]

Although there are no particular limitations on the number average molecular weight of the epoxy resin (B1), from the viewpoints of the curability of the heat-curable protective film formation layer, and the strength and heat resistance of the cured protective film, the number average molecular weight is preferably from 300 to 30,000, more preferably from 300 to 10,000, and particularly preferably from 300 to 3,000.

In this description, unless specifically stated otherwise, the "number average molecular weight" means the number average molecular weight represented as a polystyrene-equivalent value measured by a gel permeation chromatography (GPC) method. The epoxy equivalent weight of the epoxy resin (B1) is preferably from 100 to 1,100 g/eq, and more preferably from 150 to 1,000 g/eq.

In this description, the "epoxy equivalent weight" means the number of grams of the epoxy compound containing one gram equivalent of epoxy groups (g/eq), and can be measured in accordance with the method prescribed in JIS K 7236:2001.

[0189]

A single epoxy resin (B1) may be used alone, or a combination of two or more resins may be used, and in the case of a combination of two or more resins, the combination and ratio between those resins may be selected as desired.

[0190]

- Heat Curing Agent (B2)

The heat curing agent (B2) functions as a curing agent for the epoxy resin (B1).

Examples of the heat curing agent (B2) include compounds having at least two functional groups that can react with an epoxy group within each molecule. Examples of these functional groups include a phenolic hydroxyl group, alcoholic hydroxyl group, amino group, carboxyl group and acid anhydride group, and of these, a phenolic hydroxyl group, amino group or acid anhydride group is preferred, and a phenolic hydroxyl group or amino group is more preferred.

[0191]

Of the various heat curing agents (B2), examples of phenol-based curing agents having phenolic hydroxyl groups include polyfunctional phenol resins, biphenol, novolac phenol resins, dicyclopentadiene phenol resins and aralkylphenol resins.

Of the various heat curing agents (B2), examples of amine-based curing agents having amino groups include dicyandiamide (hereafter sometimes abbreviated as "DICY") and the like.

[0192]

The heat curing agent (B2) may be a compound having an unsaturated hydrocarbon group.

Examples of this heat curing agent (B2) having an unsaturated hydrocarbon group include compounds in which a portion of the hydroxyl groups of a phenol resin have each been substituted with a group containing an unsaturated hydrocarbon group, and

compounds in which a group having an unsaturated hydrocarbon group has been bonded directly to an aromatic ring of a phenol resin.

Examples of the unsaturated hydrocarbon group in the heat curing agent (B2) include the same groups as the unsaturated hydrocarbon group in the aforementioned epoxy resin having an unsaturated hydrocarbon group.

[0193]

In those cases where a phenol-based curing agent is used as the heat curing agent (B2), in terms of improving the releasability of the protective film from the support sheet, the heat curing agent (B2) preferably has high values for the softening point and glass transition temperature.

[0194]

It is preferable that the heat curing agent (B2) is solid and exhibits no curing activity relative to the epoxy resin (B1) at normal temperature, but then melts upon heating, and then exhibits curing activity relative to the epoxy resin (B1) (hereafter also referred to as a "heat-activated latent epoxy resin curing agent").

The heat-activated latent epoxy resin curing agent is dispersed stably in the epoxy resin (B1) of the heat-curable protective film formation layer at normal temperature, but then undergoes mutual dissolution with the epoxy resin (B1) upon heating, causing reaction with the epoxy resin (B1). By using a heat-activated latent epoxy resin curing agent, the storage stability of the protective film formation sheet improves markedly. For example, migration of the curing agent from the protective film formation film into the adjacent support sheet is suppressed, and any deterioration in the heat curability of the heat-curable protective film formation layer can be effectively suppressed. Consequently, because the degree of heat curing upon heating of the heat-curable

protective film formation layer can be improved, the pickup characteristics of the semiconductor chips with a protective film described below can be further improved.

[0195]

Examples of the above heat-activated latent epoxy resin curing agent include onium salts, dibasic acid hydrazides, dicyandiamide, and amine adducts of curing agents.

[0196]

Among the various heat curing agents (B2), the number average molecular weight of the resin components such as polyfunctional phenol resins, novolac phenol resins, dicyclopentadiene phenol resins and aralkylphenol resins is preferably from 300 to 30,000, more preferably from 400 to 10,000, and particularly preferably from 500 to 3,000.

Among the heat curing agents (B2), there are no particular limitations on the molecular weight of the non-resin components such as biphenol and dicyandiamide, but the molecular weight is preferably from 60 to 500.

[0197]

A single heat curing agent (B2) may be used alone, or a combination of two or more curing agents may be used, and in the case of two or more curing agents, the combination and ratio between those curing agents may be selected as desired.

[0198]

In the protective film formation layer composition (III-1) and the heat-curable protective film formation layer, the amount of the heat curing agent (B2) is preferably from 0.1 to 500 parts by mass, and more preferably from 1 to 200 parts by mass, per 100 parts by mass of the epoxy resin (B1). Ensuring that the amount of the heat curing agent (B2) is at least as large as the above lower limit enables the curing of the heat-curable protective film formation layer to proceed more readily. Further, by ensuring that the

amount of the heat curing agent (B2) is not more than the above upper limit, the coefficient of moisture absorption for the heat-curable protective film formation layer is reduced, and the reliability of a package obtained using the protective film formation sheet can be further improved.

[0199]

In the protective film formation layer composition (III-1) and the heat-curable protective film formation layer, the amount of the heat-curable component (B) (for example, the total amount of the epoxy resin (B1) and the heat curing agent (B2)) is preferably from 1 to 100 parts by mass, more preferably from 1.5 to 85 parts by mass, and particularly preferably from 2 to 70 parts by mass, per 100 parts by mass of the polymer component (A). By ensuring that the amount of the heat-curable component (B) falls within this type of range, the adhesive strength between the protective film and the support sheet is suppressed, thus improving the releasability of the support sheet.

In another aspect, the amount of the heat-curable component (B) in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer, relative to the total mass of all the components besides the solvent in the protective film formation layer composition (III-1) (namely, relative to the total mass of the heat-curable protective film formation layer), is preferably from 1 to 90% by mass, more preferably from 10 to 80% by mass, and even more preferably from 30 to 70% by mass.

[0200]

[Curing Accelerator (C)]

The protective film formation layer composition (III-1) and the heat-curable protective film formation layer may also include a curing accelerator (C). The curing accelerator (C) is a component that is used for adjusting the curing rate of the protective film formation layer composition (III-1).

Examples of preferred curing accelerators (C) include tertiary amines such as triethylenediamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol and tris(dimethylaminomethyl)phenol; imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole, and 2-phenyl-4-methyl-5-hydroxymethylimidazole (namely, imidazoles in which at least one hydrogen atom has been substituted with a group other than a hydrogen atom); organophosphines such as tributylphosphine, diphenylphosphine, and triphenylphosphine (phosphines in which at least one hydrogen atom has been substituted with an organic group); and tetraphenylborates such as tetraphenylphosphonium tetraphenylborate and triphenylphosphine tetraphenylborate.

Among the above compounds, 2-phenyl-4,5-dihydroxymethylimidazole is preferred.

[0201]

The curing accelerator (C) contained in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may be a single compound or two or more compounds, and in the case of two or more compounds, the combination and ratio between those compounds may be selected as desired.

[0202]

In those cases where the curing accelerator (C) is used, the amount of the curing accelerator (C) in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer is preferably from 0.01 to 10 parts by mass, and more preferably from 0.1 to 5 parts by mass, per 100 parts by mass of the heat-curable component (B). Ensuring that the amount of the curing accelerator (C) is at least as large as the above lower limit enables the effects obtained by using the curing accelerator (C) manifest more markedly. Further, ensuring that the amount of the curing accelerator (C)

is not more than the above upper limit enables better suppression of segregation due to migration of the high-polarity curing accelerator (C) within the heat-curable protective film formation layer to the bonding interface with the adherend under conditions of high temperature and high humidity, meaning the reliability of a package obtained using the protective film formation sheet can be further improved.

[0203]

[Filler (D)]

The protective film formation layer composition (III-1) and the heat-curable protective film formation layer may also include a filler (D). By including the filler (D) in the heat-curable protective film formation layer, the coefficient of thermal expansion of the protective film obtained by curing the heat-curable protective film formation layer can be more easily adjusted, and by optimizing this coefficient of thermal expansion for the formation target for the protective film, the reliability of a package obtained using the protective film formation sheet can be further improved. Further, by including the filler (D) in the heat-curable protective film formation layer, the coefficient of moisture absorption for the protective film can be reduced and the thermal conductivity can be improved.

[0204]

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

Examples of preferred inorganic fillers include powders of silica, alumina, talc, calcium carbonate, titanium white, red iron oxide, silicon carbide, and boron nitride and the like; beads formed by spheroidizing these inorganic fillers; surface-modified products of these inorganic fillers; single crystal fibers of these inorganic fillers; and glass fibers.

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

[0205]

The filler (D) contained in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may be a single filler or two or more fillers, and in the case of two or more fillers, the combination and ratio between those fillers may be selected as desired.

[0206]

In those cases where the filler (D) is used, the amount of the filler (D) in the protective film formation layer composition (III-1), relative to the total amount (total mass) of all the components besides the solvent (namely, the amount of the filler in the heat-curable protective film formation layer), is preferably from 5 to 80% by mass, and more preferably from 7 to 60% by mass. Provided the amount of the filler (D) falls within this type of range, the aforementioned adjustment of the coefficient of thermal expansion becomes easier.

[0207]

[Coupling Agent (E)]

The protective film formation layer composition (III-1) and the heat-curable protective film formation layer may also include a coupling agent (E). By using a compound having a functional group capable of reacting with inorganic compounds or organic compounds as a coupling agent (E), the adhesiveness and adhesion of the heat-curable protective film formation layer to adherends can be improved. Further, by using the coupling agent (E), the protective film obtained by curing the heat-curable protective film formation layer exhibits improved water resistance without losing any heat resistance.

[0208]

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

Examples of preferred silane coupling agents 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, 3-ureidopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfane, methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, vinyltriacetoxysilane and imidazole silane.

[0209]

The coupling agent (E) contained in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may be a single compound or two or more compounds, and in the case of two or more compounds, the combination and ratio between those compounds may be selected as desired.

[0210]

In those cases where the coupling agent (E) is used, the amount of the coupling agent (E) in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer is preferably from 0.03 to 20 parts by mass, more preferably from 0.05 to 10 parts by mass, and particularly preferably from 0.1 to 5 parts by mass, per 100 parts by mass of the total mass of the polymer component (A) and the heat-curable component (B). Ensuring that the amount of the coupling agent (E) is at

least as large as the above lower limit enables the effects of using the coupling agent (E), such as an improvement in the dispersibility of the filler (D) in the resin and an improvement in the adhesion between the heat-curable protective film formation layer and the adherend, to manifest more markedly. Further, ensuring that the amount of the coupling agent (E) is not more than the above upper limit better suppresses the generation of out gas.

[0211]

[Crosslinking Agent (F)]

In those cases where an aforementioned acrylic-based resin having a functional group such as a vinyl group, (meth)acryloyl group, amino group, hydroxyl group, carboxyl group or isocyanate group that can bond to other compounds is used as the polymer component (A), the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may also include a crosslinking agent (F) to achieve crosslinking by binding this functional group to other compounds. By preforming crosslinking using the crosslinking agent (F), the initial adhesive strength and the cohesion of the heat-curable protective film formation layer can be adjusted.

[0212]

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

[0213]

Examples of the organic polyvalent isocyanate compounds include aromatic polyvalent isocyanate compounds, aliphatic polyvalent isocyanate compounds and alicyclic polyvalent isocyanate compounds (hereafter, these compounds are sometimes

jointly referred to as "aromatic polyvalent isocyanate compounds and the like"); trimers, isocyanurates and adducts of these aromatic polyvalent isocyanate compounds and the like; and isocyanate-terminated urethane prepolymers and the like obtained by reacting aromatic polyvalent isocyanate compounds and the like with a polyol compound. The above "adducts" are reaction products of the aforementioned aromatic polyvalent isocyanate compounds, aliphatic polyvalent isocyanate compounds and alicyclic polyvalent isocyanate compounds with low-molecular weight active hydrogen-containing compounds such as ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane or castor oil, and a specific example is a xylylene diisocyanate adduct of trimethylolpropane described below. Further, an "isocyanate-terminated urethane prepolymer" means a prepolymer having a urethane linkage and also having isocyanate groups at the molecular terminals.

[0214]

Specific examples of the organic polyvalent isocyanate compounds include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, 3-methyldiphenylmethane diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, dicyclohexylmethane-2,4'-diisocyanate, compounds in which one or two or more of tolylene diisocyanate, hexamethylene diisocyanate and xylylene diisocyanate have been added to some or all of the hydroxyl groups of a polyol such as trimethylolpropane, and lysine diisocyanate.

[0215]

Examples of the organic polyvalent imine compounds include N,N'-diphenylmethane-4,4'-bis(1-aziridinecarboxamide), trimethylolpropane-tri-β-

aziridinypropionate, tetramethylolmethane-tri- β -aziridinypropionate, and N,N'-toluene-2,4-bis(1-aziridinecarboxamide)triethylenemelamine.

[0216]

In those cases where an organic polyvalent isocyanate compound is used as the crosslinking agent (F), a hydroxyl group-containing polymer is preferably used as the polymer component (A). When the crosslinking agent (F) has isocyanate groups and the polymer component (A) has hydroxyl groups, reaction between the crosslinking agent (F) and the polymer component (A) can easily introduce crosslinked structures into the heat-curable protective film formation layer.

[0217]

The crosslinking agent (F) contained in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may be a single compound or two or more compounds, and in the case of two or more compounds, the combination and ratio between those compounds may be selected as desired.

[0218]

In those cases where the crosslinking agent (F) is used, the amount of the crosslinking agent (F) in the protective film formation layer composition (III-1) is preferably from 0.01 to 20 parts by mass, more preferably from 0.1 to 10 parts by mass, and particularly preferably from 0.5 to 5 parts by mass, per 100 parts by mass of the polymer component (A). Ensuring that the amount of the crosslinking agent (F) is at least as large as the above lower limit enables the obtained by using the crosslinking agent (F) to manifest more markedly. Further, by ensuring that the amount of the crosslinking agent (F) is not more than the above upper limit, any excessive reduction in the adhesive strength between the heat-curable protective film formation layer and the

support sheet, or the adhesive strength between the heat-curable protective film formation layer and the semiconductor wafer or semiconductor chip can be suppressed.

In the present invention, the effects of the present invention can be satisfactorily obtained without using the crosslinking agent (F).

[0219]

[Energy Ray-Curable Resin (G)]

The protective film formation layer composition (III-1) may contain an energy ray-curable resin (G). By including the energy ray-curable resin (G), the properties of the heat-curable protective film formation layer can be altered by irradiation with energy rays.

[0220]

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

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

[0221]

Examples of the acrylate-based compounds include chain-like aliphatic skeleton-containing (meth)acrylates such as trimethylolpropane tri(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol monohydroxy penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, 1,4-butylene glycol di(meth)acrylate, and 1,6-hexanediol di(meth)acrylate; cyclic aliphatic skeleton-containing (meth)acrylates such as dicyclopentanyl di(meth)acrylate; polyalkylene glycol (meth)acrylates such as polyethylene glycol di(meth)acrylate; urethane (meth)acrylate oligomers; epoxy-

modified (meth)acrylates; polyether (meth)acrylates other than the above polyalkylene glycol (meth)acrylates; and itaconic acid oligomers.

[0222]

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

[0223]

The energy ray-curable compound used in the polymerization may be a single compound or two or more compounds, and in the case of two or more compounds, the combination and ratio between those compounds may be selected as desired.

[0224]

The energy ray-curable resin (G) contained in the protective film formation layer composition (III-1) may be a single resin or two or more resins, and in the case of two or more resins, the combination and ratio between those resins may be selected as desired.

[0225]

The amount of the energy ray-curable resin (G) in the protective film formation layer composition (III-1), relative to the total mass of all of the components besides the solvent in the protective film formation layer composition (III-1), is preferably from 1 to 95% by mass, more preferably from 2 to 90% by mass, and particularly preferably from 3 to 85% by mass.

[0226]

[Photopolymerization Initiator (H)]

In those cases where the protective film formation layer composition (III-1) contains the energy ray-curable resin (G), the composition may also include a photopolymerization initiator (H) to enable the polymerization reaction of the energy ray-curable resin (G) to proceed more efficiently.

[0227]

Examples of the photopolymerization initiator (H) in the protective film formation layer composition (III-1) include the same photopolymerization initiators as those included in the adhesive composition (ii).

[0228]

The photopolymerization initiator (H) contained in the protective film formation layer composition (III-1) may be a single initiator or two or more initiators, and in the case of two or more initiators, the combination and ratio between those initiators may be selected as desired.

[0229]

The amount of the photopolymerization initiator (H) in the protective film formation layer composition (III-1) is preferably from 0.1 to 20 parts by mass, more preferably from 1 to 10 parts by mass, and particularly preferably from 2 to 5 parts by mass, per 100 parts by mass of the energy ray-curable resin (G).

[0230]

[Colorant (I)]

The protective film formation layer composition (III-1) and the heat-curable protective film formation layer may also include a colorant (I).

Examples of the colorant (I) include conventional colorants such as inorganic pigments, organic pigments, and organic dyes and the like.

[0231]

Examples of the organic pigments and organic dyes include aminium-based colorants, cyanine-based colorants, merocyanine-based colorants, croconium-based colorants, squalium-based colorants, azulenium-based colorants, polymethine-based colorants, naphthoquinone-based colorants, pyrylium-based colorants, phthalocyanine-

based colorants, naphthalocyanine-based colorants, naphtholactam-based colorants, azo-based colorants, condensed azo-based colorants, indigo-based colorants, perinone-based colorants, perylene-based colorants, dioxazine-based colorants, quinacridone-based colorants, isoindolinone-based colorants, quinophthalone-based colorants, pyrrole-based colorants, thioindigo-based colorants, metal complex-based colorants (metal complex dyes), dithiol metal complex-based colorants, indole phenol-based colorants, triarylmethane-based colorants, anthraquinone-based colorants, naphthol-based colorants, azomethine-based colorants, benzimidazolone-based colorants, pyranthrone-based colorants, and threne-based colorants.

[0232]

Examples of the inorganic pigments include carbon blacks, cobalt-based colorants, iron-based colorants, chromium-based colorants, titanium-based colorants, vanadium-based colorants, zirconium-based colorants, molybdenum-based colorants, ruthenium-based colorants, platinum-based colorants, ITO (indium tin oxide)-based colorants, and ATO (antimony tin oxide)-based colorants.

[0233]

The colorant (I) contained in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may be a single colorant or two or more colorants, and in the case of two or more colorants, the combination and ratio between those colorants may be selected as desired.

[0234]

In those cases where the colorant (I) is used, the amount of the colorant (I) in the heat-curable protective film formation layer may be set appropriately in accordance with the intended purpose. For example, the protective film may sometimes be subjected to printing by laser irradiation, and by adjusting the amount of the colorant (I) in the heat-

curable protective film formation layer to adjust the light transmittance of the protective film, the design aesthetics of the protective film can be improved, and grinding traces on the back surface of the semiconductor wafer can be better concealed. Considering these points, the amount of the colorant (I) relative to the total amount (total mass) of all of the components besides the solvent in the protective film formation layer composition (III-1) (namely, the amount of the colorant (I) in the heat-curable protective film formation layer) is preferably from 0.1 to 10% by mass, more preferably from 0.1 to 7.5% by mass, and particularly preferably from 0.1 to 5% by mass. Ensuring that the amount of the colorant (I) is at least as large as the above lower limit enables the effects of using the colorant (I) to manifest more markedly. Further, ensuring that the amount of the colorant (I) is not more than the above upper limit suppresses any excessive reduction in the light transmittance of the heat-curable protective film formation layer.

[0235]

[General-Purpose Additives (J)]

The protective film formation layer composition (III-1) and the heat-curable protective film formation layer may also include general-purpose additives (J), provided the effects of the present invention are not impaired.

The general-purpose additives (J) may be known additives, and may be selected in accordance with the intended purpose, and although there are no particular limitations, examples of preferred additives include plasticizers, antistatic agents, antioxidants, and gettering agents.

[0236]

The general-purpose additives (I) contained in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer may be a single general-purpose additive or two or more general-purpose additives, and in the case of

two or more additives, the combination and ratio between those additives may be selected as desired.

There are no particular limitations on the amount of general-purpose additives (I) in the protective film formation layer composition (III-1) and the heat-curable protective film formation layer, and the amount may be selected appropriately in accordance with the intended purpose.

[0237]

[Solvent]

The protective film formation layer composition (III-1) preferably also includes a solvent. A protective film formation layer composition (III-1) containing a solvent exhibits improved handling properties.

There are no particular limitations on the solvent, but examples of preferred solvents include hydrocarbons such as toluene and xylene; alcohols such as methanol, ethanol, 2-propanol, isobutyl alcohol (2-methylpropan-1-ol) and 1-butanol; esters such as ethyl acetate and butyl acetate; ketones such as acetone and methyl ethyl ketone; ethers such as tetrahydrofuran; and amides (compounds having an amide linkage) such as dimethylformamide and N-methylpyrrolidone.

The solvent contained in the protective film formation layer composition (III-1) may be a single solvent or two or more solvents, and in the case of two or more solvents, the combination and ratio between those solvents may be selected as desired.

[0238]

In terms of enabling the components in the protective film formation layer composition (III-1) to be mixed more uniformly, the solvent contained in the protective film formation layer composition (III-1) is preferably methyl ethyl ketone or the like.

The amount of the solvent is preferably adjusted so that the solid fraction concentration of the protective film formation composition is from 10 to 80% by mass, more preferably from 20 to 70% by mass, and even more preferably from 30 to 65% by mass, relative to the total mass of the protective film formation composition.

[0239]

<<Manufacturing Method for Heat-Curable Protective Film Formation Layer Composition>>

The heat-curable protective film formation layer composition such as the protective film formation layer composition (III-1) can be obtained by blending together the components that constitute the composition.

There are no particular limitations on the order in which the components are added during blending, and two or more components may be added simultaneously.

In those cases where a solvent is used, the solvent may first be mixed with one of the other components besides the solvent to dilute the other component, or the solvent may simply be mixed with the other blend components without being used to first dilute one of the other components.

There are no particular limitations on the method used for mixing the components during blending, and a method may be selected from among conventional methods such as methods in which mixing is performed by rotation with a stirring bar or stirring blade, methods in which mixing is performed using a mixer, and methods in which mixing is performed by application of ultrasound.

The temperature and time during addition and mixing of each component are not particularly limited and may be set as appropriate provided the blended component does not degrade, but the temperature is preferably from 15 to 30°C.

[0240]

- Energy Ray-Curable Protective Film Formation Layer

The energy ray-curable protective film formation layer contains an energy ray-curable component (a).

The energy ray-curable component (a) is preferably in an uncured state and preferably has adhesiveness, and is more preferably in an uncured state that exhibits adhesiveness. Here, the terms "energy rays" and "energy ray-curable" are as defined above.

[0241]

<<Energy Ray-Curable Protective Film Formation Layer Composition>>

The energy ray-curable protective film formation layer can be formed from an energy ray-curable protective film formation layer composition containing the constituent materials for the layer. For example, by applying the energy ray-curable protective film formation layer composition to a formation target surface for the energy ray-curable protective film formation layer, and then performing drying as necessary, the energy ray-curable protective film formation layer can be formed in the targeted region. The ratio between the amounts of those components within the energy ray-curable protective film formation layer composition that do not volatilize at normal temperature is typically the same as the ratio between the amounts of those components in the energy ray-curable protective film formation layer. Here, "normal temperature" is as defined above.

[0242]

Application of the energy ray-curable protective film formation layer composition may be performed using a conventional method, and examples include methods that use any of various coaters such as an air knife coater, blade coater, bar coater, gravure coater,

roll coater, roll knife coater, curtain coater, die coater, knife coater, screen coater, Meyer bar coater or kiss coater.

[0243]

There are no particular limitations on the drying conditions for the energy ray-curable protective film formation layer composition, but in those cases where the energy ray-curable protective film formation layer composition contains a solvent described below, drying under heat is preferably performed, and in such cases, drying is preferably performed, for example, under conditions of 70 to 130°C for 10 seconds to 5 minutes.

[0244]

<Protective Film Formation Layer Composition (IV-1)>

An example of the energy ray-curable protective film formation layer composition is an energy ray-curable protective film formation layer composition (IV-1) (in this description, also abbreviated as "the protective film formation layer composition (IV-1)") containing the aforementioned energy ray-curable component (a).

[0245]

[Energy Ray-Curable Component (a)]

The energy ray-curable component (a) is a component that cures upon irradiation with energy rays, and is a component that is used for imparting the energy ray-curable protective film formation layer with film forming characteristics and flexibility and the like.

Examples of the energy ray-curable component (a) include polymers (a1) having an energy ray-curable group and having a weight average molecular weight of 80,000 to 2,000,000, and compounds (a2) having an energy ray-curable group and having a weight average molecular weight of 100 to 80,000. The polymer (a1) may be at least partially crosslinked with a crosslinking agent, or may have no crosslinking.

[0246]

(Polymer (a1) having an Energy Ray-Curable Group and having a Weight Average Molecular Weight of 80,000 to 2,000,000)

Examples of the polymers (a1) having an energy ray-curable group and having a weight average molecular weight of 80,000 to 2,000,000 include acrylic-based resins (a1-1) formed by an addition reaction between an acrylic-based polymer (a11) having a functional group capable of reacting with a group of another compound, and an energy ray-curable compound (a12) having a group that reacts with the functional group and also having an energy ray-curable group such as an energy ray-curable double bond or the like.

[0247]

Examples of the functional group in the acrylic-based polymer (a11) capable of reacting with a group of another compound include a hydroxyl group, carboxyl group, amino group, substituted amino group (a group in which one or two hydrogen atoms of an amino group have each been substituted with a group other than a hydrogen atom), and epoxy group. However, in terms of preventing corrosion of the circuit of the semiconductor wafer or semiconductor chip or the like, the functional group is preferably a group other than a carboxyl group.

Among the above options, the functional group is preferably a hydroxyl group.

[0248]

- Acrylic-Based Polymer (a11) having a Functional Group

Examples of the acrylic-based polymer (a11) having a functional group include polymers obtained by copolymerizing an acrylic-based monomer having the functional group and an acrylic-based monomer not having the functional group, and polymers

obtained by copolymerizing these monomers with another monomer besides the acrylic-based monomers (namely, a non-acrylic-based monomer).

The acrylic-based polymer (a11) may be a random copolymer or a block copolymer.

[0249]

Examples of the acrylic-based monomer having the aforementioned functional group include hydroxyl group-containing monomers, carboxyl group-containing monomers, amino group-containing monomers, substituted amino group-containing monomers and epoxy group-containing monomers.

[0250]

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

[0251]

Examples of the carboxyl group-containing monomers include ethylenic unsaturated monocarboxylic acids (namely, monocarboxylic acids having an ethylenic unsaturated bond) such as (meth)acrylic acid and crotonic acid; ethylenic unsaturated dicarboxylic acids (namely, dicarboxylic acids having an ethylenic unsaturated bond) such as fumaric acid, itaconic acid, maleic acid and citraconic acid; and carboxyalkyl (meth)acrylate esters such as 2-carboxyethyl methacrylate.

[0252]

The acrylic-based monomer having the functional group is preferably a hydroxyl group-containing monomer or a carboxyl group-containing monomer, and is more preferably a hydroxyl group-containing monomer.

[0253]

The acrylic-based monomer having a functional group that constitutes the acrylic-based polymer (a11) may be a single monomer or two or more monomers, and in the case of two or more monomers, the combination and ratio between those monomers may be selected as desired.

[0254]

The aforementioned acrylic-based monomer not having the functional group is preferably a (meth)acrylate ester in which the alkyl group that constitutes the alkyl ester is a chain-like structure of 1 to 18 carbon atoms, and specific examples include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (also called lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (also called myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (also called palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (also called stearyl (meth)acrylate).

[0255]

Other examples of the acrylic-based monomer not having the functional group include alkoxyalkyl group-containing (meth)acrylate esters such as methoxymethyl

(meth)acrylate, methoxyethyl (meth)acrylate, ethoxymethyl (meth)acrylate, and ethoxyethyl (meth)acrylate; (meth)acrylate esters having an aromatic group, including aryl (meth)acrylate esters such as phenyl (meth)acrylate; non-crosslinked (meth)acrylamides and derivatives thereof; and non-crosslinked (meth)acrylate esters having a tertiary amino group such as N,N-dimethylaminoethyl (meth)acrylate and N,N-dimethylaminopropyl (meth)acrylate.

[0256]

The acrylic-based monomer not having a functional group that constitutes the acrylic-based polymer (a11) may be a single monomer or two or more monomers, and in the case of two or more monomers, the combination and ratio between those monomers may be selected as desired.

[0257]

Examples of the aforementioned non-acrylic-based monomer include olefins such as ethylene and norbornene, vinyl acetate, and styrene.

The non-acrylic-based monomer that constitutes the acrylic-based polymer (a11) may be a single monomer or two or more monomers, and in the case of two or more monomers, the combination and ratio between those monomers may be selected as desired.

[0258]

In the acrylic-based polymer (a11), the proportion (amount) of structural units derived from the aforementioned acrylic-based monomer having a functional group, relative to the total mass of all the structural units that constitute the acrylic-based polymer (a11), is preferably from 0.1 to 50% by mass, more preferably from 1 to 40% by mass, and particularly preferably from 3 to 30% by mass. By ensuring that this proportion falls within this type of range, the amount of energy ray-curable groups in the

aforementioned acrylic-based resin (a1-1) obtained by copolymerizing the acrylic-based polymer (a11) and the energy ray-curable compound (a12) enables the degree of curing of the protective film to be easily adjusted to a level within the preferred range.

[0259]

The acrylic-based polymer (a11) that constitutes the acrylic-based resin (a1-1) may be a single polymer or two or more polymers, and in the case of two or more polymers, the combination and ratio between those polymers may be selected as desired.

[0260]

- Energy Ray-Curable Compound (a12)

The energy ray-curable compound (a12) is preferably a compound having one or two or more groups selected from the group consisting of an isocyanate group, an epoxy group and a carboxyl group as the group that is capable of reacting with the functional group of the acrylic-based polymer (a11), and is more preferably a compound having an isocyanate group as that group. In those cases where the energy ray-curable compound (a12) has an isocyanate group as the above group, the isocyanate group can react easily with the hydroxyl groups of an acrylic-based polymer (a11) containing hydroxyl groups as the aforementioned functional group.

[0261]

The energy ray-curable compound (a12) preferably has 1 to 5, and more preferably 1 or 2, of the energy ray-curable groups within a single molecule.

[0262]

Examples of the energy ray-curable compound (a12) include 2-methacryloyloxyethyl isocyanate, meta-isopropenyl- α,α -dimethylbenzyl isocyanate, methacryloyl isocyanate, allyl isocyanate, 1,1-(bisacryloyloxymethyl)ethyl isocyanate;

acryloyl monoisocyanate compounds obtained by reacting a diisocyanate compound or a polyisocyanate compound with hydroxyethyl (meth)acrylate; and

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

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

[0263]

The energy ray-curable compound (a12) that constitutes the acrylic-based resin (a1-1) may be a single compound or two or more compounds, and in the case of two or more compounds, the combination and ratio between those compounds may be selected as desired.

[0264]

The amount of the acrylic-based resin (a1-1), relative to the total mass of all of the components besides the solvent in the energy ray-curable protective film formation layer composition (IV-1), is preferably from 1 to 40% by mass, more preferably from 2 to 30% by mass, and particularly preferably from 3 to 20% by mass.

[0265]

In the acrylic-based resin (a1-1), the ratio of the amount of energy ray-curable groups derived from the energy ray-curable compound (a12) relative to the amount of the aforementioned functional groups derived from the acrylic-based polymer (a11) is preferably from 20 to 120 mol%, more preferably from 35 to 100 mol%, and particularly preferably from 50 to 100 mol%. Ensuring that the ratio between these amounts falls within this type of range increases the adhesive strength of the protective film following curing. In those cases where the energy ray-curable compound (a12) is a monofunctional

compound (having only one of the above groups in a single molecule), the upper limit for the above ratio becomes 100%, but when the energy ray-curable compound (a12) is a polyfunctional compound (having two or more of the groups in a single molecule), the upper limit for the above ratio may sometimes exceed 100%.

[0266]

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

Here, the "weight average molecular weight" is as defined above.

[0267]

In those cases where the polymer (a1) is at least partially crosslinked with a crosslinking agent, the polymer (a1) may be a polymer obtained by polymerizing a monomer which corresponds with none of the monomers described above for forming the acrylic-based polymer (a11) and which has a group that reacts with the crosslinking agent, and then performing crosslinking at the group that reacts with the crosslinking agent, or may be a polymer obtained by performing crosslinking at the group derived from the energy ray-curable compound (a12) that reacts with the aforementioned functional group.

[0268]

The polymer (a1) contained in the energy ray-curable protective film formation layer composition (IV-1) and the energy ray-curable protective film formation layer may be a single polymer or two or more polymers, and in the case of two or more polymers, the combination and ratio between those polymers may be selected as desired.

[0269]

(Compound (a2) having an Energy Ray-Curable Group and having a Weight Average Molecular Weight of 100 to 80,000)

Examples of the energy ray-curable group of the compound (a2) having an energy ray-curable group and having a weight average molecular weight of 100 to 80,000 include groups containing an energy ray-curable double bond, and preferred groups include a (meth)acryloyl group and a vinyl group.

[0270]

The compound (a2) is not particularly limited, provided it satisfies the conditions described above, and example include low-molecular weight compounds having an energy ray-curable group, epoxy resins having an energy ray-curable group, and phenol resins having an energy ray-curable group.

[0271]

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

Examples of the above acrylate-based compounds include difunctional (meth)acrylates such as 2-hydroxy-3-(meth)acryloyloxypropyl methacrylate, polyethylene glycol di(meth)acrylate, propoxylated ethoxylated bisphenol A di(meth)acrylate, 2,2-bis[4-((meth)acryloxypolyethoxy)phenyl]propane, ethoxylated bisphenol A di(meth)acrylate, 2,2-bis[4-((meth)acryloxydiethoxy)phenyl]propane, 9,9-bis[4-(2-(meth)acryloyloxyethoxy)phenyl]fluorene, 2,2-bis[4-((meth)acryloxypolypropoxy)phenyl]propane, tricyclodecanedimethanol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, polytetramethylene glycol di(meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate,

triethylene glycol di(meth)acrylate, 2,2-bis[4-((meth)acryloxyethoxy)phenyl]propane, neopentyl glycol di(meth)acrylate, ethoxylated propylene glycol di(meth)acrylate, and 2-hydroxy-1,3-di(meth)acryloxypropane;

polyfunctional (meth)acrylates such as tris(2-(meth)acryloxyethyl)isocyanurate, ϵ -caprolactone-modified tris(2-(meth)acryloxyethyl)isocyanurate, ethoxylated glycerol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol poly(meth)acrylate, and dipentaerythritol hexa(meth)acrylate; and

polyfunctional (meth)acrylate oligomers such as urethane (meth)acrylate oligomers.

[0272]

Among the various forms of the compound (a2), examples of epoxy resins having an energy ray-curable group and phenol resins having an energy ray-curable group that may be used include those resins disclosed in paragraph 0043 of Japanese Unexamined Patent Application, First Publication No. 2013-194102. These types of resins also correspond with the resin that constitutes the heat-curable component described below, but in this invention, is treated as the aforementioned compound (a2).

[0273]

The compound (a2) has a weight average molecular weight that is preferably from 100 to 30,000, and more preferably from 300 to 10,000.

[0274]

The compound (a2) contained in the energy ray-curable protective film formation layer composition (IV-1) and the energy ray-curable protective film formation layer may be a single compound or two or more compounds, and in the case of two or more

compounds, the combination and ratio between those compounds may be selected as desired.

[0275]

[Polymer (b) not having an Energy Ray-Curable Group]

In those cases where the energy ray-curable protective film formation layer composition (IV-1) and the energy ray-curable protective film formation layer contain the above compound (a2) as the energy ray-curable component (a), a polymer (b) not having an energy ray-curable group is preferably also included.

The polymer (b) may be at least partially crosslinked with a crosslinking agent, or may have no crosslinking.

[0276]

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

Among these, the polymer (b) is preferably an acrylic-based polymer (hereafter sometimes referred to as the "acrylic-based polymer (b-1)")

[0277]

The acrylic-based polymer (b-1) may be a conventional material, and for example, may be a homopolymer of a single acrylic-based monomer, may be a copolymer of two or more acrylic-based monomers, or may be a copolymer of one or two or more acrylic-based monomers and one or two or more monomers other than acrylic-based monomers (namely, non-acrylic-based monomers).

[0278]

Examples of the acrylic-based monomers that may constitute the acrylic-based polymer (b-1) include alkyl (meth)acrylate esters, (meth)acrylate esters having a cyclic

skeleton, glycidyl group-containing (meth)acrylate esters, hydroxyl group-containing (meth)acrylate esters, and substituted amino group-containing (meth)acrylate esters.

Here, a "substituted amino group" is as defined above.

[0279]

The above alkyl (meth)acrylate esters are preferably alkyl (meth)acrylate esters in which the alkyl group that constitutes the alkyl ester is a chain-like structure of 1 to 18 carbon atoms, and specific examples include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (also called lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (also called myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (also called palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (also called stearyl (meth)acrylate).

[0280]

Examples of the (meth)acrylate esters having a cyclic skeleton include cycloalkyl (meth)acrylate esters such as isobornyl (meth)acrylate and dicyclopentanyl (meth)acrylate;

aralkyl (meth)acrylate esters such as benzyl (meth)acrylate;

cycloalkenyl (meth)acrylate esters such as dicyclopentenyl (meth)acrylate; and

cycloalkenyloxyalkyl (meth)acrylate esters such as dicyclopentenylloxyethyl (meth)acrylate.

[0281]

Examples of the glycidyl group-containing (meth)acrylate esters include glycidyl (meth)acrylate.

Examples of the hydroxyl group-containing (meth)acrylate esters 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)acrylate esters include N-methylaminoethyl (meth)acrylate.

[0282]

Examples of the aforementioned non-acrylic-based monomers that may constitute the acrylic-based polymer (b-1) include olefins such as ethylene and norbornene, vinyl acetate, and styrene.

[0283]

Examples of the polymer (b) not having an energy ray-curable group that has been at least partially crosslinked with a crosslinking agent include polymers in which a reactive functional group in the polymer (b) has undergone reaction with the crosslinking agent.

This reactive functional group may be selected appropriately in accordance with the variety and the like of the crosslinking agent, and there are no particular limitations. For example, when the crosslinking agent is a polyisocyanate compound, examples of the reactive functional group include a hydroxyl group, carboxyl group or amino group, and among these, a hydroxyl group is preferred due to a higher reactivity with the isocyanate group. Further, when the crosslinking agent is an epoxy-based compound, examples of the reactive functional group include a carboxyl group, amino group or amide group, and among these, a carboxyl group is preferred due to a higher reactivity with the epoxy

group. However, in terms of preventing corrosion of the circuit of the semiconductor wafer or semiconductor chip, the reactive functional group is preferably a group other than a carboxyl group.

[0284]

Examples of the polymer (b) which has an aforementioned reactive functional group but does not have an energy ray-curable group include polymers obtained by polymerizing at least a monomer having the reactive functional group. In the case of the acrylic-based polymer (b-1), a monomer having the reactive functional group may be used as either one or both of the acrylic-based monomer and non-acrylic-based monomer described above as the monomer for forming the acrylic-based polymer (b-1). For example, examples of the polymer (b) which have a hydroxyl group as the reactive functional group include polymers obtained by polymerizing an aforementioned hydroxyl group-containing (meth)acrylate ester, and other examples include polymers obtained by polymerizing a monomer in which one or two or more hydrogen atoms in one of the aforementioned acrylic-based monomers or non-acrylic-based monomers have each been substituted with the reactive functional group.

[0285]

In the polymer (b) having a reactive functional group, the proportion (amount) of the structural unit derived from the monomer having the reactive functional group, relative to the total mass of all of the structural units that constitute the polymer (b), is preferably from 1 to 20% by mass, and more preferably from 2 to 10% by mass. Ensuring that the proportion falls within this type of range enables the degree of crosslinking in the polymer (b) to fall within a preferred range.

[0286]

In terms of achieving more favorable film forming characteristics for the energy ray-curable protective film formation layer composition (IV-1), the weight average molecular weight (Mw) of the polymer (b) not having an energy ray-curable group is preferably from 10,000 to 2,000,000, and is more preferably from 100,000 to 1,500,000. Here, the "weight average molecular weight" is as defined above.

[0287]

The polymer (b) not having an energy ray-curable group contained in the energy ray-curable protective film formation layer composition (IV-1) and the energy ray-curable protective film formation layer may be a single polymer or two or more polymers, and in the case of two or more polymers, the combination and ratio between those polymers may be selected as desired.

[0288]

Examples of the energy ray-curable protective film formation layer composition (IV-1) include compositions containing either one or both of the aforementioned polymer (a1) and the aforementioned compound (a2). In those cases where the energy ray-curable protective film formation layer composition (IV-1) contains the compound (a2), the composition preferably also contains the polymer (b) not having an energy ray-curable group, and in this case, preferably also contains the aforementioned (a1). The energy ray-curable protective film formation layer composition (IV-1) may also contain both the polymer (a1) and the polymer (b) not having an energy ray-curable group, but not contain the compound (a2).

[0289]

In those cases where the energy ray-curable protective film formation layer composition (IV-1) contains the polymer (a1), the compound (a2) and the polymer (b) not having an energy ray-curable group, the amount of the compound (a2) in the energy

ray-curable protective film formation layer composition (IV-1) is preferably from 10 to 400 parts by mass, and more preferably from 30 to 350 parts by mass, per 100 parts by mass of the total amount of the polymer (a1) and the polymer (b) not having an energy ray-curable group.

[0290]

In the energy ray-curable protective film formation layer composition (IV-1), the total amount of the energy ray-curable component (a) and the polymer (b) not having an energy ray-curable group relative to the total amount (total mass) of all of the components besides the solvent (namely, the total amount of the energy ray-curable component (a) and the polymer (b) not having an energy ray-curable group in the energy ray-curable protective film formation layer) is preferably from 5 to 90% by mass, more preferably from 10 to 80% by mass, and particularly preferably from 20 to 70% by mass. Ensuring that the proportion of energy ray-curable components falls within this type of range makes the energy ray-curability of the energy ray-curable protective film formation layer more favorable.

The amount of the energy ray-curable component (a) relative to the total mass of all of the components besides the solvent in the energy ray-curable protective film formation layer composition (IV-1) is preferably from 1 to 80% by mass.

The amount of the energy ray-curable component (a1) relative to the total mass of all of the components besides the solvent in the energy ray-curable protective film formation layer composition (IV-1) is preferably from 1 to 80% by mass.

The amount of the energy ray-curable component (a2) relative to the total mass of all of the components besides the solvent in the energy ray-curable protective film formation layer composition (IV-1) is preferably from 1 to 80% by mass.

The amount of the polymer (b) not having an energy ray-curable group relative to the total mass of all of the components besides the solvent in the energy ray-curable protective film formation layer composition (IV-1) is preferably from 1 to 80% by mass.

The total amount of the aforementioned component (a1), component (a2) and component (b) must not exceed 100% by mass.

[0291]

Besides the energy ray-curable components described above, the energy ray-curable protective film formation layer composition (IV-1) may also contain one or two or more components selected from the group consisting of heat-curable components, photopolymerization initiators, fillers, coupling agents, crosslinking agents, colorants and general-purpose additives depending on the intended purpose of the composition. For example, by using an energy ray-curable protective film formation layer composition (IV-1) containing an aforementioned energy ray-curable component and a heat-curable component, the adhesive strength of the formed energy ray-curable protective film formation layer to an adherend can be improved by heating the layer, and the strength of the protective film formed from this energy ray-curable protective film formation layer can also be improved.

[0292]

Examples of heat-curable components, photopolymerization initiators, fillers, coupling agents, crosslinking agents, colorants and general-purpose additives that may be included in the energy ray-curable protective film formation layer composition (IV-1) include the same materials as those described above for the heat-curable component (B), the photopolymerization initiator (H), the filler (D), the colorant (E), the crosslinking agent (F), the colorant (I) and the general-purpose additives (J) in the protective film formation layer composition (III-1).

[0293]

In the energy ray-curable protective film formation layer composition (IV-1) for each of the heat-curable components, photopolymerization initiators, fillers, coupling agents, crosslinking agents, colorants and general-purpose additives, a single component may be used alone, or a combination of two or more components may be used, and in the case of a combination of two or more components, the combination and ratio between those components may be selected as desired.

There are no particular limitations on the amounts of the heat-curable components, photopolymerization initiators, fillers, coupling agents, crosslinking agents, colorants and general-purpose additives in the energy ray-curable protective film formation layer composition (IV-1), and these amounts may be set appropriately in accordance with the intended purpose.

[0294]

Because the handling of the energy ray-curable protective film formation layer composition (IV-1) improves upon dilution, the composition preferably also contains a solvent.

Examples of the solvent contained in the energy ray-curable protective film formation layer composition (IV-1) include the same solvents as those mentioned above for use in the protective film formation layer composition (III-1).

The solvent contained in the energy ray-curable protective film formation layer composition (IV-1) may be a single solvent or two or more solvents.

[0295]

<<Manufacturing Method for Energy Ray-Curable Protective Film Formation Layer Composition>>

The energy-curable protective film formation layer composition such as the protective film formation layer composition (IV-1) can be obtained by blending together the components that constitute the composition.

There are no particular limitations on the order in which the components are added during blending, and two or more components may be added simultaneously.

In those cases where a solvent is used, the solvent may first be mixed with one of the other components besides the solvent to dilute the other component, or the solvent may simply be mixed with the other blend components without being used to first dilute one of the other components.

There are no particular limitations on the method used for mixing the components during blending, and a method may be selected from among conventional methods such as methods in which mixing is performed by rotation with a stirring bar or stirring blade, methods in which mixing is performed using a mixer, and methods in which mixing is performed by application of ultrasound.

The temperature and time during addition and mixing of each component are not particularly limited and may be set as appropriate provided the blended component does not degrade, but the temperature is preferably from 15 to 30°C.

[0296]

> Release Film

There are no particular limitations on the release film, provided it satisfies the static friction force condition (not more than 29 N) described above. Examples of preferred release films include conventional release films having a release-treated surface that are typically used in this field. Examples of the release treatment performed on the above release-treated surface include treatments performed with any of various release agents such as alkyd-based, silicone-based, fluorine-based, unsaturated polyester-based,

polyolefin-based and wax-based release agents. In terms of having superior heat resistance, the release agent is preferably an alkyd-based, silicone-based or fluorine-based release agent.

[0297]

The thickness of the release film, although not particularly limited, is preferably from 20 to 85 μm , and more preferably from 25 to 75 μm . Ensuring that the thickness of the release film is at least as large as the above lower limit facilitates removal of the release film at the desired stage, and also suppresses the formation of winding marks on the release film when the protective film formation sheet is wound into a roll. On the other hand, ensuring that the thickness of the release film is not more than the above upper limit enhances the suppression effect on detachment of the release film at a stage other than the desired stage.

[0298]

In the protective film formation sheet, provided that the surface (the exposed surface) of the release film on the opposite side from the surface on which the protective film formation layer is provided has an aforementioned static friction force of not more than 29 N, the surface may be smooth or uneven, and may, for example, be selected with due consideration of the surface roughness of the surface (the exposed surface) of the support sheet on the opposite side from the side on which the protective film formation layer is provided.

[0299]

In the protective film formation sheet according to the present invention, the static friction force between the surface (the exposed surface) of the support sheet on the opposite side from the side on which the protective film formation layer is provided and the surface (the exposed surface) of the release film on the opposite side from the side on

which the protective film formation layer is provided is, as already mentioned above, not more than 29 N, and is preferably not more than 25 N, more preferably not more than 20 N, even more preferably not more than 15 N, and particularly preferably 13 N or less, and for example, may be not more than 10 N, or even 8.5 N or less.

On the other hand, although there are no particular limitations on the above static friction force, the lower limit may be 1 N, 2 N, or 3 N or the like, but this is not a limitation.

In other words, the static friction force may be within a range from 1 N to 29 N, preferably from 1 N to 25 N, more preferably from 2 N to 20 N, even more preferably from 2 N to 15 N, and particularly preferably from 3 N to 13 N.

Further, the static friction force may be from 5 N to 12 N, or from 5 N to 7 N.

The static friction force can be adjusted by appropriate selection of the combination of the support sheet and the release film, with due consideration of the degree of smoothness of the above surface (the exposed surface) of the support sheet, and the degree of smoothness of the above surface (the exposed surface) of the release film. Further, the static friction force can also be adjusted by appropriate selection of the combination of the support sheet and the release film, with due consideration of the material used for the surface (the exposed surface) of the support sheet, and the material used for the surface (the exposed surface) of the release film.

[0300]

<Manufacturing Method for Protective Film Formation Sheet>

The protective film formation sheet according to the present invention can be manufactured using a manufacturing method that includes a step of forming a laminated structure of the support sheet and the protective film formation layer so that the surface roughness of the surface of the support sheet on the opposite side from the side on which

the protective film formation layer is provided is not more than 0.5 μm (hereafter also referred to as the "lamination step (P1)"), and a step of forming a laminated structure of the protective film formation layer and the release film so that the static friction force between the surface of the support sheet on the opposite side from the side on which the protective film formation layer is provided and the surface of the release film on the opposite side from the side on which the protective film formation layer is provided is not more than 29 N (hereafter also referred to as the "lamination step (P2)").

[0301]

In those cases where the support sheet is composed of a plurality of layers, the plurality of layers may be laminated together to form the support sheet.

When manufacturing a support sheet in which another layer (for example, an adhesive layer, intermediate layer, or coating layer or the like) is laminated to the substrate, a composition containing the components for forming the other layer (for example, an adhesive composition, intermediate layer formation composition, or coating composition or the like) may be applied to the surface of the substrate and then dried as necessary, thus forming the other layer on the substrate. Furthermore, when manufacturing a support sheet in which another layer is laminated to the substrate, the other layer may be laminated to the substrate by applying a composition containing the components for forming the other layer to the release-treated surface of a release material and drying the composition as necessary to initially form the other layer on the release material, and subsequently bonding the surface (the exposed surface) of the formed other layer to the surface of the substrate. In this case, the release material may be removed, as necessary, when some form of operation is to be performed on the other layer, such as the lamination of the protective film formation layer to the other layer.

A conventional material typically used in this field may be used as the release material, and for example, the same material as that used for the aforementioned release film that constitutes part of the protective film formation sheet according to the present invention may be used.

[0302]

For example, applying a targeted composition to a substrate already having another layer formed on either one or both surfaces of the substrate, thereby forming an additional other layer, is also possible. However, in this type of case, as mentioned above, a method is preferably employed in which the additional other layer is formed in advance on a release material, and is subsequently bonded to the substrate or the other layer already laminated to the substrate.

[0303]

In the lamination step (P1), the laminated structure of the support sheet and the protective film formation layer can be formed, for example, by applying the protective film formation layer composition to the support sheet and then performing drying as necessary to form the protective film formation layer (hereafter this particular step is sometimes referred to as the "lamination step (P1)-11"). However, in this step, the surface of the support sheet to which the protective film formation layer composition is applied is selected so that the surface roughness of the surface of the support sheet to which the protective film formation layer composition is not applied (the uncoated surface) is not more than 0.5 μm . For example, if the surface roughness of one surface of the support sheet is not more than 0.5 μm but the surface roughness of the other surface is greater than 0.5 μm , then the surface having a surface roughness greater than 0.5 μm is used as the application surface for the protective film formation layer composition. On the other hand, if both surfaces of the support sheet have surface roughness of not more

than 0.5 μm , then either surface may be used as the application surface for the protective film formation layer composition.

[0304]

Further, in the lamination step (P1), the laminated structure of the support sheet and the protective film formation layer can also be formed using the same method as that used in the preparation of a support sheet composed of a plurality of layers. In other words, the laminated structure of the support sheet and the protective film formation layer can also be formed by first applying the protective film formation layer composition to the release-treated surface of a release material and then performing drying as necessary to form the protective film formation layer in advance on the release material, and subsequently bonding the surface of this formed protective film formation layer on which the release material is not provided to the surface of the support sheet (hereafter this particular step is sometimes referred to as the "lamination step (P1)-12"). However, in this step, the surface of the support sheet to which the protective film formation layer is bonded (hereafter also referred to as the "bonding surface") is selected so that the surface roughness of the surface of the support sheet to which the protective film formation layer is not bonded (hereafter also referred to as the "non-bonded surface") is not more than 0.5 μm . At this time, selection of the bonding surface may be conducted in the same manner as the aforementioned selection of the coating surface in the case where the protective film formation layer composition is applied to a surface of the support sheet.

In this method, conventional materials typically used in this field may be used as the above release material, and the same materials as the aforementioned release films used in forming the protective film formation sheet according to the present invention are preferred.

[0305]

For example, even in those cases where the support sheet is a sheet prepared by laminating another layer described above to one or both surfaces of a substrate, a protective film formation layer can still be formed by applying the protective film formation layer composition directly to this type of support sheet. However, in this type of case, it is preferable to employ a method in which a protective film formation layer that has been formed in advance on a release material is bonded to the support sheet, in a similar manner to that described above in the lamination step (P1).

[0306]

If the lamination step (P1)-11 described above is used as the lamination step (P1), then in the lamination step (P2), the release film described above is bonded to the surface of the protective film formation layer on which the support sheet is not provided. However, in this step, the type of release film is selected so that the static friction force between the exposed surface of the support sheet having a surface roughness of not more than $0.5\ \mu\text{m}$, and the surface of the release film on the opposite side from the side to which the protective film formation layer is bonded is not more than 29 N.

[0307]

On the other hand, if the lamination step (P1)-12 described above is used as the lamination step (P1), then in the lamination step (P2), the release material provided on the surface of the protective film formation layer on the opposite side from the side on which the support sheet is provided is removed to expose one surface of the protective film formation layer, and the release film described above is bonded to this exposed surface of the protective film formation layer. However, in this step, the type of release film is selected so that the static friction force between the exposed surface of the support sheet having a surface roughness of not more than $0.5\ \mu\text{m}$, and the surface of the release

film on the opposite side from the side to which the protective film formation layer is bonded is not more than 29 N.

[0308]

Furthermore, if the lamination step (P1)-12 described above is used as the lamination step (P1), then by using the aforementioned release film (the release film that constitutes the protective film formation sheet according to the present invention) as the release material on which the protective film formation layer is formed in advance, this lamination step (P1)-12 also combines the lamination step (P2). This particular method is preferable in terms of simplifying the manufacturing steps. The step of forming the laminated structure of the support sheet and the protective film formation layer in this particular manufacturing method is hereafter sometimes referred to as the "lamination step (P1)".

In other words, the protective film formation sheet according to the present invention can also be manufactured by a manufacturing method that has a step (the lamination step (P1')) of using the protective film formation layer composition to form a protective film formation layer on the release-treated surface of an aforementioned release film, and then bonding the surface of the formed protective film formation layer on which the release film is not provided to the surface of an aforementioned support sheet, wherein the bonding surface of the support sheet is selected so that the surface roughness of the surface of the support sheet to which the protective film formation layer is not bonded is not more than 0.5 μm , and the release film is selected so that the static friction force between the surface of the support sheet having a surface roughness of not more than 0.5 μm , and the surface of the release film on the opposite side from the release-treated surface is not more than 29 N.

[0309]

When manufacturing a protective film formation sheet in which, as illustrated in FIG. 7 and the like, the protective film formation layer has a smaller surface area than the adhesive layer when the protective film formation sheet is viewed in plan view from above the release film, a protective film formation layer that has been cut in advance to the required size and shape may be provided on the adhesive layer in the above manufacturing method.

[0310]

During manufacture of the protective film formation sheet according to the present invention, the protective film formation layer can be formed, for example, by applying the protective film formation layer composition to the formation target surface for the protective film formation layer, and then preferably performing drying. Application of the protective film formation layer composition may be performed using a conventional method, and examples include methods that use any of various coaters such as an air knife coater, blade coater, bar coater, gravure coater, roll coater, roll knife coater, curtain coater, die coater, knife coater, screen coater, Meyer bar coater or kiss coater.

[0311]

There are no particular limitations on the drying conditions for the protective film formation layer composition, but the protective film formation layer composition is preferably dried under heat, and in such cases, drying is preferably performed, for example, under conditions of 70 to 130°C for 1 to 5 minutes.

[0312]

During manufacture of the protective film formation sheet according to the present invention, the adhesive layer can be formed, for example, by applying the aforementioned adhesive composition to the formation target surface for the adhesive

layer, and then preferably performing drying. The adhesive composition may be applied using the same method as that described for the protective film formation layer composition.

[0313]

The applied adhesive composition may be subjected to crosslinking by heating, and this crosslinking under heat may also combined the function of drying. The heating conditions are, for example, 100 to 130°C for 1 to 5 minutes, but the conditions are not limited to these values.

[0314]

During manufacture of the protective film formation sheet according to the present invention, a coating layer can be formed, for example, by applying the coating composition described above to the formation target surface for the coating layer, preferably performing drying, and then if required, curing the coating film formed by the application. The coating composition may be applied using the same method as that described for the protective film formation layer composition.

[0315]

There are no particular limitations on the drying conditions for the coating composition, and for example, drying is preferably performed using the same conditions as those described for the protective film formation layer composition.

[0316]

There are no particular limitations on the curing conditions for the coating film formed from the coating composition, and the curing may be performed using a conventional method.

In the case of curing by irradiation with energy rays, if ultraviolet rays are used for the irradiation, then the irradiation may be performed using a high-pressure mercury

lamp, a fusion H lamp, or a xenon lamp or the like as the ultraviolet source, with an irradiation dose that is preferably from 100 to 500 mJ/cm². On the other hand, if an electron beam is used for the irradiation, then the electron beam is typically generated using an electron accelerator or the like, and the irradiation dose is preferably from 150 to 350 kV. Among these options, formation of the coating layer is preferably performed by irradiation of ultraviolet rays.

[0317]

In those cases where the coating layer is formed for the purpose of covering an uneven surface of the substrate or the like and improving the degree of smoothness of the surface of the support sheet, the coating composition is preferably applied directly to the uneven surface to form the coating layer. By using this method, the generation of voids between the surface of the coating layer and the uneven surface can be better suppressed, and for example, irregular reflection of light at the interface between the surface of the coating layer and the uneven surface can be suppressed, and the aforementioned infrared examination of the semiconductor chips can be performed more favorably.

In order to suppress the occurrence of voids, a coating composition having a low viscosity is preferably used. Further, a coating composition containing an energy ray-curable compound is usually ideal for suppressing the occurrence of voids.

[0318]

In those cases where it is necessary to adjust the surface roughness of a surface of the support sheet, that adjustment may be performed using a conventional method. For example, in those cases where the layer that requires adjustment of the surface roughness is a layer formed by applying an aforementioned composition such as the protective film formation layer composition, adhesive composition or coating composition, the surface

roughness of that layer can be adjusted by altering the surface roughness of the layer to which the composition is applied.

Further, in those cases where the layer that requires adjustment of the surface roughness includes a meltable component such as a filler that melts upon heating on the surface of the layer, the surface roughness can be reduced by heating the surface and melting the meltable component. In those cases where the layer that requires adjustment of the surface roughness does not include an aforementioned meltable component on the surface of the layer, the surface roughness may be reduced by heating the entire surface and smoothing the layer.

Further, as described above, the surface roughness can also be reduced by forming a coating layer on the layer that requires adjustment of the surface roughness.

On the other hand, the surface roughness can also be increased by subjecting the layer that requires adjustment of the surface roughness to a surface roughening treatment such as a sand blasting treatment.

[0319]

In those cases where it is necessary to adjust the surface roughness of the surface of the release film on the opposite side from the release-treated surface in order to alter the aforementioned static friction force (also called the static friction coefficient), the adjustment may be performed using a conventional method, in the same manner as that described above for the support sheet. The aforementioned surface of the release film usually has a higher degree of smoothness, and for example if it is desirable to increase the surface roughness, then a surface roughening treatment such as a sand blasting treatment may be performed.

However, adjusting the surface roughness of the surface of the support sheet is easier than adjusting the surface roughness of the above surface of the release film.

Accordingly, the static friction force is preferably adjusted by adjusting the surface roughness of the surface of the support sheet.

[0320]

A manufacturing method that includes the lamination step (P1') is described below, with reference to FIG. 9, as a manufacturing method for a sheet having the structure illustrated in FIG. 2, which represents one example of the protective film formation sheet according to the present invention. The manufacturing method described here is merely one example, and in those cases where another manufacturing method for the protective film formation sheet of the structure illustrated in FIG. 2 or a manufacturing method for a different protective film formation sheet includes the same steps or similar steps to those described below, those steps may be performed in the same manner as the steps described below.

[0321]

In this method, a heat-curable protective film formation layer composition or an energy ray-curable protective film formation layer composition is applied to the release-treated surface 15b of the release film 15, thus forming the protective film formation layer 13 as shown in FIG. 9(a). At this time, the release film 15 is selected so that the static friction force between a surface (surface 11b) of the substrate 11 having a surface roughness of not more than 0.5 μm and a surface (surface 15a) of the release film 15 on the opposite side from the release-treated surface 15b is not more than 29 N. Here, in order to facilitate comparison with the protective film formation sheet 1B, an example is shown in which the protective film formation layer 13 is disposed as a lower layer beneath the release film 15, but this does not mean that the orientation of the release-treated surface 15b of the release film 15 is limited to the downward-facing orientation illustrated in FIG. 9(a) during application of the protective film formation composition,

and the opposite upward-facing orientation may also be used, with this upward orientation being preferred.

Further, a separate release material may also be bonded to the surface (the exposed surface) of the protective film formation layer 13 on the opposite side from the side that contacts the release film 15 (not shown in the figure). Examples of this release material include the same materials as the release material that represents the coating target for the adhesive composition described below.

[0322]

In this method, next, an adhesive composition is applied to a release-treated surface 90b of a release material 90, thus forming the adhesive layer 12 as shown in FIG. 9(b). Here, in order to facilitate comparison with the protective film formation sheet 1B, an example is shown in which the adhesive layer 12 is disposed as a lower layer beneath the release material 90, but this does not mean that the orientation of the release-treated surface 90b of the release material 90 is limited to the downward-facing orientation illustrated in FIG. 9(b) during application of the adhesive composition, and the opposite upward-facing orientation may also be used, with this upward orientation being preferred.

[0323]

In this method, subsequently, the substrate 11 is bonded to the surface (the exposed surface) of the adhesive layer 12 on the opposite side from the side that contacts the release material 90. At this time, the bonding surface for the adhesive layer 12 on the substrate 11 is selected so that the surface roughness of the surface 11b of the substrate 11 to which the adhesive layer 12 is not bonded is not more than 0.5 μm .

The above operations yield the support sheet 10.

[0324]

Next in this method, as illustrated in FIG. 9(d), an exposed surface of the adhesive layer 12 in the support sheet 10, which is exposed by removing the release material 90 provided on the adhesive layer 12, is bonded to the exposed surface of the protective film formation layer 13, thus obtaining the protective film formation sheet 1B illustrated in FIG. 9(e). In those cases where a separate release material described above is affixed to the surface (the exposed surface) of the protective film formation layer 13 on the opposite side from the side that contacts the release film 15, this release material is removed before bonding the exposed surface of the protective film formation layer 13 to the exposed surface of the adhesive layer 12.

[0325]

Next is a description of a manufacturing method for a protective film formation sheet according to the present invention having the structure illustrated in FIG. 1 (this method is not shown in the drawings).

In this method, the manufacturing method for the protective film formation sheet 1B described above can be used.

[0326]

First, a laminated sheet having a release film 15 laminated to one surface of an adhesive tape used for forming the jig adhesive layer 16 is cut to a target shape so that the adhesive tape exists in the target region. This target shape is, for example, a circular shape when the surface of the laminated sheet is viewed from above in plan view.

Subsequently, the adhesive tape having this target shape (for example, a circular shape when viewed in plan view) is removed from the laminated sheet, thus forming a processed laminated sheet having the release material exposed in the region from which the adhesive tape has been removed. In other words, in the case where a circular region

of the adhesive tape is removed when viewed in plan view, this processed laminated sheet has the adhesive tape completely removed in the target region.

Next, the release film 15 is removed from the protective film formation sheet 1B, and by bonding the exposed surface of the protective film formation layer 13 to the adhesive tape of this processed laminated sheet, the protective film formation sheet 1A illustrated in FIG. 1 is obtained. In this method, in those cases where a sheet that has not been wound into a roll is used as the protective film formation sheet 1B, a protective film formation sheet which, with the exception of being provided with a conventional release material instead of the release film 15, has the same structure as the protective film formation sheet 1B may also be used as the bonding target for the aforementioned processed laminated sheet.

[0327]

The manufacturing method described above is merely one example, and the manufacturing method for the protective film formation sheet 1A is not limited to this method.

[0328]

<Method for Using Protective Film Formation Sheet>

A method for using the protective film formation sheet according to the present invention is, for example, as described below.

First is a description of a method for using the protective film formation sheet in the case where the protective film formation layer is heat-curable.

In this method, the back surface of a semiconductor wafer is first affixed to the protective film formation layer of the protective film formation sheet, and the protective film formation sheet is secured in a dicing apparatus.

Subsequently, the protective film formation layer is cured by heating to form a protective film. In those cases where a back grind tape is affixed to the surface (the electrode formation surface) of the semiconductor wafer, this back grind tape is usually removed from the semiconductor wafer prior to formation of the protective film.

[0329]

Next, the semiconductor wafer, together with the protective film, is subjected to dicing to form semiconductor chips. In the period following formation of the protective film until the dicing is performed, the protective film may be irradiated with a laser light from the support sheet side of the protective film formation sheet to form printing (laser printing) on the surface of the protective film.

In the protective film formation sheet according to the present invention, the surface roughness of the surface of the support sheet on the opposite side to the side on which the protective film formation layer is provided is not more than $0.5\ \mu\text{m}$, meaning the surface (the back surface of the support sheet) is either a smooth surface or a surface having a low degree of unevenness. Accordingly, when the semiconductor chips obtained upon dicing are inspected from the back surface of the semiconductor chips (namely, the surface of the semiconductor chips to which the protective film formation sheet is affixed) using an infrared camera or the like, scattering of the infrared rays at the surface (the back surface) of the support sheet is suppressed, and therefore a clear examination image can be acquired, and an infrared examination of the semiconductor chips can be performed favorably. As a result, the existence of damage such as chipping and cracking of the semiconductor chips can be easily ascertained.

[0330]

Subsequently, semiconductor chips with a protective film are obtained by picking up each of the semiconductor chips, together with the cut protective film affixed to the

back surface of the chip, from the support sheet. For example, in the case where the support sheet is a multilayer sheet prepared by laminating a substrate and an adhesive layer, and the adhesive layer is an energy ray-curable layer, the adhesive layer is first cured by irradiation with energy rays, and the semiconductor chips with a protective film can be obtained easily by picking up each of the semiconductor chips, together with the protective film affixed to the back surface of the chip, from this cured adhesive layer.

From this point onward, conventional methods may be used to perform a flip-chip connection of the semiconductor chip of each of the obtained semiconductor chips with a protective film to the circuit surface of a substrate, and then encapsulate the entire structure in a resin to obtain a semiconductor package. Using this semiconductor package, a targeted semiconductor device can then be produced.

[0331]

Up until this point, the case has been described in which the protective film formation layer is first cured to form a protective film and dicing is then performed, but dicing may be performed without curing the protective film formation layer, with the protective film formation layer then being cured after the dicing to form the protective film.

Further, up until this point, the case has been described in which the semiconductor chips are subjected to an infrared examination after dicing, but an infrared examination may also be performed on the semiconductor wafer prior to dicing, in a state where the protective film formation sheet has been affixed. In this case, the infrared examination may be performed either before or after formation of the protective film by curing of the protective film formation layer.

[0332]

Next is a description of a method for using the protective film formation sheet in the case where the protective film formation layer is an energy ray-curable layer.

In this case, in a similar manner to that described above for the case where the protective film formation layer was heat-curable, the back surface of a semiconductor wafer is first affixed to the protective film formation layer of the protective film formation sheet, and the protective film formation sheet is secured in a dicing apparatus.

Next, the protective film formation layer is cured by irradiation with energy rays, thus forming a protective film. In those cases where a back grind tape is affixed to the surface (the electrode formation surface) of the semiconductor wafer, this back grind tape is usually removed from the semiconductor wafer prior to formation of the protective film.

[0333]

Next, the semiconductor wafer, together with the protective film, is subjected to dicing to form semiconductor chips. In the period following formation of the protective film until the dicing is performed, the protective film may be irradiated with a laser light from the support sheet side of the protective film formation sheet to perform printing onto the surface of the protective film. During this period, in a similar manner to that described above for the case where the protective film formation layer was heat-curable, either the semiconductor wafer prior to dicing or the semiconductor chips obtained upon dicing may be subjected to a high-precision infrared examination using an infrared camera or the like.

[0334]

Subsequently, semiconductor chips with a protective film are obtained by picking up each of the semiconductor chips, together with the cut protective film affixed to the back surface of the chip, from the support sheet.

This method is particularly suitable in those cases where, for example, the protective film formation sheet includes a support sheet that is prepared by laminating a substrate and an adhesive layer, and the adhesive layer is not an energy ray-curable layer.

[0335]

For example, in the case where a protective film formation sheet is used in which the support sheet is prepared by laminating a substrate and an adhesive layer, and the adhesive layer is an energy ray-curable layer, the method described below is preferred.

In other words, in a similar manner to that described above, the back surface of a semiconductor wafer is first affixed to the protective film formation layer of the protective film formation sheet, and the protective film formation sheet is secured in a dicing apparatus.

Next, if required, the protective film formation layer may be irradiated with a laser light from the support sheet side of the protective film formation sheet to perform printing onto the surface of the protective film formation layer, and the semiconductor wafer is then subjected to dicing to form semiconductor chips. During this period, in a similar manner to that described above for the case where the protective film formation layer is heat-curable, either the semiconductor wafer prior to dicing or the semiconductor chips obtained upon dicing may be subjected to a high-precision infrared examination using an infrared camera or the like.

[0336]

Subsequently, irradiation of energy rays is performed to cure the protective film formation layer to form a protective film and also cure the adhesive layer, and semiconductor chips with a protective film are then obtained by picking up each of the semiconductor chips, together with the protective film affixed to the back surface of the

chip, from the cured adhesive layer. The printing performed on the surface of the protective film formation layer is retained in the same state on the protective film.

[0337]

From this point onward, conventional methods may be used to perform a flip-chip connection of the semiconductor chip of each of the obtained semiconductor chips with a protective film to the circuit surface of a substrate, and then encapsulate the entire structure in a resin to obtain a semiconductor package. Using this semiconductor package, a targeted semiconductor device can then be produced. This process is the same in all those cases where the protective film formation layer is an energy ray-curable layer.

[0338]

In a similar manner to the method described above for the case where the protective film formation layer is heat-curable, various alterations can be made to the method described here. In other words, up until this point, the case has been described in which the protective film formation layer is first cured to form a protective film and dicing is then performed, but dicing may be performed without curing the protective film formation layer, with the protective film formation layer then being cured after the dicing to form the protective film.

Further, up until this point, the case has been described in which the semiconductor chips are subjected to an infrared examination after dicing, but an infrared examination may also be performed on the semiconductor wafer prior to dicing, in a state where the protective film formation sheet has been affixed. In this case, the infrared examination may be performed either before or after formation of the protective film by curing of the protective film formation layer.

[0339]

On the other hand, when a long protective film formation sheet is wound into a roll, a protective film formation sheet is usually used in which a release film (for example, the release film 15 in FIGS. 1 to 8) has been laminated to the exposed surface of the protective film formation layer on the opposite side from the surface on which the support sheet is provided. Then, regardless of the structure of the protective film formation sheet (for example, in any of the protective film formation sheets illustrated in FIGS. 1 to 8), the winding of the protective film formation sheet according to the present invention into a roll yields a roll in which laminated units having the support sheet, the protective film formation layer and the release film laminated in that order are sequentially stacked on top of one another in the radial direction of the roll. As a result, where adjacent laminated units contact one another in the radial direction of the roll, the surface of the release film of one laminated unit (the surface of the release film on the opposite side from the side on which the protective film formation layer is provided) and the surface of the support sheet of the other laminated unit (the surface of the support sheet on the opposite side from the surface on which the protective film formation layer is provided) make contact and are pressed against one another, and the protective film formation sheet is stored in this state. However, in the protective film formation sheet according to the present invention, because the static friction force between the surface of the release film and the surface of the support sheet that contact one another in this manner is not more than 29 N, blocking between the adjacent laminated units is suppressed, and the sheet can be fed favorably from the roll.

[0340]

[Manufacturing Method for Semiconductor Device]

As described above, the protective film formation sheet according to the present invention is ideal for use during the manufacture of a semiconductor device. In other

words, one embodiment of a manufacturing method a semiconductor device that uses the protective film formation sheet according to the present invention is a manufacturing method that includes a step of removing the release film from the protective film formation sheet and then affixing the protective film formation layer to the back surface of a semiconductor wafer on the opposite side from the surface on which a circuit is provided, a step of curing the protective film formation layer following affixing to the semiconductor wafer to form a protective film, a step of dicing the semiconductor wafer with the protective film formation sheet formed thereon to form semiconductor chips, a step of examining the semiconductor chips by irradiating infrared rays onto the semiconductor chips from the support sheet side of the protective film formation sheet, a step of obtaining semiconductor chips with a protective film by detaching each semiconductor chip, together with the protective film affixed to the back surface of the chip, from the support sheet, and a step of performing flip-chip connection of the semiconductor chip of the semiconductor chip with a protective film to the circuit surface of a circuit board.

[0341]

One aspect of the protective film formation sheet that represents one embodiment of the present invention is a protective film formation sheet containing:

a protective film formation layer provided on a support sheet of the present invention, and a release film provided on the protective film formation layer, wherein

the surface roughness of a surface of the support sheet on the opposite side from the side on which the protective film formation layer is provided is from 0 to 0.5 μm , preferably from 0 to 0.45 μm , more preferably from 0.01 to 0.4 μm , even more preferably from 0.01 to 0.35 μm , and particularly preferably from 0.03 to 0.3 μm , and

the static friction force, measured in accordance with JIS K7125, between the aforementioned surface of the support sheet and a surface of the release film on the opposite side from the side on which the protective film formation layer is provided is from 1 N to 29 N, preferably from 1 N to 25 N, more preferably from 2 N to 20 N, even more preferably from 2 N to 15 N, and particularly preferably from 3 N to 13 N, or may be from 5 N to 12 N, or from 5 N to 7 N.

EXAMPLES

[0342]

The present invention is described below in further detail using a series of specific examples. However, the present invention is in no way limited by the examples described below.

[0343]

The raw materials used in the manufacture of the protective film formation layer compositions are listed below.

[Polymer Component (A)]

(A)-1: an acrylic-based resin (weight average molecular weight: 400,000, glass transition temperature: -1°C) obtained 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.

[Heat-Curable Component (B)]

- Epoxy Resin (B1)

(B1)-1: a bisphenol A epoxy resin (JER828, manufactured by Mitsubishi Chemical Corporation, epoxy equivalent weight: 183 to 194 g/eq, number average molecular weight: 370)

(B1)-2 a bisphenol A epoxy resin (JER1055, manufactured by Mitsubishi Chemical Corporation, epoxy equivalent weight: 800 to 900 g/eq, number average molecular weight: 1,600)

(B1)-3: a dicyclopentadiene epoxy resin (EPICLON HP-7200HH, manufactured by DIC Corporation, epoxy equivalent weight: 274 to 286 g/eq)

- Heat Curing Agent (B2)

(B2)-1: dicyandiamide (a heat-activated latent epoxy resin curing agent, ADEKA HARDNER EH-3636AS, manufactured by ADEKA Corporation, amount of active hydrogen: 21 g/eq)

[Curing Accelerator (C)]

(C)-1: 2-phenyl-4,5-dihydroxymethylimidazole (CUREZOL 2PHZ, manufactured by Shikoku Corporation)

[Filler (D)]

(D)-1: a silica filler (SC2050MA, manufactured by Admatechs Co., Ltd., surface-modified with an epoxy-based compound, average particle size: 0.5 μm)

[Coupling Agent (E)]

(E)-1: 3-glycidoxypentyltrimethoxysilane (a silane coupling agent, KBM403, manufactured by Shin-Etsu Chemical Co., Ltd.)

[Colorant (I)]

(I)-1: a carbon black (MA600B, manufactured by Mitsubishi Chemical Corporation, average particle size: 28 nm)

[0344]

The substrates used during manufacture of the support sheets are listed below.

Substrate (r1): a polypropylene substrate in which one surface is a smooth surface having a surface roughness (Ra) of 0.1 μm and the other surface is a matte-treated

surface having a surface roughness (Ra) of 0.3 μm (manufactured by Gunze Limited, thickness: 80 μm)

Substrate (r2): a polyvinyl chloride substrate in which both surfaces are smooth surfaces having a surface roughness (Ra) of 0.03 μm (manufactured by Achilles Corporation, thickness: 80 μm)

Substrate (r3): an ethylene/methacrylic acid copolymer substrate in which one surface is a smooth surface having a surface roughness (Ra) of 0.1 μm and the other surface is a matte-treated surface having a surface roughness (Ra) of 0.6 μm (manufactured by DuPont-Mitsui Polychemicals Co., Ltd., thickness: 80 μm)

Substrate (r4): a polypropylene substrate in which one surface is a smooth surface having a surface roughness (Ra) of 0.1 μm and the other surface is a matte-treated surface having a surface roughness (Ra) of 1.0 μm (manufactured by Mitsubishi Plastics, Inc., thickness: 80 μm)

[0345]

The release films used in the various steps during manufacture of the protective film formation sheets are listed below.

Release film (s1): a polyethylene terephthalate release film in which one surface has undergone a release treatment and the other surface is a smooth surface that has not undergone a release treatment (SP-PET382150, manufactured by Lintec Corporation, thickness: 38 μm)

Release film (s2): a polyethylene terephthalate release film in which one surface has undergone a release treatment and the other surface is a smooth surface that has not undergone a release treatment (SP-PET381130, manufactured by Lintec Corporation, thickness: 38 μm)

Release film (s3): a polyethylene terephthalate release film in which one surface has undergone a release treatment and the other surface is a matte-treated surface that has not undergone a release treatment (SP-PMF381031H, manufactured by Lintec Corporation, thickness: 38 μm)

[0346]

The surface roughness (Ra) values of the substrates, and the static friction force values between the substrates and the release films were measured using the methods described below.

[0347]

(Measurement of Surface Roughness)

The surface roughness (Ra) values of the above substrates were measured in accordance with JIS B 0601:2001, using a contact surface shape measuring apparatus (SURFTEST SV-3000, manufactured by Mitutoyo Corporation), with the cutoff value λ_c set to 0.8 μm , and the evaluation length L_n set to 10 mm.

The results are shown in Table 1.

[0348]

(Measurement of Static Friction Force)

The static friction force was measured using a universal material testing instrument (RTG-1225, manufactured by A&D Company, Limited), in accordance with JIS K7125, using the method described below.

In other words, the release film was cut to dimensions of 10 cm $\times$ 20 cm and the substrate was cut to dimensions of 6 cm $\times$ 10 cm to form a pair of test pieces.

The release film test piece was secured to a flat static friction force measurement jig using a tape. At this time, the release-treated surface of the release film test piece was oriented to face the securing surface of the jig, and the release film was secured such that

no wrinkles were generated. The jig was then set in this state in the universal material testing instrument.

The substrate test piece was secured to the 6 cm × 10 cm surface of a metal weight having dimensions of 6 cm × 10 cm × 2 cm and a weight of 1 kg. At this time, a double-sided tape was affixed to the surface of the substrate test piece on the opposite side from the static friction force measurement target surface, and the substrate test piece was secured to the metal weight via this double-sided tape.

Subsequently, the substrate test piece secured to the metal weight was positioned so that the static friction force measurement target surface of the substrate test piece was brought into direct contact with the static friction force measurement target surface (the surface on the opposite side from the release-treated surface) of the secured release film test piece, meaning the release film test piece, the substrate test piece and the metal weight were laminated together in that order. The metal weight was then moved in the horizontal direction, namely in a direction parallel with the static friction force measurement target surface of the release film test piece, at a speed of 10 mm/minute, and the loading (peak test force) prior to the start of the movement of the metal weight was measured, and recorded as the static friction force.

The results are shown in Table 1.

[0349]

[Example 1]

<Manufacture of Protective Film Formation Sheet>

(Manufacture of Heat-Curable Protective Film Formation Layer Composition)

As shown in Table 1, the polymer component (A)-1 (150 parts by mass), the epoxy resin (B1)-1 (60 parts by mass), the epoxy resin (B1)-2 (10 parts by mass), the epoxy resin (B1)-3 (30 parts by mass), the heat curing agent (B2)-1 (2 parts by mass), the

curing accelerator (C)-1 (2 parts by mass), the filler (D)-1 (320 parts by mass), the coupling agent (E)-1 (2 parts by mass), and the colorant (I)-1 (1.2 parts by mass) were mixed, methyl ethyl ketone was then added and mixed, and the resulting mixture was stirred at 23°C for 60 minutes, thus obtaining a protective film formation layer composition (III-1) having a solid fraction content of 53.0% by mass. The blend amounts of the components other than the methyl ethyl ketone shown in Table 1 all represent solid fraction amounts.

[0350]

(Formation of Protective Film Formation Layer)

The protective film formation layer composition (III-1) obtained above was applied to the release-treated surface of the release film (s1) using a knife coater, and the composition was dried at 110°C for 2 minutes to form a protective film formation layer with a thickness of 25 μm . The release-treated surface of the release film (s2) was then bonded to the exposed surface of this protective film formation layer on the opposite side from the side on which the release film (s1) had been provided.

[0351]

(Manufacture of Adhesive Composition)

An alkyl (meth)acrylate ester copolymer (weight average molecular weight: 400,000, glass transition temperature: -1°C) (100 parts by mass) and a trifunctional xylylene diisocyanate-based crosslinking agent (TAKENATE D110N, manufactured by Mitsui Takeda Chemicals, Inc.) (5 parts by mass) were mixed, methyl ethyl ketone was then added and mixed, and the resulting mixture was stirred at 23°C for 30 minutes, thus obtaining an adhesive composition (iii) having a solid fraction content of 30.0% by mass. The alkyl (meth)acrylate ester copolymer was obtained by copolymerizing methyl methacrylate (30 parts by mass), 2-ethylhexyl acrylate (60 parts by mass) and 2-

hydroxyethyl acrylate (10 parts by mass). The blend amounts of the components other than the methyl ethyl ketone shown in the table all represent solid fraction amounts.

[0352]

(Formation of Adhesive Layer, Manufacture of Support Sheet)

The adhesive composition (iii) obtained above was applied to the release-treated surface of the release film (s1) using a knife coater, and the composition was dried at 110°C for 2 minutes to form an adhesive layer with a thickness of 10 μm .

The flat surface of the substrate (r1) was then bonded to the exposed surface of this adhesive layer on the opposite side from the side on which the release film (s1) had been provided, thus obtaining a support sheet.

[0353]

(Manufacture of Protective Film Formation Sheet)

The release film (s2) was removed from one surface of the protective film formation layer obtained above, the release film (s1) provided on the adhesive layer of the support sheet was also removed, and the exposed surface of the protective film formation layer and the exposed surface of the adhesive layer were laminated together, thus obtaining a protective film formation sheet having the structure illustrated in FIG. 2, wherein the substrate (r1), the adhesive layer, the protective film formation layer and the release film (s1) were laminated together in that order, the surface (the exposed surface) of the support sheet on the opposite side from the side on which the adhesive layer was provided was the matte-treated surface of the substrate (r1), and the surface (the exposed surface) of the release film on the opposite side from the side on which the protective film formation layer was provided was a smooth surface.

[0354]

<Evaluations of Protective Film Formation Sheet>

(Feedability from Roll)

A long protective film formation sheet having a width of 0.4 m and a length of 100 m obtained in the manner described above was wound into a roll. Ten of these types of rolls were prepared, these rolls were stored at 23°C for 30 days, and feeding of the protective film formation sheet from the rolls was then tested. If the protective film formation sheet was able to be fed from all of the rolls with no problems, an evaluation of A was recorded, if one or two rolls of the protective film formation sheet were unable to be fed smoothly without any practical problems, and evaluation of B was recorded, and if some form of problem was detected in all of the rolls, such as an inability to feed the protective film formation sheet due to the occurrence of blocking, or peeling of the release film during feeding of the protective film formation sheet, then an evaluation of C was recorded. The results are shown in Table 1.

[0355]

(Infrared Examination Characteristics)

The release film (s1) was removed from the protective film formation sheet obtained above, and a tape mounter (Adwill RAD-2700, manufactured by Lintec Corporation) was used to affix the protective film formation layer of the protective film formation sheet to the #2000 polished surface of a silicon wafer (diameter: 200 mm, thickness: 350 μ m) while heating was performed at 70°C. Subsequently, the protective film formation layer was cured by heating at 130°C for 2 hours, thus forming a protective film. This process yielded a laminated body containing the support sheet (a laminated sheet of the substrate and the adhesive layer), the protective film and the silicon wafer laminated in that order.

Subsequently, using an infrared microscope (BX-51, manufactured by Olympus Corporation), the obtained laminated body was inspected from the side of the support

sheet, and if grinding traces could be detected on the polished surface of the silicon wafer through the support sheet and the protective film, an evaluation of A was recorded, whereas if grinding traces could not be detected, an evaluation of B was recorded. The results are shown in Table 1.

[0356]

An entry of "-" in Table 1 means that the item was either not measured or not evaluated.

[0357]

[Example 2]

<Manufacture of Protective Film Formation Sheet>

(Manufacture of Heat-Curable Protective Film Formation Layer Composition, Manufacture of Adhesive Composition)

The protective film formation layer composition (III-1) and the adhesive composition (iii) were manufactured using the same methods as Example 1.

[0358]

(Formation of Protective Film Formation Layer)

The protective film formation layer composition (III-1) obtained above was applied to the release-treated surface of the release film (s3) using a knife coater, and the composition was dried at 110°C for 2 minutes to form a protective film formation layer with a thickness of 25 μm . The release-treated surface of the release film (s2) was then bonded to the exposed surface of this protective film formation layer on the opposite side from the side on which the release film (s3) had been provided.

[0359]

(Formation of Adhesive Layer, Manufacture of Support Sheet)

The adhesive composition (iii) obtained above was applied to the release-treated surface of the release film (s1) using a knife coater, and the composition was dried at 110°C for 2 minutes to form an adhesive layer with a thickness of 10 μm .

One of the flat surfaces of the substrate (r2) was then bonded to the exposed surface of this adhesive layer on the opposite side from the side on which the release film (s1) had been provided, thus obtaining a support sheet.

[0360]

(Manufacture of Protective Film Formation Sheet)

The release film (s2) was removed from one surface of the protective film formation layer obtained above, the release film (s1) provided on the adhesive layer of the support sheet was also removed, and the exposed surface of the protective film formation layer and the exposed surface of the adhesive layer were laminated together, thus obtaining a protective film formation sheet having the substrate (r2), the adhesive layer, the protective film formation layer and the release film (s3) laminated together in that order, wherein the surface (the exposed surface) of the support sheet on the opposite side from the side on which the adhesive layer was provided was the other smooth surface of the substrate (r2), and the surface (the exposed surface) of the release film on the opposite side from the side on which the protective film formation layer was provided was a matte-treated surface.

[0361]

<Evaluations of Protective Film Formation Sheet>

The protective film formation sheet obtained above was evaluated using the same methods as Example 1. The results are shown in Table 1.

[0362]

[Example 3]

<Manufacture of Protective Film Formation Sheet>

(Manufacture of Heat-Curable Protective Film Formation Layer Composition,
Manufacture of Adhesive Composition)

The protective film formation layer composition (III-1) and the adhesive composition (iii) were manufactured using the same methods as Example 1.

[0363]

(Formation of Protective Film Formation Layer)

The protective film formation layer composition (III-1) obtained above was applied to the release-treated surface of the release film (s3) using a knife coater, and the composition was dried at 110°C for 2 minutes to form a protective film formation layer with a thickness of 25 μm . The release-treated surface of the release film (s2) was then bonded to the exposed surface of this protective film formation layer on the opposite side from the side on which the release film (s3) had been provided.

[0364]

(Formation of Adhesive Layer, Manufacture of Support Sheet)

The adhesive composition (iii) obtained above was applied to the release-treated surface of the release film (s1) using a knife coater, and the composition was dried at 110°C for 2 minutes to form an adhesive layer with a thickness of 10 μm .

The matte-treated surface of the substrate (r3) was then bonded to the exposed surface of this adhesive layer on the opposite side from the side on which the release film (s1) had been provided, thus obtaining a support sheet.

[0365]

(Manufacture of Protective Film Formation Sheet)

The release film (s2) was removed from one surface of the protective film formation layer obtained above, the release film (s1) provided on the adhesive layer of

the support sheet was also removed, and the exposed surface of the protective film formation layer and the exposed surface of the adhesive layer were laminated together, thus obtaining a protective film formation sheet having the substrate (r3), the adhesive layer, the protective film formation layer and the release film (s3) laminated together in that order, wherein the surface (the exposed surface) of the support sheet on the opposite side from the side on which the adhesive layer was provided was the smooth surface of the substrate (r3), and the surface (the exposed surface) of the release film on the opposite side from the side on which the protective film formation layer was provided was the matte-treated surface.

[0366]

<Evaluations of Protective Film Formation Sheet>

The protective film formation sheet obtained above was evaluated using the same methods as Example 1. The results are shown in Table 1.

[0367]

[Example 4]

<Manufacture of Protective Film Formation Sheet>

(Manufacture of Heat-Curable Protective Film Formation Layer Composition, Formation of Protective Film Formation Layer, Manufacture of Adhesive Composition)

Using the same methods as Example 1, the protective film formation layer composition (III-1) was manufactured, and a protective film formation layer was obtained having the release film (s1) on one surface and the release film (s2) on the other surface.

Further, the adhesive composition (iii) was also manufactured using the same method as Example 1.

[0368]

(Formation of Adhesive Layer, Manufacture of Support Sheet)

Using the same method as Example 1, an adhesive layer with a thickness of 10 μm was formed on the release-treated surface of the release film (s1).

The matte-treated surface of the substrate (r4) was then bonded to the exposed surface of this adhesive layer on the opposite side from the side on which the release film (s1) had been provided, thus obtaining a support sheet.

[0369]

(Manufacture of Protective Film Formation Sheet)

The release film (s2) was removed from one surface of the protective film formation layer obtained above, the release film (s1) provided on the adhesive layer of the support sheet was also removed, and the exposed surface of the protective film formation layer and the exposed surface of the adhesive layer were laminated together, thus obtaining a protective film formation sheet having the substrate (r4), the adhesive layer, the protective film formation layer and the release film (s1) laminated together in that order, wherein the surface (the exposed surface) of the support sheet on the opposite side from the side on which the adhesive layer was provided was the smooth surface of the substrate (r4), and the surface (the exposed surface) of the release film on the opposite side from the side on which the protective film formation layer was provided was a smooth surface.

[0370]

<Evaluations of Protective Film Formation Sheet>

The protective film formation sheet obtained above was evaluated using the same methods as Example 1. The results are shown in Table 1.

[0371]

[Comparative Example 1]

<Manufacture of Protective Film Formation Sheet>

(Manufacture of Heat-Curable Protective Film Formation Layer Composition, Formation of Protective Film Formation Layer, Manufacture of Adhesive Composition)

Using the same methods as Example 1, the protective film formation layer composition (III-1) was manufactured, and a protective film formation layer was obtained having the release film (s1) on one surface and the release film (s2) on the other surface.

Further, the adhesive composition (iii) was also manufactured using the same method as Example 1.

[0372]

(Formation of Adhesive Layer, Manufacture of Support Sheet)

Using the same method as Example 1, an adhesive layer with a thickness of 10 μm was formed on the release-treated surface of the release film (s1).

The smooth surface of the substrate (r4) was then bonded to the exposed surface of this adhesive layer on the opposite side from the side on which the release film (s1) had been provided, thus obtaining a support sheet.

[0373]

(Manufacture of Protective Film Formation Sheet)

The release film (s2) was removed from one surface of the protective film formation layer obtained above, the release film (s1) provided on the adhesive layer of the support sheet was also removed, and the exposed surface of the protective film formation layer and the exposed surface of the adhesive layer were laminated together, thus obtaining a protective film formation sheet having the substrate (r4), the adhesive layer, the protective film formation layer and the release film (s1) laminated together in that order, wherein the surface (the exposed surface) of the support sheet on the opposite

side from the side on which the adhesive layer was provided was the matte-treated surface of the substrate (r4), and the surface (the exposed surface) of the release film on the opposite side from the side on which the protective film formation layer was provided was a smooth surface.

[0374]

<Evaluations of Protective Film Formation Sheet>

The protective film formation sheet obtained above was evaluated using the same methods as Example 1. The results are shown in Table 1.

[0375]

[Comparative Example 2]

<Manufacture of Protective Film Formation Sheet>

(Manufacture of Heat-Curable Protective Film Formation Layer Composition, Formation of Protective Film Formation Layer, Manufacture of Adhesive Composition)

Using the same methods as Example 1, the protective film formation layer composition (III-1) was manufactured, and a protective film formation layer was obtained having the release film (s1) on one surface and the release film (s2) on the other surface.

Further, the adhesive composition (iii) was also manufactured using the same method as Example 1.

[0376]

(Formation of Adhesive Layer, Manufacture of Support Sheet)

Using the same method as Example 1, an adhesive layer with a thickness of 10 μm was formed on the release-treated surface of the release film (s1).

[0377]

(Manufacture of Coating Composition)

An alkyl (meth)acrylate ester copolymer (weight average molecular weight: 400,000, glass transition temperature: -1°C) (100 parts by mass) and a trifunctional xylylene diisocyanate-based crosslinking agent (TAKENATE D110N, manufactured by Mitsui Takeda Chemicals, Inc.) (40 parts by mass) were mixed, methyl ethyl ketone was then added and mixed, and the resulting mixture was stirred at 23°C for 30 minutes, thus obtaining a coating composition having a solid fraction content of 30.0% by mass. The alkyl (meth)acrylate ester copolymer was obtained by copolymerizing methyl methacrylate (30 parts by mass), 2-ethylhexyl acrylate (60 parts by mass) and 2-hydroxyethyl acrylate (10 parts by mass). The blend amounts of the components other than the methyl ethyl ketone shown in the table all represent solid fraction amounts.

[0378]

(Formation of Coating Layer, Manufacture of Support Sheet)

The coating composition obtained above was applied to the matte-treated surface of the substrate (r1) using a knife coater, and the composition was dried at 110°C for 2 minutes to form a coating layer with a thickness of 10 μm .

The smooth surface of the substrate (r1) on the opposite side from the side on which the coating layer had been provided was then bonded to the exposed surface of the aforementioned adhesive layer on the opposite side from the side on which the release film (s1) had been provided, thus obtaining a support sheet.

[0379]

(Manufacture of Protective Film Formation Sheet)

The release film (s2) was removed from one surface of the protective film formation layer obtained above, the release film (s1) provided on the adhesive layer of the support sheet was also removed, and the exposed surface of the protective film formation layer and the exposed surface of the adhesive layer were laminated together,

thus obtaining a protective film formation sheet having the coating layer, the substrate (r1), the adhesive layer, the protective film formation layer and the release film (s1) laminated together in that order, wherein the surface (the exposed surface) of the support sheet on the opposite side from the side on which the adhesive layer was provided was the surface of the coating layer, and the surface (the exposed surface) of the release film on the opposite side from the side on which the protective film formation layer was provided was a smooth surface.

[0380]

<Evaluations of Protective Film Formation Sheet>

The protective film formation sheet obtained above was evaluated using the same methods as Example 1. The results are shown in Table 1.

[0381]

[Comparative Example 3]

<Manufacture of Protective Film Formation Sheet>

(Manufacture of Heat-Curable Protective Film Formation Layer Composition, Formation of Protective Film Formation Layer, Manufacture of Adhesive Composition)

Using the same methods as Example 1, the protective film formation layer composition (III-1) was manufactured, and a protective film formation layer was obtained having the release film (s1) on one surface and the release film (s2) on the other surface.

Further, the adhesive composition (iii) was also manufactured using the same method as Example 1.

[0382]

(Formation of Adhesive Layer, Manufacture of Support Sheet)

The adhesive composition (iii) obtained above was applied to the release-treated surface of the release film (s1) using a knife coater, and the composition was dried at 110°C for 2 minutes to form an adhesive layer with a thickness of 10 μm .

One of the flat surfaces of the substrate (r2) was then bonded to the exposed surface of this adhesive layer on the opposite side from the side on which the release film (s1) had been provided, thus obtaining a support sheet.

[0383]

(Manufacture of Protective Film Formation Sheet)

The release film (s2) was removed from one surface of the protective film formation layer obtained above, the release film (s1) provided on the adhesive layer of the support sheet was also removed, and the exposed surface of the protective film formation layer and the exposed surface of the adhesive layer were laminated together, thus obtaining a protective film formation sheet having the substrate (r2), the adhesive layer, the protective film formation layer and the release film (s1) laminated together in that order, wherein the surface (the exposed surface) of the support sheet on the opposite side from the side on which the adhesive layer was provided was the other smooth surface of the substrate (r2), and the surface (the exposed surface) of the release film on the opposite side from the side on which the protective film formation layer was provided was a smooth surface.

[0384]

<Evaluations of Protective Film Formation Sheet>

The protective film formation sheet obtained above was evaluated using the same methods as Example 1. The results are shown in Table 1.

[0385]

[Comparative Example 4]

<Manufacture of Protective Film Formation Sheet>

(Manufacture of Heat-Curable Protective Film Formation Layer Composition, Formation of Protective Film Formation Layer, Manufacture of Adhesive Composition)

Using the same methods as Example 1, the protective film formation layer composition (III-1) was manufactured, and a protective film formation layer was obtained having the release film (s1) on one surface and the release film (s2) on the other surface.

Further, the adhesive composition (iii) was also manufactured using the same method as Example 1.

[0386]

(Formation of Adhesive Layer, Manufacture of Support Sheet)

The adhesive composition (iii) obtained above was applied to the release-treated surface of the release film (s1) using a knife coater, and the composition was dried at 110°C for 2 minutes to form an adhesive layer with a thickness of 10 μm .

The matte-treated surface of the substrate (r3) was then bonded to the exposed surface of this adhesive layer on the opposite side from the side on which the release film (s1) had been provided, thus obtaining a support sheet.

[0387]

(Manufacture of Protective Film Formation Sheet)

The release film (s2) was removed from one surface of the protective film formation layer obtained above, the release film (s1) provided on the adhesive layer of the support sheet was also removed, and the exposed surface of the protective film formation layer and the exposed surface of the adhesive layer were laminated together, thus obtaining a protective film formation sheet having the substrate (r3), the adhesive layer, the protective film formation layer and the release film (s1) laminated together in

that order, wherein the surface (the exposed surface) of the support sheet on the opposite side from the side on which the adhesive layer was provided was the smooth surface of the substrate (r3), and the surface (the exposed surface) of the release film on the opposite side from the side on which the protective film formation layer was provided was a smooth surface.

[0388]

<Evaluations of Protective Film Formation Sheet>

The protective film formation sheet obtained above was evaluated using the same methods as Example 1. The results are shown in Table 1.

[0389]

[Table 1]

	Exposed surface of support sheet (Ra (μm))	Exposed surface of release film	Static friction force (N)	Evaluation results	
				Feedability from roll	Infrared examination characteristics
Example 1	matte-treated surface of substrate (0.3)	smooth surface	5	A	A
Example 2	smooth surface of substrate (0.03)	matte-treated surface	7	A	A
Example 3	smooth surface of substrate (0.1)	matte-treated surface	5	A	A
Example 4	smooth surface of substrate (0.1)	smooth surface	12	B	A
Comparative Example 1	matte-treated surface of substrate (1.0)	smooth surface	5	A	B
Comparative Example 2	surface of coating layer covering matte-treated surface of substrate (-)	smooth surface	30	C	A
Comparative Example 3	smooth surface of substrate (0.03)	smooth surface	33	C	A
Comparative Example 4	smooth surface of substrate (0.1)	smooth surface	34	-	A

[0390]

As is evident from the above results, in the protective film formation sheets of Examples 1 to 4, by ensuring that the surface roughness of the surface (the exposed surface) of the support sheet on the opposite side from the side on which the protective film formation layer was provided was not more than 0.3 μm , infrared examination of the semiconductor chips could be performed favorably, and moreover, by ensuring that the static friction force between the above surface (the exposed surface) of the support sheet and the surface (the exposed surface) of the release film on the opposite side from the side on which the protective film formation layer was provided was not more than 12 N, feeding of the protective film formation sheet from a roll could be performed favorably.

As is clearly evident from these results, it was confirmed that by ensuring that the aforementioned exposed surface of the support sheet was a smooth surface or a surface having little unevenness, and the aforementioned exposed surface of the release film was either a smooth surface or an uneven surface, thereby adjusting the combination between these exposed surfaces, the static friction force described above could be reduced, and the protective film formation sheet could be fed favorably from a roll.

[0391]

In contrast, in the protective film formation sheet of Comparative Example 1, although the sheet was able to be fed favorably from a roll due to the small static friction force, because the aforementioned surface roughness was large, infrared examination of the semiconductor chips could not be performed normally.

Further, in the protective film formation sheet of Comparative Example 2, although the infrared examination of the semiconductor chips could be performed favorably, abnormalities were observed when feeding the sheet from a roll. Although it was assumed that, despite not being measured, the surface roughness of the surface of the

coating layer that covered the matte-treated surface of the substrate was probably sufficiently small, because the material of this coating layer was unsuitable, it is thought that the aforementioned static friction force became too large, despite the fact that the exposed surface of the release film was a smooth surface.

Furthermore, in the protective film formation sheet of Comparative Example 3, although the infrared examination of the semiconductor chips could be performed favorably due to the small surface roughness, because the aforementioned static friction force was large, abnormalities were observed when feeding the sheet from a roll.

In the protective film formation sheet of Comparative Example 4, although the infrared examination of the semiconductor chips could be performed favorably due to the small surface roughness, it is assumed that because the static friction force was large, abnormalities would be observed when feeding the sheet from a roll, in a similar manner to that observed for Comparative Example 3.

INDUSTRIAL APPLICABILITY

[0392]

The present invention can be used in the manufacture of semiconductor chips or the like in which the back surface is protected with a protective film, and is therefore extremely useful industrially.

DESCRIPTION OF THE REFERENCE SIGNS

[0393]

1A, 1B, 1C, 1D, 1E, 1F, 1G, 1H: Protective film formation sheet

10: Support sheet

10a: Surface of support sheet

10b: Back surface (exposed surface) of support sheet

11: Substrate

11a: Surface of substrate

11b: Back surface of substrate

12: Adhesive layer

12a: Surface of adhesive layer

13, 23: Protective film formation layer

13a, 23a: Surface of protective film formation layer

14: Coating layer

14a: Surface of coating layer

14b: Back surface of coating layer

15: Release film

15a: Surface of release film

CLAIMS

1. A protective film formation sheet having a protective film formation layer provided on a support sheet, and a release film provided on the protective film formation layer, wherein

a surface roughness of a surface of the support sheet on an opposite side from a side on which the protective film formation layer is provided is not more than 0.5 μm ,

and

a static friction force, measured in accordance with JIS K7125, between the surface of the support sheet and a surface of the release film on an opposite side from a side on which the protective film formation layer is provided is not more than 29 N.
2. The protective film formation sheet according to Claim 1, wherein the support sheet has a substrate, and a surface of the substrate has been subjected to a roughening treatment using a sand blasting treatment.
3. The protective film formation sheet according to Claim 1, wherein the support sheet comprises an adhesive layer laminated to a substrate.
4. The protective film formation sheet according to Claim 2, wherein the support sheet comprises an adhesive layer laminated to the substrate.
5. The protective film formation sheet according to Claim 3 or 4, wherein a thickness of the adhesive layer is from 1 to 100 μm .

6. A manufacturing method for a protective film formation sheet, wherein the protective film formation sheet is the protective film formation sheet according to any one of Claims 1 to 5, and

the method comprises:

a step of forming a laminated structure of the support sheet and the protective film formation layer so that a surface roughness of the surface of the support sheet on an opposite side from a side on which the protective film formation layer is provided is not more than 0.5 μm , and

a step of forming a laminated structure of the protective film formation layer and the release film so that a static friction force, measured in accordance with JIS K7125, between a surface of the support sheet on an opposite side from a side on which the protective film formation layer is provided and a surface of the release film on an opposite side from a side on which the protective film formation layer is provided is not more than 29 N.

7. A manufacturing method for a semiconductor device, the method comprising:

a step of removing the release film from the protective film formation sheet according to any one of Claims 1 to 4, and then affixing the protective film formation layer to a back surface of a semiconductor wafer on an opposite side from a surface on which a circuit is provided,

a step of curing the protective film formation layer following affixing to the semiconductor wafer to form a protective film,

a step of dicing the semiconductor wafer with the protective film formation sheet formed thereon to form semiconductor chips,

a step of examining the semiconductor chips by irradiating infrared rays onto the semiconductor chips from the support sheet side of the protective film formation sheet,

a step of obtaining semiconductor chips with a protective film by detaching each semiconductor chip, together with the protective film affixed to a back surface of the chip, from the support sheet, and

a step of performing flip-chip connection of the semiconductor chip of the semiconductor chip with a protective film to a circuit surface of a circuit board.