

DESCRIPTION

SUPPORTING SHEET AND COMPOSITE SHEET FOR PROTECTIVE FILM FORMATION

TECHNICAL FIELD

[0001]

The present invention relates to a supporting sheet and a composite sheet for protective film formation.

Priority is claimed on Japanese Patent Application No. 2016-060577, filed on March 24, 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 semiconductor 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 semiconductor chip, and the semiconductor chip with the protective film obtained by formation of the protective film in this manner is then incorporated in a semiconductor device. The protective film is used for preventing

cracks and chips from occurring in the semiconductor chip, so-called chipping, in the steps from the dicing step onward.

[0004]

A composite sheet for protective film formation containing a film for protective film formation (a protective film formation layer) provided on a supporting sheet is used for formation of this type of protective film. A laminated sheet produced by laminating an adhesive layer to a resin substrate can be used, for example, as the supporting sheet. In this composite sheet for protective film formation, the film for protective film formation has a protective film formation ability, whereas the supporting sheet can function as a dicing sheet, meaning the composite sheet for protective film formation can be used as an integrated combination of a film for protective film formation and a dicing sheet.

[0005]

Prior to processing, the substrate used in the supporting sheet typically has an uneven shape on either one or both surfaces. When the substrate prior to processing, the supporting sheet obtained using this substrate, or the composite sheet for protective film formation is wound into a roll for storage, if the substrate does not have a surface having this type of uneven shape (namely, an uneven surface), then blocking tends to occur in which the contact surfaces of the roll stick to each other, making subsequent use of the roll problematic. The contact surfaces mentioned here, in the case of a roll of the substrate, refer to the two surfaces of the substrate, or in the case of a supporting sheet or a composite sheet for protective film formation, refer to the exposed surface of the substrate that represents the bottom layer, and the exposed surface of the uppermost layer such as a release film. Particularly in the case of a composite sheet for protective film formation, if blocking occurs then wrinkles tend to occur in the sheet, and when the sheet

is fed from the roll, the uppermost layer (typically a release film) may detach from the sheet.

In contrast, if one of the contact surfaces of the roll is the uneven surface of the substrate, then blocking is suppressed as a result of the reduction in the surface area of the roll contact surface.

[0006]

On the other hand, in the production process for a semiconductor device, printing by irradiation with a laser light (sometimes referred to as "laser printing" in this description) is sometimes performed on the supporting sheet-side surface of the protective film affixed to the semiconductor wafer or semiconductor chip. In this case, the laser light is irradiated through the supporting sheet from the opposite side of the supporting sheet (substrate) from the side on which the protective film is formed. In other words, the laser light passes through the supporting sheet from the exposed surface side of the substrate, and reaches the protective film. Accordingly, if the exposed surface of the substrate is an uneven surface, then a problem arises in that the laser light undergoes irregular reflection at the surface, making the laser printing indistinct.

Further, in the production process for a semiconductor device, the state of the composite sheet for protective film formation, or the state of the semiconductor wafer or semiconductor chip provided with a protective film, is sometimes examined through the sheet or the like using an infrared camera or the like. However, in cases such as those described above where laser light undergoes irregular reflection at the exposed surface of the substrate, a problem arises in that a distinct examination image cannot be obtained.

[0007]

One example of a disclosed composite sheet for protective film formation that can prevent this type of irregular reflection of light such as laser light is a composite sheet (a

dicing tape-integrated semiconductor back surface protective film) which uses a substrate in which only one surface is an uneven surface, with this uneven surface disposed not as the exposed surface, but rather as the surface that faces the film for protective film formation (see Patent Document 1). With this film for protective film formation, the haze of the laminated sheet (dicing tape) obtained by laminating the substrate and the adhesive layer is 45% or less.

[0008]

However, in the composite sheet for protective film formation disclosed in Patent Document 1, because the exposed surface of the substrate is a smooth surface, a problem arises in that when the composite sheet is wound into a roll, the blocking described above cannot be suppressed.

Moreover, in those cases where an adhesive layer is provided on the uneven surface of the substrate, in order to reduce the effect the uneven surface has on the adhesive layer, the adhesive layer must be comparatively soft and also formed with adequate thickness. If the adhesive layer is comparatively hard, then the adhesive layer is sometimes unable to fill the regions near the bases of the protrusions on the substrate surface, and voids can develop. Further, if the adhesive layer is thin, then the uneven shape of the substrate surface is reflected, and the substrate-side surface (back surface) of the film for protective film formation also becomes an uneven surface. If a protective film is formed from a film for protective film formation having these types of problems of inadequate filling and coating of the uneven shape on the substrate surface, and laser printing is then performed on the supporting sheet-side surface of the protective film, then the printing becomes indistinct. Further, a distinct examination image of the semiconductor wafer or semiconductor chip can also not be obtained. On the other hand, if the adhesive layer is too thick, then the adhesive layer is prone to vibration during

cutting in the dicing step, and therefore the semiconductor chips and the semiconductor wafer undergoing cutting to produce the semiconductor chips are also likely to vibrate, resulting in the application of unwanted forces to the semiconductor chips or semiconductor wafer, and an increased likelihood of cracks or chips occurring in the semiconductor chips (namely, an increased likelihood of chipping).

PRIOR ART LITERATURE

Patent Documents

[0009]

Patent Document 1: Japanese Unexamined Patent Application, First Publication
No. 2012-033741

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0010]

The present invention has objects of providing a composite sheet for protective film formation that enables suppression of blocking, distinct laser printing to the protective film, and acquisition of a distinct examination image of the semiconductor wafer or semiconductor chip, without the problems of unsatisfactory filling and coating of the substrate surface by the adhesive layer and the occurrence of chipping, and also providing a supporting sheet used in the production of the composite sheet for protective film formation.

Means for Solving the Problems

[0011]

The present invention provides a supporting sheet having a substrate, and an adhesive layer laminated to the substrate, wherein the surface roughness (Ra) of the surface of the substrate on the side on which the adhesive layer is provided is 0.4 μm or less, and the surface roughness (Ra) of the surface of the substrate on the opposite side from the side on which the adhesive layer is provided is greater than the surface roughness of the surface on which the adhesive layer is provided, and is from 0.053 to 0.48 μm .

[0012]

In the supporting sheet of the present invention, the thickness of the adhesive layer may be 15 μm or less.

In the supporting sheet of the present invention, the adhesive layer may be non-energy-curable.

Further, the present invention also provides a composite sheet for protective film formation containing the above supporting sheet, and also containing a film for protective film formation provided on the adhesive layer in the supporting sheet.

Effects of the Invention

[0013]

By using the supporting sheet and the composite sheet for protective film formation of the present invention, suppression of blocking, distinct laser printing to the protective film, and acquisition of a distinct examination image of the semiconductor wafer or semiconductor chip can all be achieved without the problems of unsatisfactory filling and coating of the substrate surface by the adhesive layer and the occurrence of chipping.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

FIG. 1 is a cross-sectional view schematically illustrating one embodiment of the supporting sheet of the present invention.

FIG. 2 is a cross-sectional view schematically illustrating one embodiment of the composite sheet for protective film formation of the present invention.

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

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

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0015]

◇ Supporting Sheet, Composite Sheet for Protective Film Formation

The supporting sheet of the present invention has a substrate, and an adhesive layer laminated to the substrate, wherein the surface roughness (Ra) of the surface of the substrate on the side on which the adhesive layer is provided (hereafter sometimes referred to as "the first surface") is 0.4 μm or less, and the surface roughness (Ra) of the surface of the substrate on the opposite side from the side on which the adhesive layer is provided (hereafter sometimes referred to as "the second surface") is greater than the surface roughness of the surface (the first surface) on the side on which the adhesive layer is provided, and is from 0.053 to 0.48 μm .

The supporting sheet is used for producing the composite sheet for protective film formation described below, and can be used, for example, as a semiconductor wafer processing sheet such as a dicing sheet.

[0016]

In the present description, for the sake of convenience, of the two surfaces of a substrate, the surface having lower surface roughness (for example, the surface having a surface roughness of $0.4\ \mu\text{m}$ or less, the first surface) is sometimes referred to as the smooth surface, and the surface having greater surface roughness (for example, the surface having surface roughness of 0.053 to $0.48\ \mu\text{m}$, the second surface) is sometimes referred to as the uneven surface. In other words, the names smooth surface and uneven surface used for the substrate do not necessarily indicate the absolute degree of smoothness of these surfaces, but rather indicate the relative size relationship between the degrees of smoothness of these surfaces.

[0017]

The composite sheet for protective film formation of the present invention contains the above supporting sheet, and also has a film for protective film formation provided on the adhesive layer in the supporting sheet.

By including a substrate in which the surface roughness values of the first surface and the second surface are within specific ranges, and in which the surface roughness of the second surface is greater than the surface roughness of the first surface, the composite sheet for protective film formation of the present invention can achieve suppression of blocking, distinct laser printing to the protective film, and acquisition of a distinct examination image of the semiconductor wafer or semiconductor chip. Further, because the surface roughness of the first surface of the substrate is within a specific range (and is a small value) that represents a low degree of unevenness, the adhesive layer need not be

comparatively soft or have a certain adequate thickness, and the problems of unsatisfactory filling and coating of the first surface by the adhesive layer and the occurrence of chipping can also be suppressed.

[0018]

First, the overall structures of the supporting sheet and the composite sheet for protective film formation of the present invention are described below, with reference to the drawings. The drawings used in the following description may sometimes be drawn with the main portions enlarged as appropriate to facilitate comprehension of the features of the present invention, meaning the dimensional ratios and the like between the constituent elements may differ from the actual values.

[0019]

FIG. 1 is a cross-sectional view schematically illustrating one embodiment of the supporting sheet of the present invention.

The illustrated supporting sheet 1 has an adhesive layer 12 provided on a substrate 11, and has a release film 15 provided on the adhesive layer 12.

The adhesive layer 12 is laminated to one surface (a first surface) 11a of the substrate 11, and the other surface of the substrate 11, namely the surface (a second surface) 11b on the opposite side from the side on which the adhesive layer 12 is provided, is an exposed surface.

[0020]

In the substrate 11, the first surface 11a has a surface roughness of $0.4\ \mu\text{m}$ or less, and the second surface 11b has a surface roughness that is greater than the surface roughness of the first surface 11a, and is from 0.053 to $0.48\ \mu\text{m}$.

In the present description, unless specifically stated otherwise, the "surface roughness" means the so-called arithmetical mean roughness measured in accordance with JIS B 0601:2001, and is sometimes abbreviated as "Ra".

[0021]

The release film 15 is provided on one surface of the adhesive layer 12, namely the surface (hereafter sometimes referred to as "the first surface") 12a on the opposite side from the side on which the substrate 11 is provided, but at the time of use of the supporting sheet 1, this release film 15 is removed, and a film for protective film formation, for example, is laminated to the surface to form a composite sheet for protective film formation. The reference numeral 12b denotes the other surface of the adhesive layer 12, namely the surface (hereafter sometimes referred to as "the second surface") on the side on which the substrate 11 is provided.

[0022]

FIG. 2 is a cross-sectional view schematically illustrating one embodiment of the composite sheet for protective film formation of the present invention. In the figures from FIG. 2 onward, structural elements that are the same as elements illustrated in figures that have already been described are labeled with the same symbols as those used in the previously described figures, and detailed descriptions of those elements are omitted.

The illustrated composite sheet for protective film formation 101 has an adhesive layer 12 provided on a substrate 11, and a film for protective film formation 13 provided on the adhesive layer 12. The composite sheet for protective film formation 101 can be produced using the supporting sheet 1, and can also be described as a structure in which the film for protective film formation 13 is provided on the adhesive layer 12 in the supporting sheet 1.

[0023]

The film for protective film formation 13 is laminated across the entire surface of the first surface 12a of the adhesive layer 12.

Further, a jig adhesive layer 14 is laminated to a portion, namely a region near the periphery, of a surface (hereafter sometimes referred to as "the first surface") 13a of the film for protective film formation 13 on the opposite side from the side on which the adhesive layer 12 is provided.

Then, a release film 15 is laminated to the portion of the first surface 13a of the film for protective film formation 13 to which the jig adhesive layer 14 has not been laminated, and surfaces (a first surface 14a and a side surface 14c) of the jig adhesive layer 14 that do not contact the film for protective film formation 13. Here, the first surface 14a of the jig adhesive layer 14 is the surface of the jig adhesive layer 14 on the opposite side from the side that contacts the film for protective film formation 13, and in some cases, the boundary between the first surface 14a and the side surface 14c of the jig adhesive layer 14 may not be able to be clearly distinguished. Further, the release film 15 may sometimes not contact the side surface 14c of the jig adhesive layer 14. The supporting sheet 1 is usually stored in this state, with the release film 15 attached. In FIG. 2, symbol 15a indicates the surface (hereafter sometimes referred to as "the first surface") of the release film 15 on the opposite side from the side that contacts the film for protective film formation 13.

[0024]

The composite sheet for protective film formation 101 is used in a state where the release film 15 has been removed, by affixing the first surface 13a of the film for protective film formation 13 to the surface (in this description, sometimes referred to as "the back surface") of a semiconductor wafer (not shown in the figure) on the opposite

side from the surface on which the circuit is formed (in this description, sometimes referred to as "the circuit forming surface"), and affixing the first surface 14a of the jig adhesive layer 14 to a jig such as a ring frame.

[0025]

In the composite sheet for protective film formation 101, the second surface 11b of the substrate 11 has a surface roughness of 0.053 to 0.48 μm , and this surface roughness is greater than the surface roughness of the first surface 11a of the substrate 11, and has an appropriate uneven shape. As a result, when the composite sheet for protective film formation 101 is wound into a roll, the contact surfaces within the roll, namely, for the stacked portions of the composite sheet for protective film formation 101, the second surface 11b of the substrate 11 of one portion and the first surface 15a of the release film 15 of another portion, are prevented from sticking together, and blocking is suppressed.

[0026]

Further, in the production process for a semiconductor device, the film for protective film formation 13 is sometimes cured to form a protective film while affixed to the surface (the back surface) of the semiconductor wafer or semiconductor chip on the opposite side from the circuit forming surface, and irradiation of a laser light from the second surface 11b side of the substrate 11 is then performed to perform printing (laser printing). At this time, the laser light is irradiated through the supporting sheet 1 from the second surface 11b side of the substrate 11, and reaches the protective film. Accordingly, as mentioned above, because the second surface 11b of the substrate 11 has an appropriate uneven shape with a low degree of unevenness, irregular reflection of the laser light at the second surface 11b of the substrate 11 is suppressed, enabling distinct laser printing to be performed on the protective film.

[0027]

Furthermore, in the production process of a semiconductor device, a semiconductor wafer or semiconductor chip provided with the composite sheet for protective film formation 101 or a protective film is sometimes examined with an infrared camera or the like through the composite sheet for protective film formation 101 or the protective film. At this time, as mentioned above, because the second surface 11b of the substrate 11 has an appropriate uneven shape with a low degree of unevenness, irregular reflection of the infrared rays at the second surface 11b of the substrate 11 is suppressed, enabling a distinct examination image to be acquired.

[0028]

Furthermore, when the adhesive layer is provided on the uneven surface of a substrate, as in the case of a conventional composite sheet for protective film formation, in order to reduce the effect the uneven surface has on the adhesive layer, the adhesive layer must be comparatively soft and formed with adequate thickness. This is because if the adhesive layer is comparatively hard, then the adhesive layer is sometimes unable to fill the regions near the bases of the protrusions on the substrate surface, meaning voids can develop, whereas if the adhesive layer is thin, then the uneven shape of the substrate surface is reflected, and the substrate-side surface (back surface) of the film for protective film formation also becomes an uneven surface. In these types of cases where the filling and coating of the uneven shape of the substrate surface by the adhesive layer is inadequate, if laser printing of the protective film is conducted in the manner described above, then the printing becomes indistinct, and a distinct examination image of the semiconductor wafer or semiconductor chip can also not be obtained. However, if the adhesive layer is too thick, then the adhesive layer is prone to vibration, for example during cutting in the dicing step, and therefore the semiconductor chips and the

semiconductor wafer undergoing cutting to produce the semiconductor chips are also likely to vibrate, resulting in the application of unwanted forces to the semiconductor chips, and an increased likelihood of cracks or chips occurring (namely, an increased likelihood of chipping). In this manner, various problems can easily arise when providing an adhesive layer on the uneven surface of a substrate.

However, in the composite sheet for protective film formation 101 of the present invention, the first surface 11a of the substrate 11 on which the adhesive layer 12 is provided has a surface roughness of $0.4\text{ }\mu\text{m}$ or less, indicating a high level of smoothness (a low degree of unevenness), and therefore the types of problems described above can be avoided. In other words, in the composite sheet for protective film formation 101, the first surface 11a of the substrate 11 can be satisfactorily filled and coated by the adhesive layer 12, and because there is no need to form the adhesive layer 12 as a thick layer, chipping can be suppressed.

[0029]

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

With the exceptions of having a different shape for the film for protective film formation and not including a jig adhesive layer, the illustrated composite sheet for protective film formation 102 is the same as the composite sheet for protective film formation 101 illustrated in FIG. 2. In other words, the composite sheet for protective film formation 102 has an adhesive layer 12 provided on the substrate 11, and a film for protective film formation 23 provided on the adhesive layer 12, and also has a release film 15 provided on the film for protective film formation 23.

[0030]

The film for protective film formation 23 is laminated to a portion of the first surface 12a of the adhesive layer 12, namely a central region in the width direction (the left-right direction in FIG. 3) of the supporting sheet 1.

Further, a release film 15 is laminated to the portion of the first surface 12a of the adhesive layer 12 to which the film for protective film formation 23 is not laminated, and to the surfaces (a first surface 23a and a side surface 23c) of the film for protective film formation 23 that do not contact the adhesive layer 12. Here, the first surface 23a of the film for protective film formation 23 is the surface of the film for protective film formation 23 on the opposite side from the side that contacts the adhesive layer 12, and in some cases, the boundary between the first surface 23a and the side surface 23c of the film for protective film formation 23 may not be able to be clearly distinguished. Furthermore, the release film 15 may sometimes not contact the side surface 23c of the film for protective film formation 23. The composite sheet for protective film formation 102 is usually stored in this state, with the release film 15 attached.

[0031]

The composite sheet for protective film formation 102 is used in a state where the release film 15 has been removed, by affixing the first surface 23a of the film for protective film formation 23 to the back surface of a semiconductor wafer (not shown in the figure), and affixing the portion of the first surface 12a of the adhesive layer 12 to which the film for protective film formation 23 has not been laminated to a jig such as a ring frame.

[0032]

In the composite sheet for protective film formation 102, the surface roughness of the first surface 11a of the substrate 11 is $0.4\text{ }\mu\text{m}$ or less, and the surface roughness of the second surface 11b is greater than the surface roughness of the first surface 11a of the

substrate 11, and is from 0.053 to 0.48 μm . As a result, in a similar manner to the composite sheet for protective film formation 101, with the composite sheet for protective film formation 102, suppression of blocking, distinct laser printing to the protective film, and acquisition of a distinct examination image of the semiconductor wafer or semiconductor chip can all be achieved without the problems of unsatisfactory filling and coating of the first surface 11a of the substrate 11 by the adhesive layer 12, and the occurrence of chipping.

[0033]

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

With the exception that a jig adhesive layer 14 is also laminated to the portion of the first surface 12a of the adhesive layer 12 to which the film for protective film formation 23 has not been laminated, namely the region near the periphery, the illustrated composite sheet for protective film formation 103 is the same as the composite sheet for protective film formation 102 illustrated in FIG. 3.

[0034]

The composite sheet for protective film formation 103 is used in a state where the release film 15 has been removed, by affixing the first surface 23a of the film for protective film formation 23 to the back surface of a semiconductor wafer (not shown in the figure), and affixing the first surface 14a of the jig adhesive layer 14 to a jig such as a ring frame.

[0035]

In the composite sheet for protective film formation 103, the surface roughness of the first surface 11a of the substrate 11 is 0.4 μm or less, and the surface roughness of the

second surface 11b is greater than the surface roughness of the first surface 11a of the substrate 11, and is from 0.053 to 0.48 μm . As a result, in a similar manner to the composite sheet for protective film formation 101, with the composite sheet for protective film formation 103, suppression of blocking, distinct laser printing to the protective film, and acquisition of a distinct examination image of the semiconductor wafer or semiconductor chip can all be achieved without the problems of unsatisfactory filling and coating of the first surface 11a of the substrate 11 by the adhesive layer 12, and the occurrence of chipping.

[0036]

The composite sheet for protective film formation of the present invention is not limited to the structures illustrated in FIGS. 2 to 4, and structures in which a portion of one of the structures illustrated in one of FIGS. 2 to 4 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.

Next is a description of the composition of each layer of the supporting sheet and the composite sheet for protective film formation of the present invention.

[0037]

◎ Substrate

The surface roughness of the surface (the first surface) of the substrate on the side on which the adhesive layer is provided is 0.4 μm or less, and for example, may be set to any one of 0.37 μm or less, 0.3 μm or less, 0.2 μm or less, 0.1 μm or less, 0.09 μm or less, 0.08 μm or less, 0.07 μm or less, or 0.06 μm or less or the like, but these are merely examples.

There are no particular limitations on the lower limit for the surface roughness of the first surface of the substrate, and for example the surface roughness may be 0.01 μm or greater, but this is merely one example.

Examples of preferred ranges for the surface roughness of the first surface include ranges from 0.01 to 0.4 μm , from 0.01 to 0.37 μm , from 0.01 to 0.3 μm , from 0.01 to 0.2 μm , from 0.01 to 0.1 μm , from 0.01 to 0.09 μm , from 0.01 to 0.08 μm , from 0.01 to 0.07 μm , and from 0.01 to 0.06 μm .

[0038]

The surface roughness of the surface (the second surface) of the substrate on the opposite side from the side on which the adhesive layer is provided is from 0.053 to 0.48 μm , and within this range, the surface roughness may be set, for example, to at least 0.055 μm , at least 0.08 μm , at least 0.15 μm , at least 0.25 μm , or at least 0.35 μm or the like, and may be set to not more than 0.47 μm , not more than 0.45 μm , not more than 0.35 μm , not more than 0.25 μm , or not more than 0.15 μm or the like, but these are merely examples.

Examples of preferred ranges for the surface roughness of the second surface include ranges from 0.053 to 0.47 μm , from 0.053 to 0.45 μm , from 0.053 to 0.35 μm , from 0.053 to 0.25 μm , and from 0.053 to 0.15 μm .

Other examples of preferred ranges for the surface roughness of the second surface include ranges from 0.055 to 0.48 μm , from 0.08 to 0.48 μm , from 0.15 to 0.48 μm , from 0.25 to 0.48 μm , and from 0.35 to 0.48 μm .

The surface roughness of the second surface must be greater than the surface roughness of the first surface.

[0039]

The substrate can be produced, for example, using a substrate that functions as the raw material (hereafter sometimes abbreviated as "the raw material substrate"), either by a method in which the smooth surface and the uneven surface are formed simultaneously, or a method in which the smooth surface and the uneven surface are formed separately.

[0040]

One example of a method for producing the substrate by forming the smooth surface and the uneven surface simultaneously is a method in which the raw material substrate is sandwiched between a pair of rollers having different degrees of smoothness on the roller surfaces, and then passing the raw material substrate between the two rollers while the rollers are rotated, thereby forming a smooth surface on the raw material substrate from the roller surface having a higher degree of smoothness (the smooth surface roller), and forming an uneven surface on the raw material substrate from the roller surface having a lower degree of smoothness (the uneven surface roller).

[0041]

On the other hand, one example of a method for producing the substrate by forming the smooth surface and the uneven surface separately is a method in which a raw material substrate having a surface roughness of $0.4\text{ }\mu\text{m}$ or less on one or both surfaces is used, one surface is designated as the final smooth surface (the surface having a surface roughness of $0.4\text{ }\mu\text{m}$ or less), and the other surface is subjected to a smoothing treatment or a roughening treatment to form an uneven surface (the surface having a surface roughness of 0.053 to $0.48\text{ }\mu\text{m}$) having a surface roughness that is greater than that of the smooth surface. In this method, an example of the method used for the smoothing treatment or roughening treatment is the so-called stamping method in which the raw

material substrate is pressed against an aforementioned smooth surface or uneven surface of a roller.

In those cases where, as described above, a smooth surface or an uneven surface is formed on the raw material substrate by transferring the shape of a roller surface or the like, the surface roughness of the substrate can be adjusted by altering the degree of smoothness of the smooth surface, or the degree of unevenness of the uneven surface, of the roller.

In the method described above, if necessary, the surface of the raw material substrate designated as the final smooth surface (the surface having a surface roughness of $0.4\text{ }\mu\text{m}$ or less) may also be subjected to a smoothing treatment or a roughening treatment to adjust the surface roughness to a value of $0.4\text{ }\mu\text{m}$ or less.

[0042]

A description was provided above of a method in which the smooth surface or uneven surface of a roller was used to adjust the surface roughness of one surface of the substrate to a value within a range from 0.053 to $0.48\text{ }\mu\text{m}$, but the pattern used to transfer the smooth surface or uneven surface is not limited to rollers, and other shapes such as plates and blocks may also be used.

Further, besides the stamping method described above, other examples of methods for performing a roughening treatment of the surface of the raw material substrate include sand blasting treatment methods and solvent treatment methods.

[0043]

Up until this point, a method has been described in which a raw material substrate having a surface roughness of $0.4\text{ }\mu\text{m}$ or less on one or both surfaces is used to produce a substrate for which the surface roughness of both surfaces satisfy the conditions

described above, but the substrate can also be produced, for example, using the method described below.

In other words, another method for producing the substrate is a method in which a raw material substrate having a surface roughness of at least $0.053\ \mu\text{m}$ on one or both surfaces is used, one surface is designated as the final uneven surface (the surface having a surface roughness of 0.053 to $0.48\ \mu\text{m}$), and the other surface is subjected to a smoothing treatment or a roughening treatment to form a smooth surface (the surface having a surface roughness of $0.4\ \mu\text{m}$ or less) having a surface roughness that is less than that of the uneven surface.

In this method, if necessary, the surface of the raw material substrate designated as the final uneven surface (the surface having a surface roughness of 0.053 to $0.48\ \mu\text{m}$) may also be subjected to a smoothing treatment or a roughening treatment to adjust the surface roughness to a value within a range from 0.053 to $0.48\ \mu\text{m}$.

[0044]

Among these options, a method in which a raw material substrate is used, and the smooth surface and the uneven surface are formed simultaneously is preferred as the method for producing the substrate.

[0045]

The constituent material for the substrate is preferably any of various types of resin, and these resins may be known materials.

However, the substrate preferably exhibits transmittance to light having a wavelength of $532\ \text{nm}$ and light having a wavelength of $1,600\ \text{nm}$. Light having a wavelength of $532\ \text{nm}$ is ideal for performing laser printing to the protective film, and light having a wavelength of $1,600\ \text{nm}$ is ideal for performing infrared examinations of the semiconductor wafer or semiconductor chips.

Moreover, in those cases where the adhesive layer described below is energy ray-curable, the substrate preferably also exhibits transmittance of light in the ultraviolet region.

The specific constituent material for the substrate will be described later.

[0046]

The constituent material for a single layer substrate may be composed of a single material or two or more materials, and in the case of two or more materials, the combination of materials and the ratio between the materials may be adjusted as desired.

[0047]

The tensile modulus of elasticity of the substrate is not particularly limited, but is preferably from 240 to 700 MPa, more preferably from 280 to 650 MPa, and particularly preferably from 320 to 600 MPa.

[0048]

The substrate may be composed of one layer (a single layer), or may be composed of a plurality of two or more layers. When the substrate is composed of a plurality of layers, the plurality of layers may be the same or different. In other words, 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. In those cases where the plurality of layers are mutually different, the combination of the plurality of layers is not particularly limited. In this description, the expression that the plurality of layers are mutually different is not limited to the case of the substrate, and means that at least one of the constituent material or the thickness of each layer is different from the other layers.

[0049]

The thickness of the substrate may be selected appropriately in accordance with the intended purpose, but is preferably from 15 to 300 μm and more preferably from 20

to 200 μm , and for example, may be from 30 to 160 μm or from 40 to 120 μm or the like. By ensuring that the thickness of the substrate falls within this type of range, the flexibility of the composite sheet for protective film formation and the fixability to a semiconductor wafer or semiconductor chip can be improved.

Here, "the thickness of the substrate" means the thickness of the overall substrate, and for example, the thickness of a substrate composed of a plurality of layers means the total thickness of all of the layers that constitute the substrate.

At least one surface of the substrate is a non-smooth surface having an uneven shape with a surface roughness of at least 0.053 μm , and the thickness of the substrate can be calculated more accurately in a region that includes a substrate protrusion, by including the tip of the protrusion as one measurement point.

[0050]

© Adhesive Layer

The adhesive layer may be a conventional layer, and there are no particular limitations. For example, the adhesive layer may be energy ray-curable or non-energy ray-curable.

In the present invention, the term "energy ray-curable" means a property wherein the material cures upon irradiation with energy rays. In contrast, a property wherein a material does not cure even when irradiated with energy rays is termed "non-energy ray-curable".

In the present invention, "energy rays" means rays among electromagnetic waves and charged particle beams that have an energy quantum, and specific examples include ultraviolet rays, radiation, and electron beams and the like.

Ultraviolet rays can be irradiated, for example, using a high-pressure mercury lamp, a fusion H lamp, a xenon lamp, a black light, or an LED lamp or the like as an

ultraviolet source. Electron beams can be generated and irradiated from an electron beam accelerator or the like.

[0051]

Examples of the constituent materials of the adhesive layer include adhesives such as adhesive resins, and crosslinking agents and the like.

The adhesive layer preferably exhibits transmittance of both light having a wavelength of 532 nm and light having a wavelength of 1,600 nm. Light having a wavelength of 532 nm is ideal for performing laser printing to the protective film, and light having a wavelength of 1,600 nm is ideal for performing infrared examinations of the semiconductor wafer or semiconductor chips.

[0052]

The adhesive layer is preferably either energy ray-curable or non-energy ray-curable, and is more preferably non-energy ray-curable.

[0053]

The storage modulus of the adhesive layer is not particularly limited, but typically, is preferably from 0.01 to 1,000 MPa, more preferably from 0.01 to 500 MPa, and particularly preferably from 0.01 to 300 MPa.

The storage modulus of the adhesive layer can be adjusted by altering the types of constituent components in the adhesive layer, or the amounts of those components.

In the present description, unless specifically stated otherwise, "the storage modulus of the adhesive layer" in those cases where the adhesive layer is a curable layer, means "the storage modulus of the adhesive layer prior to curing".

[0054]

The storage modulus of the adhesive layer is determined using the method described below.

In other words, two adhesive layers are bonded together to produce an adhesive layer laminate having a thickness of 800 μm , this laminate is stamped to form a circular test piece with a diameter of 10 mm, a measurement apparatus such as a viscoelasticity measurement device is used to impart a strain with a frequency of 1 Hz to the test piece, and the storage modulus is then measured within a range from -50 to 150°C, with the value of the storage modulus at 23°C being recorded as the aforementioned storage modulus of the adhesive layer.

[0055]

The adhesive layer may be composed of one layer (a single layer), or may be composed of a plurality of two or more layers. When the adhesive layer is composed of a plurality of layers, the plurality of layers may be the same or different. Here, the expression that "the plurality of layers may be the same or different" has the same meaning as that described above for the substrate. In those cases where the plurality of layers are mutually different, the combination of the plurality of layers is not particularly limited.

[0056]

The thickness of the adhesive layer may be selected appropriately in accordance with the intended purpose, but is preferably from 1 to 50 μm , more preferably from 1 to 40 μm , and particularly preferably from 1 to 30 μm . By ensuring that the thickness of the adhesive layer is at least as large as the above lower limit, the bonding strength of the adhesive layer to the film for protective film formation can be further improved. Moreover, the effect of the adhesive layer in filling and coating the uneven shape of the first surface of the substrate is also enhanced, and the effect of this uneven shape on the adhesive layer can be further reduced. On the other hand, by ensuring that the thickness

of the adhesive layer is not more than the above upper limit, the suppression effect on chipping is further enhanced, and the dicing step can be better stabilized.

[0057]

Here, "the thickness of the adhesive layer" means the thickness of the overall adhesive layer, and for example, the thickness of an adhesive layer composed of a plurality of layers means the total thickness of all of the layers that constitute the adhesive layer.

As described above, the surface roughness of the first surface of the substrate is $0.4\text{ }\mu\text{m}$ or less, and depending on the uneven shape of this surface, the surface of the adhesive layer on the side on which the substrate is provided (namely, the second surface) may sometimes be a non-smooth surface having an uneven shape with a surface roughness of $0.1\text{ }\mu\text{m}$ or greater. In such cases, the thickness of the adhesive layer can be calculated more accurately in a region that includes a protrusion in the adhesive layer, by including the tip of the protrusion as one measurement point.

[0058]

The hardness of the adhesive layer is preferably adjusted in accordance with the thickness of the layer. An example of an indicator that can be used for determining the hardness of the adhesive layer is the storage modulus described above.

[0059]

For example, in those cases where the thickness of the adhesive layer preferably exceeds $15\text{ }\mu\text{m}$ (is thicker than $15\text{ }\mu\text{m}$), or is more preferably $18\text{ }\mu\text{m}$ or greater, the storage modulus of the adhesive layer is preferably at least 30 kPa , more preferably at least 40 kPa , and particularly preferably 50 kPa or greater. The upper limit for the storage modulus of the adhesive layer in this case may be the same as the upper limit described above for a typical case. In this manner, if the adhesive layer is comparatively

hard, then even if the adhesive layer is thick, the adhesive layer is unlikely to vibrate during cutting in the dicing step. As a result, the semiconductor chips and the semiconductor wafer undergoing cutting to produce the semiconductor chips are also unlikely to vibrate, meaning application of unwanted forces to the semiconductor chips or semiconductor wafer, resulting in an increased likelihood of cracks or chips occurring in the semiconductor chips, namely so-called chipping, can be suppressed.

[0060]

On the other hand, in those cases where the thickness of the adhesive layer is preferably 15 μm or less, or more preferably an even thinner value of 10 μm or less, there are no particular limitations on the storage modulus of the adhesive layer. In this case, even if the adhesive layer is comparatively soft, the adhesive layer is unlikely to vibrate during cutting in the dicing step, and therefore similar effects can be obtained to those described above for the case in which the adhesive layer is comparatively hard but thick.

In this case (where the adhesive layer is thin), the storage modulus of the adhesive layer may be set to a value within the typical range described above, but this is merely one example. However, even in this case, in order to further enhance the chipping suppression effect, the storage modulus of the adhesive layer is preferably set to a value within the range described above for the case where the adhesive layer is thick.

[0061]

In other words, in the supporting sheet, by ensuring that the thickness of the adhesive layer is preferably not more than 15 μm , and more preferably 10 μm or less, a superior chipping suppression effect can be obtained without being affected by the storage modulus of the adhesive layer.

[0062]

The adhesive layer can be formed using an adhesive composition containing an adhesive. For example, the adhesive layer can be formed in the targeted region by applying the adhesive composition to the formation target surface for the adhesive layer, and then performing drying as necessary. A more specific method for forming the adhesive layer is described below in further detail, together with the method for forming other layers. 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.

[0063]

The adhesive composition 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 necessary.

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 appropriately from among conventional methods such as methods in which mixing is performed by rotation of 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 taken 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.

[0064]

Application of the adhesive 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.

[0065]

There are no particular limitations on the drying conditions for the adhesive composition, but in those cases where the adhesive composition contains a solvent described below, drying by heating is preferred. An adhesive composition containing a solvent is preferably dried, for example, under conditions of 70 to 130°C for 10 seconds to 5 minutes.

[0066]

Examples of supporting sheets containing a substrate and an adhesive layer composed of the types of materials described above include adhesive sheets composed of a substrate film and an adhesive layer formed thereon, as disclosed in Japanese Patent (Granted) Publication No. 4805549, adhesive sheets composed of a substrate film and an adhesive layer formed thereon, as disclosed in Japanese Patent (Granted) Publication No. 4781633, dicing sheets containing a substrate and an adhesive layer laminated to at least one surface of the substrate, as disclosed in Japanese Patent (Granted) Publication No. 5414953, and sheets for work processing having a pressure-sensitive adhesive resin layer (an adhesive layer) on at least one surface of a substrate, as disclosed in Japanese Unexamined Patent Application, First Publication No. 2013-199562.

The supporting sheet of the present invention is preferably a sheet in which the constituent materials are the same as these sheets, and in which the surface roughness of

the first surface and the second surface have been adjusted to values within the above numerical ranges.

[0067]

© Film for Protective Film Formation

The film for protective film formation has curability, and forms a protective film upon curing.

The film for protective film formation may be either heat-curable or energy ray-curable.

[0068]

○ Heat-Curable Film for Protective Film Formation

An example of a preferred heat-curable film for protective film formation contains a polymer component (A) and a heat-curable component (B). The polymer component (A) is a component that can be 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.

[0069]

The heat-curable film for protective film formation may be composed of one layer (a single layer), or may be composed of a plurality of two or more layers. When the heat-curable film for protective film formation is composed of a plurality of layers, the plurality of layers may be the same or different. Here, the expression that "the plurality of layers may be the same or different" has the same meaning as that described above for the substrate. In those cases where the plurality of layers are mutually different, the combination of the plurality of layers is not particularly limited.

[0070]

The thickness of the heat-curable film for protective film formation is preferably from 1 to 100 μm , more preferably from 5 to 75 μm , and particularly preferably from 5 to 50 μm . By ensuring that the thickness of the heat-curable film for protective film formation is at least as large as the above lower limit, a protective film having a superior protective function can be formed. Further, by ensuring that the thickness of the heat-curable film for protective film formation is not more than the above upper limit, the protective film can be prevented from becoming excessively thick.

Here, "the thickness of the heat-curable film for protective film formation" means the thickness of the overall heat-curable film for protective film formation, and for example, the thickness of a heat-curable film for protective film formation composed of a plurality of layers means the total thickness of all of the layers that constitute the heat-curable film for protective film formation.

[0071]

The curing conditions when affixing the heat-curable film for protective film formation to the back surface of a semiconductor wafer, and then curing the film to form a protective film are not particularly limited, provided the degree of curing is sufficient to enable the resulting protective film to function satisfactorily, and these curing conditions may be selected appropriately in accordance with the type of heat-curable film for protective film formation being used.

For example, the heating temperature during curing of the heat-curable film for protective film formation is preferably from 100 to 200°C, more preferably from 110 to 180°C, and particularly preferably from 120 to 170°C. The heating time during curing is preferably from 0.5 to 5 hours, more preferably from 0.5 to 3 hours, and particularly preferably from 1 to 2 hours.

[0072]

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

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

[0073]

Application of the composition for heat-curable protective film formation can be performed, for example, using the same methods as those described above for application of the adhesive composition.

[0074]

The drying conditions for the composition for heat-curable protective film formation are not particularly limited, but in those cases where the composition for heat-curable protective film formation has a solvent described below, drying by heating is preferred. A composition for heat-curable protective film formation containing a solvent is preferably dried, for example, under conditions of 70 to 130°C for 10 seconds to 5 minutes.

[0075]

<Composition for Heat-Curable Protective Film Formation (III-1)>

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

[0076]

[Polymer Component (A)]

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

The polymer component (A) contained in the composition (III-1) and the film for protective film formation 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.

[0077]

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

[0078]

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

"acrylic acid" and "methacrylic acid", and "(meth)acrylate" is deemed to include both "acrylate" and "methacrylate".

[0079]

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. By ensuring that 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 film for protective film formation improves. Further, by ensuring that the weight average molecular weight of the acrylic-based resin is not more than the above upper limit, the heat-curable film for protective film formation 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 film for protective film formation.

In this description, unless specifically stated otherwise, the weight average molecular weight represents the polystyrene-equivalent value measured by a gel permeation chromatography (GPC) method.

[0080]

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 supporting sheet (adhesive layer) is suppressed, thus improving the releasability of the supporting 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 film for protective film formation and the protective film adherend can be increased.

[0081]

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.

[0082]

Examples of the (meth)acrylate ester 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 (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (stearyl (meth)acrylate);

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 dicyclopentenyoxyethyl (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.

[0083]

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.

[0084]

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.

[0085]

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 composite sheet for protective film formation.

[0086]

In the present invention, a thermoplastic resin other than an acrylic-based resin (hereafter sometimes abbreviated as simply "the thermoplastic resin") may be used alone without using an acrylic-based resin, or 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 supporting sheet and make the heat-curable film for protective film formation 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 film for protective film formation.

[0087]

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.

[0088]

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.

[0089]

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

[0090]

The thermoplastic resin contained in the composition (III-1) and the heat-curable film for protective film formation 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.

[0091]

In the composition (III-1), regardless of the type of polymer component (A), the proportion of the amount of the polymer component (A) relative to the total mass of all the components besides the solvent (namely, the amount of the polymer component (A) in the heat-curable film for protective film formation) is preferably from 5 to 85% by mass, and more preferably from 5 to 80% by mass, and for example, may be any one of 10 to 70% by mass, 20 to 60% by mass, or 30 to 50% by mass.

[0092]

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

[0093]

[Heat-Curable Component (B)]

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

The heat-curable component (B) contained in the composition (III-1) and the heat-curable film for protective film formation 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.

[0094]

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

[0095]

(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 composition (III-1) and the heat-curable film for protective film formation 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.

[0096]

- Epoxy Resin (B1)

Examples of the epoxy resin (B1) include conventional resins such as polyfunctional epoxy resins, biphenyl compounds, bisphenol A diglycidyl 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.

[0097]

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 semiconductor chips with a protective film obtained using the composite sheet for protective film formation can be improved.

[0098]

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 group.

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.

[0099]

The number average molecular weight of the epoxy resin (B1) is not particularly limited, but from the viewpoints of the curability of the heat-curable film for protective film formation, 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.

The epoxy equivalent weight of the epoxy resin (B1) is preferably from 100 to 1,000 g/eq, and more preferably from 150 to 950 g/eq.

[0100]

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.

[0101]

- 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.

[0102]

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.

[0103]

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 having 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.

[0104]

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 supporting sheet, the heat curing agent (B2) preferably has a high value for the softening point or glass transition temperature.

[0105]

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.

[0106]

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.

[0107]

In the composition (III-1) and the heat-curable film for protective film formation, the amount of the heat curing agent (B2), per 100 parts by mass of the epoxy resin (B1), is preferably from 0.1 to 500 parts by mass, and more preferably from 1 to 200 parts by mass, and for example, may be from 1 to 100 parts by mass, from 1 to 50 parts by mass, or from 1 to 25 parts by mass. 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 film for protective film formation 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 film for protective film formation is reduced, and the reliability of a package obtained using the composite sheet for protective film formation can be further improved.

[0108]

In the composition (III-1) and the heat-curable film for protective film formation, the amount of the heat-curable component (B) (for example, the total amount of the epoxy resin (B1) and the heat curing agent (B2)), per 100 parts by mass of the polymer component (A), is preferably from 20 to 500 parts by mass, more preferably from 30 to 300 parts by mass, and particularly preferably from 40 to 150 parts by mass, and for example, may be from 40 to 125 parts by mass, from 40 to 100 parts by mass, or from 40 to 75 parts by mass. 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 supporting sheet is suppressed, thus improving the releasability of the supporting sheet.

[0109]

[Curing Accelerator (C)]

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

[0110]

The curing accelerator (C) contained in the composition (III-1) and the heat-curable film for protective film formation 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.

[0111]

In those cases where the curing accelerator (C) is used, the amount of the curing accelerator (C) in the composition (III-1) and the heat-curable film for protective film formation is preferably from 0.01 to 10 parts by mass, and more preferably from 0.1 to 7 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) to 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 film for protective film formation to the bonding interface with the adherend under conditions of high temperature and high humidity, meaning the reliability of semiconductor chips with a protective film obtained using the composite sheet for protective film formation can be further improved.

[0112]

[Filler (D)]

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

[0113]

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 silica or alumina.

[0114]

The filler (D) contained in the composition (III-1) and the heat-curable film for protective film formation 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.

[0115]

In those cases where the filler (D) is used, the proportion of the amount of the filler (D) relative to the total mass of all the components besides the solvent in the composition (III-1) (namely, the amount of the filler (D) in the heat-curable film for protective film formation) is preferably from 5 to 80% by mass, and more preferably from 7 to 60% by mass, and for example, may be any one of 10 to 50% by mass, 15 to 45% by mass, or 20 to 40% 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.

[0116]

[Coupling Agent (E)]

The composition (III-1) and the heat-curable film for protective film formation 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 film for protective film formation to adherends can be improved. Further, by using the coupling agent (E), the protective

film obtained by curing the heat-curable film for protective film formation exhibits improved water resistance without losing any heat resistance.

[0117]

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.

[0118]

The coupling agent (E) contained in the composition (III-1) and the heat-curable film for protective film formation 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.

[0119]

In those cases where the coupling agent (E) is used, the amount of the coupling agent (E) in the composition (III-1) and the heat-curable film for protective film formation 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 film for protective film formation 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.

[0120]

[Crosslinking Agent (F)]

In those cases where a compound 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 such as the aforementioned acrylic-based resin is used as the polymer component (A), the composition (III-1) and the heat-curable film for protective film formation may also include a crosslinking agent (F). The crosslinking agent (F) is a component that is used to achieve crosslinking by bonding the functional group in the polymer component (A) to another compound, and by performing crosslinking in this manner, the initial adhesive strength and the cohesion of the heat-curable film for protective film formation can be adjusted.

[0121]

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).

[0122]

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 an aromatic polyvalent isocyanate compound or the like with a polyol compound. The above term "adduct" means a reaction product of an aforementioned aromatic polyvalent isocyanate compound, aliphatic polyvalent isocyanate compound or alicyclic polyvalent isocyanate compounds with a low-molecular weight active hydrogen-containing compound such as ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane or castor oil. A specific example is a xylylene diisocyanate adduct of trimethylolpropane described below. Further, an "isocyanate-terminated urethane prepolymer" is as described above.

[0123]

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.

[0124]

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.

[0125]

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 film for protective film formation.

[0126]

The crosslinking agent (F) contained in the composition (III-1) and the heat-curable film for protective film formation 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.

[0127]

In those cases where the crosslinking agent (F) is used, the amount of the crosslinking agent (F) in the 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 effects 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, excessive use of the crosslinking agent (F) is suppressed.

[0128]

[Energy Ray-Curable Resin (G)]

The 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 film for protective film formation can be altered by irradiation with energy rays.

[0129]

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.

[0130]

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

[0131]

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.

[0132]

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.

[0133]

The energy ray-curable resin (G) contained in the 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.

[0134]

In those cases where the energy ray-curable resin (G) is used, the amount of the energy ray-curable resin (G) in the composition (III-1) is preferably from 1 to 95% by mass, more preferably from 5 to 90% by mass, and particularly preferably from 10 to 85% by mass.

[0135]

[Photopolymerization Initiator (H)]

In those cases where the 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.

[0136]

Examples of the photopolymerization initiator (H) in the composition (III-1) include benzoin compounds such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin benzoic acid, methyl benzoin benzoate, and benzoin dimethyl ketal; acetophenone compounds such as acetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, and 2,2-dimethoxy-1,2-diphenylethan-1-one; acyl phosphine oxides such as bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide

and 2,4,6-trimethylbenzoyldiphenylphosphine oxide; sulfide compounds such as benzyl phenyl sulfide and tetramethylthiuram monosulfide; α -ketol compounds such as 1-hydroxycyclohexyl phenyl ketone; azo compounds such as azobisisobutyronitrile; titanocene compounds such as titanocene; thioxanthone compounds such as thioxanthone; peroxide compounds; diketone compounds such as diacetyl; as well as benzil, benzophenone, 2,4-diethylthioxanthone, 1,2-diphenylmethane, 2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone, and 2-chloroanthraquinone.

Further examples of the photopolymerization initiator include quinone compounds such as 1-chloroanthraquinone; and photosensitizers such as amines.

[0137]

The photopolymerization initiator (H) contained in the 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.

[0138]

In those cases where the photopolymerization initiator (H) is used, the amount of the photopolymerization initiator (H) in the 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).

[0139]

[Colorant (I)]

The composition (III-1) and the heat-curable film for protective film formation 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.

[0140]

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, dioxazine-based colorants, naphthol-based colorants, azomethine-based colorants, benzimidazolone-based colorants, pyranthrone-based colorants, and threne-based colorants.

[0141]

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.

[0142]

The colorant (I) contained in the composition (III-1) and the heat-curable film for protective film formation 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.

[0143]

In those cases where the colorant (I) is used, the amount of the colorant (I) in the heat-curable film for protective film formation may be set appropriately in accordance with the intended purpose. For example, by adjusting the amount of the colorant (I) in the heat-curable film for protective film formation to adjust the light transmittance of the protective film, the printing legibility can be adjusted in those cases where laser printing is performed on the protective film. Further, by adjusting the amount of the colorant (I) in the heat-curable film for protective film formation, 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 proportion of the amount of the colorant (I) relative to the total mass of all the components besides the solvent in the composition (III-1) (namely, the amount of the colorant (I) in the heat-curable film for protective film formation) 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, by ensuring that the amount of the colorant (I) is not more than the above upper limit, any excessive reduction in the light transmittance of the heat-curable film for protective film formation can be suppressed.

[0144]

[General-Purpose Additives (J)]

The composition (III-1) and the heat-curable film for protective film formation 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.

[0145]

Either a single general-purpose additive or two or more general-purpose additives may be included in the composition (III-1) and the heat-curable film for protective film formation, 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 in the composition (III-1) and the heat-curable film for protective film formation, and the amount may be selected appropriately in accordance with the intended purpose.

[0146]

[Solvent]

The composition (III-1) preferably also includes a solvent. A 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; 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 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.

[0147]

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

[0148]

<<Method for Producing Composition for Heat-Curable Protective Film Formation>>

The composition for heat-curable protective film formation such as the 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.

[0149]

○ Energy Ray-Curable Film for Protective Film Formation

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

In the energy ray-curable film for protective film formation, 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.

[0150]

The energy ray-curable film for protective film formation may be composed of only one layer (a single layer), or may be composed of 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 there are no particular limitations on the combination of the plurality of layers.

[0151]

The thickness of the energy ray-curable film for protective film formation is preferably from 1 to 100 μm , more preferably from 5 to 75 μm , and particularly preferably from 5 to 50 μm . By ensuring that the thickness of the energy ray-curable film for protective film formation is at least as large as the above lower limit, a protective film having a superior protective function can be formed. Further, by ensuring that the thickness of the energy ray-curable film for protective film formation is not more than the above upper limit, the protective film can be prevented from becoming excessively thick.

Here, "the thickness of the energy ray-curable film for protective film formation" means the thickness of the overall energy ray-curable film for protective film formation, and for example, the thickness of an energy ray-curable film for protective film formation composed of a plurality of layers means the total thickness of all of the layers that constitute the energy ray-curable film for protective film formation.

[0152]

The curing conditions when affixing the energy ray-curable film for protective film formation to the back surface of a semiconductor wafer, and then curing the film to form a protective film are not particularly limited, provided the degree of curing is sufficient to enable the resulting protective film to function satisfactorily, and these curing conditions may be selected appropriately in accordance with the type of energy ray-curable film for protective film formation being used.

For example, the energy ray illuminance when curing the energy ray-curable film for protective film formation is preferably from 120 to 280 mW/cm². Further, the energy ray irradiation dose during curing is preferably from 200 to 1,000 mJ/cm².

[0153]

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

The energy ray-curable film for protective film formation can be formed from a composition for energy ray-curable protective film formation containing the constituent materials for the energy ray-curable film for protective film formation. For example, by applying the composition for energy ray-curable protective film formation to a formation target surface for the energy ray-curable film for protective film formation, and then performing drying as necessary, the energy ray-curable film for protective film formation can be formed in the targeted region. The ratio between the amounts of those components within the composition for energy ray-curable protective film formation 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 film for protective film formation. Here, "normal temperature" is as defined above.

[0154]

Application of the composition for energy ray-curable protective film formation may be performed, for example, using the same methods as those described above for application of the adhesive composition.

[0155]

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

[0156]

<Composition for Energy Ray-Curable Protective Film Formation (IV-1)>

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

[0157]

[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 film for protective film formation with film forming characteristics and flexibility, as well as forming the hard protective film upon curing.

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

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.

[0158]

(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 a 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.

[0159]

Examples of the aforementioned functional group 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.

[0160]

- 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, and the polymerization method may employ a conventional method.

[0161]

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.

[0162]

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 (unsaturated alcohols not having a (meth)acryloyl skeleton) such as vinyl alcohol and allyl alcohol.

[0163]

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

[0164]

The acrylic-based monomer having the functional group is preferably a hydroxyl group-containing monomer.

[0165]

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.

[0166]

Examples of the aforementioned acrylic-based monomer not having the functional group 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, 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 (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (stearyl (meth)acrylate).

[0167]

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.

[0168]

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.

[0169]

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

[0170]

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.

[0171]

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.

[0172]

In the composition for resin layer formation (IV-1), the proportion of the amount of the acrylic-based resin (a1-1) relative to the total mass of all the components besides the solvent (namely, the amount of the acrylic-based resin (a1-1) in the energy ray-curable film for protective film formation) is preferably from 1 to 70% by mass, more preferably from 5 to 60% by mass, and particularly preferably from 10 to 50% by mass, and for example, may be from 15 to 50% by mass, from 25 to 50% by mass, or from 35 to 50% by mass.

[0173]

- 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.

[0174]

The energy ray-curable compound (a12) preferably has 1 to 5, and more preferably 1 to 3, of the energy ray-curable groups within a single molecule.

[0175]

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.

[0176]

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.

[0177]

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 mol%, 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 mol%.

[0178]

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.

[0179]

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.

[0180]

The polymer (a1) contained in the composition (IV-1) and the energy ray-curable film for protective film formation 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.

[0181]

(Compound (a2) having an Energy Ray-Curable Group and having a 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 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.

[0182]

The compound (a2) is not particularly limited, provided it satisfies the conditions described above, and examples 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.

[0183]

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 polypropylene 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.

[0184]

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, are treated as the aforementioned compound (a2).

[0185]

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.

[0186]

The compound (a2) contained in the composition (IV-1) and the energy ray-curable film for protective film formation 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.

[0187]

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

In those cases where the composition (IV-1) and the energy ray-curable film for protective film formation 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.

[0188]

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)")

[0189]

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).

[0190]

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.

[0191]

Examples of the above alkyl (meth)acrylate esters 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 (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (stearyl (meth)acrylate).

[0192]

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 dicyclopentenyoxyethyl (meth)acrylate.

[0193]

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.

[0194]

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

[0195]

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, amino group, or the like, 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, amide group or the like, 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.

[0196]

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). 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.

[0197]

In the polymer (b) having a reactive functional group, the proportion (amount) of structural units 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.

[0198]

In terms of achieving more favorable film forming characteristics for the composition (IV-1), the weight average molecular weight (M_w) 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.

[0199]

The polymer (b) not having an energy ray-curable group contained in the composition (IV-1) and the energy ray-curable film for protective film formation 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.

[0200]

Examples of the 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 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 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).

[0201]

In those cases where the 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 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.

[0202]

In the composition (IV-1), the proportion represented by 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 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 film for protective film formation) 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 the energy ray-curable component falls within this type of range makes the energy ray-curability of the energy ray-curable film for protective film formation more favorable.

[0203]

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

[0204]

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

[0205]

In the composition (IV-1) for each of the heat-curable component, filler, coupling agent, crosslinking agent, photopolymerization initiator, colorant 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.

The amounts of the heat-curable components, fillers, coupling agents, crosslinking agents, photopolymerization initiators, colorants and general-purpose additives in the composition (IV-1) may be set appropriately in accordance with the intended purpose, and there are no particular limitations.

[0206]

Because the handling of the composition (IV-1) improves upon dilution, the composition preferably also contains a solvent.

Examples of the solvent contained in the composition (IV-1) include the same solvents as those mentioned above for use in the composition (III-1).

The solvent contained in the composition (IV-1) may be a single solvent or two or more solvents.

[0207]

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

The energy-curable composition for protective film formation such as the 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.

[0208]

◇ Method for Producing Supporting Sheet, Method for Producing Composite Sheet for Protective Film Formation

The supporting sheet and the composite sheet for protective film formation described above can be produced by sequentially laminating the various layers described

above to achieve the desired positional relationships between the layers. The method used for forming each layer is as described above.

For example, when producing the supporting sheet, when laminating the adhesive layer to the substrate, the adhesive composition described above may be applied to the substrate, with drying then performed if necessary.

[0209]

On the other hand, when producing the composite sheet for protective film formation, when the film for protective film formation is laminated onto the adhesive layer that has already been laminated to the substrate, the film for protective film formation can be formed directly by coating the composition for heat-curable protective film formation or the composition for energy ray-curable protective film formation onto the adhesive layer. In these cases where one of the compositions is used to form a continuous two-layer laminated structure, an additional composition may be applied to the layer formed from the above composition to form another new layer. However, it is preferable that the continuous two-layer laminated structure is produced by forming the second of these two laminated layers in advance by application of the composition to a separate release film, and then subsequently affixing the exposed surface of this preformed layer, on the opposite side from the side that contacts the release film, to the exposed surface of the other layer that has already been formed. In this case, the above composition is preferably applied to a release-treated surface of the release film. The release film may be removed if necessary after formation of the laminated structure.

[0210]

In other words, when producing the composite sheet for protective film formation, the composite sheet for protective film formation can be obtained by laminating the adhesive layer to the substrate by applying the adhesive composition to

the substrate and performing drying as necessary, forming the film for protective film formation separately on a release film by applying the composition for heat-curable protective film formation or the composition for energy ray-curable protective film formation to a release film and performing drying as necessary, and then affixing the exposed surface of the film for protective film formation to the exposed surface of the adhesive layer laminated to the substrate, thereby laminating the film for protective film formation to the adhesive layer.

[0211]

On the other hand, when laminating the adhesive layer to the substrate, instead of using the method of applying the adhesive composition to the substrate, the adhesive layer may also be laminated to the substrate by first forming the adhesive layer on a release film by applying the adhesive composition to the release film and performing drying as necessary, and subsequently affixing the exposed surface of this adhesive layer to one surface of the substrate.

In either method, the release film may be removed at any arbitrary timing following formation of the target laminated structure.

[0212]

In this manner, any of the layers besides the substrate (namely, the adhesive layer or the film for protective film formation) that constitute the composite sheet for protective film formation may be formed in advance on a release film, and then laminated using a method in which the exposed surface is affixed to the surface of the target layer, and the composite sheet for protective film formation may be produced by appropriately selecting, as necessary, the layers for which these types of steps are employed.

[0213]

However, in the present invention, in those cases where the surface roughness of the surface of the substrate to which the adhesive layer is laminated, namely the first surface, is from 0.1 to 0.4 μm or is a value close to this range, meaning the degree of unevenness of the surface cannot be ignored, the adhesive layer is preferably formed (thereby forming the supporting sheet) by the method in which the adhesive composition is applied to the substrate. This is because if an adhesive layer that has been formed in advance is affixed to this type of uneven surface, then the adhesive layer tends to be unable to fill the regions near the bases of the protrusions on the surface, meaning voids develop, and the filling and coating of the surface (the first surface) by the adhesive layer is inadequate. If this type of inadequate filling and coating of the first surface occurs, then the types of problems described above tend to occur.

[0214]

In contrast, when the adhesive layer is formed by applying an adhesive composition to the first surface of the substrate, because the adhesive composition has fluidity, the composition readily fills even the regions near the bases of the protrusions on the first surface, and as a result, these regions are satisfactorily coated with the adhesive layer, enabling occurrence of the types of problems described above to be well suppressed. However, when affixing the adhesive layer to the first surface of the substrate, occurrence of the voids described above can also be suppressed by heating and softening the adhesive layer. Accordingly, in some cases the method in which an adhesive layer that has been formed in advance is affixed to the first surface may also be used.

[0215]

The composite sheet for protective film formation is typically stored in a state where a release film has been affixed to the surface of the outermost layer on the

opposite side from the supporting sheet (for example, the film for protective film formation). Accordingly, the composite sheet for protective film formation can also be obtained by applying the composition for forming the layer that constitutes the outermost layer, such as the composition for heat-curable protective film formation or the composition for energy ray-curable protective film formation, to this release film (preferably a release-treated surface of the release film) and performing drying as necessary to form the layer that constitutes the outermost layer on the release film, subsequently using one of the above methods to laminate each of the remaining layers to the exposed surface of this layer on the opposite side from the side that contacts the release film, and then not removing the release film, but rather keeping the release film affixed to the laminated structure.

EXAMPLES

[0216]

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.

The composition of each of the layers of the composite sheets for protective film formation described in the following examples and the like is shown below.

[0217]

<Substrate>

The substrates that constitute the supporting sheets are shown below.

Substrate Bm1: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, a

surface roughness (Ra) of the smooth surface of 0.05 μm , and a surface roughness (Ra) of the uneven surface of 0.1 μm .

Substrate Bm2: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, a surface roughness (Ra) of the smooth surface of 0.05 μm , and a surface roughness (Ra) of the uneven surface of 0.2 μm .

Substrate Bm3: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, a surface roughness (Ra) of the smooth surface of 0.05 μm , and a surface roughness (Ra) of the uneven surface of 0.3 μm .

Substrate Bm4: a substrate containing polybutylene terephthalate as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 500 MPa, a surface roughness (Ra) of the smooth surface of 0.05 μm , and a surface roughness (Ra) of the uneven surface of 0.3 μm .

Substrate Bm5: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, and a surface roughness (Ra) for both surfaces of 0.05 μm .

Substrate Bm6: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, a surface roughness (Ra) of the smooth surface of 0.05 μm , and a surface roughness (Ra) of the uneven surface of 0.5 μm .

Substrate Bm7: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, a surface roughness (Ra) of the smooth surface of 0.05 μm , and a surface roughness (Ra) of the uneven surface of 0.055 μm .

Substrate Bm8: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, a surface roughness (Ra) of the smooth surface of 0.03 μm , and a surface roughness (Ra) of the uneven surface of 0.4 μm .

Substrate Bm9: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, a surface roughness (Ra) of the smooth surface of 0.03 μm , and a surface roughness (Ra) of the uneven surface of 0.47 μm .

Substrate Bm10: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, a surface roughness (Ra) of the smooth surface of 0.35 μm , and a surface roughness (Ra) of the uneven surface of 0.4 μm .

Substrate Bm11: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, a surface roughness (Ra) of the smooth surface of 0.37 μm , and a surface roughness (Ra) of the uneven surface of 0.47 μm .

Substrate Bm12: a substrate containing polypropylene as the main constituent material, having a thickness of 80 μm , a tensile modulus of elasticity of 360 MPa, a surface roughness (Ra) of the smooth surface of 0.43 μm , and a surface roughness (Ra) of the uneven surface of 0.47 μm .

The above tensile modulus of elasticity and surface roughness values represent values measured using the methods described below.

[0218]

(Measurement of Substrate Tensile Modulus of Elasticity)

The substrate was cut to prepare a test piece, and the tensile modulus of elasticity (Young's modulus) of the test piece at 23°C was measured in accordance with JIS K 7161:1994. At this time, the width of the test piece during measurement was 15 mm, and the distance between the grippers was 100 mm.

(Measurement of Substrate Surface Roughness)

The surface roughness (Ra) values of the substrate surfaces 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 mm, and the evaluation length L_n set to 10 mm.

[0219]

<Adhesive Resin>

The adhesive resins used for forming the adhesive layers are shown below.

Adhesive resin (i)-1: an acrylic-based polymer obtained by copolymerizing n-butyl acrylate (hereafter abbreviated as "BA") (85 parts by mass) and 2-hydroxyethyl acrylate (hereafter abbreviated as "HEA") (15 parts by mass), weight average molecular weight: 600,000.

Adhesive resin (i)-2: an acrylic-based polymer obtained by copolymerizing 2-ethylhexyl acrylate (hereafter abbreviated as "2EHA") (30 parts by mass), isobornyl acrylate (hereafter abbreviated as "iBA") (50 parts by mass), and HEA (20 parts by mass), weight average molecular weight: 800,000.

[0220]

<Production Raw Materials for Compositions for Protective Film Formation>

The raw materials used in the production of the compositions for protective film formation are shown below.

[Polymer Component (A)]

(A)-1: an acrylic-based resin obtained by copolymerizing BA (10 parts by mass), methyl acrylate (70 parts by mass), glycidyl methacrylate (5 parts by mass) and HEA (15 parts by mass) (weight average molecular weight: 800,000, glass transition temperature: -1°C)

[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: 255 to 260 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 (3-glycidyloxypropyltrimethoxysilane)

(a silane coupling agent, KBM403, manufactured by Shin-Etsu Chemical Co., Ltd.,

methoxy equivalent weight: 12.7 mmol/g, molecular weight: 236.3)

[Crosslinking Agent (F)]

(F)-1: tolylene diisocyanate-based crosslinking agent (BHS 8515, manufactured

by TOYOCEM Co., Ltd.)

[Photopolymerization Initiator (H)]

Photopolymerization initiator (H)-1: 1-hydroxycyclohexyl phenyl ketone

(IRGACURE (a registered trademark) 184, manufactured by BASF Corporation)

[Colorant (I)]

(I)-1: a carbon black (MA600B, manufactured by Mitsubishi Chemical

Corporation, average particle size: 28 nm)

[Energy Ray-Curable Component (a)]

Energy ray-curable component (a)-1: an ultraviolet ray-curable acrylic-based

copolymer having methacryloyloxy groups as side chains, and having a weight average

molecular weight of 800,000 and a glass transition temperature of -10°C, obtained by

reacting an acrylic-based polymer obtained by copolymerizing 2EHA (80 parts by mass)

and HEA (20 parts by mass) with 2-methacryloyloxyethyl isocyanate (hereafter

sometimes abbreviated as "MOI") (an amount sufficient to provide a total number of

moles of isocyanate groups in the 2-methacryloyloxyethyl isocyanate that is 0.8 times the

total number of moles of hydroxyl groups derived from HEA in the acrylic-based

polymer).

[0221]

<Production of Composite Sheet for Protective Film Formation>

[Example 1]

(Production of Composition for Heat-Curable Protective Film Formation (III-1))

The polymer component (A)-1 (40 parts by mass), the epoxy resin (B1)-1 (5 parts by mass), the epoxy resin (B1)-2 (4 parts by mass), the epoxy resin (B1)-3 (10 parts by mass), the heat curing agent (B2)-1 (1 part by mass), the curing accelerator (C)-1 (1 part by mass), the filler (D)-1 (36 parts by mass), the coupling agent (E)-1 (1 part by mass) and the colorant (I)-1 (2 parts by mass) were mixed together and then diluted with sufficient methyl ethyl ketone to obtained a solid fraction concentration of 45% by mass, thus obtaining a composition for heat-curable protective film formation (III-1). The above blend amounts of all of the components except the methyl ethyl ketone represent solid fraction amounts.

[0222]

(Formation of Film for Protective film Formation)

The composition (III-1) obtained above was applied to the release-treated surface of a release film prepared by subjecting one surface of a polyethylene terephthalate film to a silicone release treatment (SP-PET381031, manufactured by Lintec Corporation, thickness: 38 μm), and the composition was then dried at 100°C for 3 minutes, thus forming a film for protective film formation Pf1 having a thickness of 25 μm .

[0223]

(Production of Adhesive Composition)

The adhesive resin (i)-1 (100 parts by mass) and the tolylene diisocyanate-based crosslinking agent (BHS 8515 manufactured by TOYOCEM Co., Ltd.) (1 part by mass) were mixed together and then diluted with sufficient methyl ethyl ketone to obtained a solid fraction concentration of 35% by mass, thus obtaining a non-energy-curable

adhesive composition (I-4)-1. The above blend amounts of all of the components except the methyl ethyl ketone represent solid fraction amounts.

[0224]

(Formation of Adhesive Layer, Production of Supporting Sheet)

The adhesive composition (I-4)-1 obtained above was applied to the smooth surface of the aforementioned substrate Bm1 having a surface roughness of 0.05 μm , and by drying the adhesive composition at 100°C for one minute, a non-energy-curable adhesive layer Ad1 having a thickness of 5 μm was formed, thus obtaining a supporting sheet Ss1.

[0225]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the obtained film for protective film formation Pf1 on the side not provided with the release film, and the exposed surface of the adhesive layer Ad1 of the supporting sheet Ss1 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm1, the adhesive layer Ad1, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm1 on the side on which the adhesive layer Ad1 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm1 on the opposite side from the side on which the adhesive layer Ad1 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 1.

[0226]

[Example 2]

With the exception of using a supporting sheet Ss2 obtained by altering the amount of the adhesive composition (I-4)-1 applied during formation of the adhesive layer, so as to form a non-energy-curable adhesive layer Ad2 having a thickness of 20 μm rather than 5 μm , the same method as Example 1 was used to produce a composite sheet for protective film formation.

In other words, this composite sheet for protective film formation was composed of the substrate Bm1, the adhesive layer Ad2, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm1 on the side on which the adhesive layer Ad2 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm1 on the opposite side from the side on which the adhesive layer Ad2 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 1.

[0227]

[Example 3]

(Production of Adhesive Composition)

The adhesive resin (i)-2 (100 parts by mass) and the tolylene diisocyanate-based crosslinking agent (BHS 8515 manufactured by TOYO CHEM Co., Ltd.) (10 parts by mass) were mixed together and then diluted with sufficient methyl ethyl ketone to obtain a solid fraction concentration of 35% by mass, thus obtaining a non-energy-curable adhesive composition (I-4)-2. The above blend amounts of all of the components except the methyl ethyl ketone represent solid fraction amounts.

[0228]

(Formation of Adhesive Layer, Production of Supporting Sheet)

The adhesive composition (I-4)-2 obtained above was applied to the smooth surface of the aforementioned substrate Bm1 having a surface roughness of 0.05 μm , and by drying the adhesive composition at 100°C for one minute, a non-energy-curable adhesive layer Ad3 having a thickness of 5 μm was formed, thus obtaining a supporting sheet Ss3.

[0229]

(Production of Composite Sheet for Protective Film Formation)

With the exception of using the supporting sheet Ss3 obtained above instead of the supporting sheet Ss1, the same method as Example 1 was used to produce a composite sheet for protective film formation.

In other words, this composite sheet for protective film formation was composed of the substrate Bm1, the adhesive layer Ad3, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm1 on the side on which the adhesive layer Ad3 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm1 on the opposite side from the side on which the adhesive layer Ad3 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 1.

[0230]

[Example 4]

(Production of Adhesive Composition)

The adhesive composition (I-4)-2 was obtained using the same method as Example 3.

[0231]

(Formation of Adhesive Layer, Production of Supporting Sheet)

The adhesive composition (I-4)-2 obtained above was applied to the smooth surface of the aforementioned substrate Bm2 having a surface roughness of 0.05 μm , and by drying the adhesive composition at 100°C for one minute, a non-energy-curable adhesive layer Ad3 having a thickness of 5 μm was formed, thus obtaining a supporting sheet Ss4.

[0232]

(Production of Composite Sheet for Protective Film Formation)

With the exception of using the supporting sheet Ss4 obtained above instead of the supporting sheet Ss1, the same method as Example 1 was used to produce a composite sheet for protective film formation.

In other words, this composite sheet for protective film formation was composed of the substrate Bm2, the adhesive layer Ad3, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm2 on the side on which the adhesive layer Ad3 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm2 on the opposite side from the side on which the adhesive layer Ad3 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 1.

[0233]

[Example 5]

(Production of Adhesive Composition)

The adhesive composition (I-4)-2 was obtained using the same method as Example 3.

[0234]

(Formation of Adhesive Layer, Production of Supporting Sheet)

The adhesive composition (I-4)-2 obtained above was applied to the smooth surface of the aforementioned substrate Bm3 having a surface roughness of 0.05 μm , and by drying the adhesive composition at 100°C for one minute, a non-energy-curable adhesive layer Ad3 having a thickness of 5 μm was formed, thus obtaining a supporting sheet Ss5.

[0235]

(Production of Composite Sheet for Protective Film Formation)

With the exception of using the supporting sheet Ss5 obtained above instead of the supporting sheet Ss1, the same method as Example 1 was used to produce a composite sheet for protective film formation.

In other words, this composite sheet for protective film formation was composed of the substrate Bm3, the adhesive layer Ad3, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm3 on the side on which the adhesive layer Ad3 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm3 on the opposite side from the side on which the adhesive layer Ad3 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 1.

[0236]

[Example 6]

(Production of Adhesive Composition)

The adhesive composition (I-4)-2 was obtained using the same method as Example 3.

[0237]

(Formation of Adhesive Layer, Production of Supporting Sheet)

The adhesive composition (I-4)-2 obtained above was applied to the smooth surface of the aforementioned substrate Bm4 having a surface roughness of 0.05 μm , and by drying the adhesive composition at 100°C for one minute, a non-energy-curable adhesive layer Ad3 having a thickness of 5 μm was formed, thus obtaining a supporting sheet Ss6.

[0238]

(Production of Composite Sheet for Protective Film Formation)

With the exception of using the supporting sheet Ss6 obtained above instead of the supporting sheet Ss1, the same method as Example 1 was used to produce a composite sheet for protective film formation.

In other words, this composite sheet for protective film formation was composed of the substrate Bm4, the adhesive layer Ad3, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm4 on the side on which the adhesive layer Ad3 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm4 on the opposite side from the side on which the adhesive layer Ad3 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 1.

[0239]

[Example 7]

(Production of Composition for Energy Ray-Curable Protective Film Formation (IV-1))

The energy ray-curable component (a)-1 (42 parts by mass), the filler (D)-1 (55 parts by mass), the coupling agent (E)-1 (0.3 parts by mass), the crosslinking agent (F)-1 (1 part by mass), the photopolymerization initiator (H)-1 (0.3 parts by mass), and the colorant (I)-1 (1 part by mass) were mixed together and then diluted with sufficient

methyl ethyl ketone to obtain a solid fraction concentration of 45% by mass, thus obtaining a composition for energy ray-curable protective film formation (IV-1). The above blend amounts of all of the components except the methyl ethyl ketone represent solid fraction amounts.

[0240]

(Formation of Film for Protective film Formation)

The composition (IV-1) obtained above was applied to the release-treated surface of a release film prepared by subjecting one surface of a polyethylene terephthalate film to a silicone release treatment (SP-PET381031, manufactured by Lintec Corporation, thickness: 38 μm), and the composition was then dried at 100°C for 3 minutes, thus forming a film for protective film formation Pf2 having a thickness of 25 μm .

[0241]

(Production of Adhesive Composition)

The adhesive composition (I-4)-2 was obtained using the same method as Example 3.

[0242]

(Formation of Adhesive Layer, Production of Supporting Sheet)

The adhesive layer Ad3 was formed and the supporting sheet Ss5 was obtained using the same method as Example 5.

[0243]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad3 of the supporting sheet Ss5 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm3, the adhesive layer Ad3, the film for protective film formation Pf2 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm3 on the side on which the adhesive layer Ad3 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm3 on the opposite side from the side on which the adhesive layer Ad3 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 1.

[0244]

[Example 8]

(Formation of Film for Protective film Formation)

The film for protective film formation Pf1 was formed using the same method as Example 1.

[0245]

(Formation of Adhesive Layer, Production of Supporting Sheet)

With the exception of using the substrate Bm7 described above instead of the substrate Bm1, and using the smooth surface of the substrate Bm7 having a surface roughness of 0.05 μm as the surface for formation of the adhesive layer Ad1, the same method as Example 1 was used to obtain a supporting sheet Ss11.

[0246]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation Pf1 obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad1 of the supporting sheet Ss11 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm7, the adhesive layer Ad1, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm7 on the side on which the adhesive layer Ad1 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm7 on the opposite side from the side on which the adhesive layer Ad1 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 2.

[0247]

[Example 9]

(Formation of Film for Protective film Formation)

The film for protective film formation Pf1 was formed using the same method as Example 1.

[0248]

(Formation of Adhesive Layer, Production of Supporting Sheet)

With the exception of using the substrate Bm8 described above instead of the substrate Bm1, and using the smooth surface of the substrate Bm8 having a surface roughness of 0.03 μm as the surface for formation of the adhesive layer Ad1, the same method as Example 1 was used to obtain a supporting sheet Ss12.

[0249]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation Pf1 obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad1 of the supporting sheet Ss12 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm8, the adhesive layer Ad1, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm8 on the side on which the adhesive layer Ad1 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm8 on the opposite side from the side on which the adhesive layer Ad1 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 2.

[0250]

[Example 10]

(Formation of Film for Protective film Formation)

The film for protective film formation Pf1 was formed using the same method as Example 1.

[0251]

(Formation of Adhesive Layer, Production of Supporting Sheet)

With the exception of using the substrate Bm9 described above instead of the substrate Bm1, and using the smooth surface of the substrate Bm9 having a surface roughness of 0.03 μm as the surface for formation of the adhesive layer Ad1, the same method as Example 1 was used to obtain a supporting sheet Ss13.

[0252]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation Pf1 obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad1 of the supporting sheet Ss13 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm9, the adhesive layer Ad1, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm9 on the side on which the adhesive layer Ad1 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm9 on the opposite side from the side on which the adhesive layer Ad1 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 2.

[0253]

[Example 11]

(Formation of Film for Protective film Formation)

The film for protective film formation Pf1 was formed using the same method as Example 1.

[0254]

(Formation of Adhesive Layer, Production of Supporting Sheet)

With the exception of using the substrate Bm10 described above instead of the substrate Bm1, and using the smooth surface of the substrate Bm10 having a surface roughness of 0.35 μm as the surface for formation of the adhesive layer Ad1, the same method as Example 1 was used to obtain a supporting sheet Ss14.

[0255]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation Pf1 obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad1 of the supporting sheet Ss14 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm10, the adhesive layer Ad1, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm10 on the side on which the adhesive layer Ad1 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm10 on the opposite side from the side on which the adhesive layer Ad1 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 2.

[0256]

[Example 12]

(Formation of Film for Protective film Formation)

The film for protective film formation Pf1 was formed using the same method as Example 1.

[0257]

(Formation of Adhesive Layer, Production of Supporting Sheet)

With the exception of using the substrate Bm11 described above instead of the substrate Bm1, and using the smooth surface of the substrate Bm11 having a surface roughness of $0.37\ \mu\text{m}$ as the surface for formation of the adhesive layer Ad1, the same method as Example 1 was used to obtain a supporting sheet Ss15.

[0258]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation Pf1 obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad1 of the supporting sheet Ss15 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm11, the adhesive layer Ad1, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm11 on the side on which the adhesive layer Ad1 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm11 on the opposite side from the side on which the adhesive layer Ad1 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 2.

[0259]

[Reference Example 1]

(Formation of Film for Protective film Formation)

The film for protective film formation Pf1 was formed using the same method as Example 1.

[0260]

(Formation of Adhesive Layer, Production of Supporting Sheet)

With the exception of altering the amount of the adhesive composition (I-4)-2 applied during formation of the adhesive layer, so as to form an adhesive layer Ad4 having a thickness of 20 μm rather than 5 μm , the same method as Example 4 was used to obtain a supporting sheet Ss7.

[0261]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation Pf1 obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad4 of the supporting sheet Ss7 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm2, the adhesive layer Ad4, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm2 on the side on which the adhesive layer Ad4 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm2 on the opposite side from the side on which the adhesive layer Ad4 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 3.

[0262]

[Comparative Example 1]

(Formation of Film for Protective film Formation)

The film for protective film formation Pf1 was formed using the same method as Example 1.

[0263]

(Formation of Adhesive Layer, Production of Supporting Sheet)

With the exception of using the substrate Bm5 described above instead of the substrate Bm1, and forming the adhesive layer Ad1 with a thickness of 5 μm on one surface (the smooth surface) of the substrate Bm5, the same method as Example 1 was used to obtain a supporting sheet Ss8.

[0264]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation Pf1 obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad1 of the supporting sheet Ss8 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm5, the adhesive layer Ad1, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm5 on the side on which the adhesive layer Ad1 was provided, and the surface (exposed surface) of the substrate Bm5 on the opposite side from the side on which the adhesive layer Ad1 was provided were both smooth surfaces. The composition of this composite sheet for protective film formation is shown in Table 3.

[0265]

[Comparative Example 2]

(Formation of Film for Protective film Formation)

The film for protective film formation Pf1 was formed using the same method as Example 1.

[0266]

(Formation of Adhesive Layer, Production of Supporting Sheet)

With the exception of using the substrate Bm6 described above instead of the substrate Bm1, and forming the adhesive layer Ad2 by applying the adhesive composition (I-4)-1 obtained above to the uneven surface of the substrate Bm6 having a surface roughness of 0.5 μm , the same method as Example 2 was used to obtain a supporting sheet Ss9.

[0267]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation Pf1 obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad2 of the supporting sheet Ss9 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm6, the adhesive layer Ad2, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm6 on the side on which the adhesive layer Ad2 was provided was the uneven surface, and the surface (exposed surface) of the substrate Bm6 on the opposite side from the side on which the adhesive layer Ad2 was provided was the smooth surface. The composition of this composite sheet for protective film formation is shown in Table 3.

[0268]

[Comparative Example 3]

(Formation of Film for Protective film Formation)

The film for protective film formation Pf1 was formed using the same method as Example 1.

[0269]

(Formation of Adhesive Layer, Production of Supporting Sheet)

With the exception of using the substrate Bm6 described above instead of the substrate Bm1, and forming the adhesive layer Ad1 by applying the adhesive composition (I-4)-1 obtained above to the smooth surface of the substrate Bm6 having a surface roughness of 0.05 μm , the same method as Example 1 was used to obtain a supporting sheet Ss10.

[0270]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation Pf1 obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad1 of the supporting sheet Ss10 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm6, the adhesive layer Ad1, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm6 on the side on which the adhesive layer Ad1 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm6 on the opposite side from the side on which the adhesive layer Ad1 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 3.

[0271]

[Comparative Example 4]

(Formation of Film for Protective film Formation)

The film for protective film formation Pf1 was formed using the same method as Example 1.

[0272]

(Formation of Adhesive Layer, Production of Supporting Sheet)

With the exception of using the substrate Bm12 described above instead of the substrate Bm1, and using the smooth surface of the substrate Bm12 having a surface roughness of 0.43 μm as the surface for formation of the adhesive layer Ad1, the same method as Example 1 was used to obtain a supporting sheet Ss16.

[0273]

(Production of Composite Sheet for Protective Film Formation)

The exposed surface of the film for protective film formation Pf1 obtained above, on the side not provided with the release film, and the exposed surface of the adhesive layer Ad1 of the supporting sheet Ss16 were laminated together, thus obtaining a composite sheet for protective film formation of the structure illustrated in FIG. 2.

This composite sheet for protective film formation was composed of the substrate Bm12, the adhesive layer Ad1, the film for protective film formation Pf1 and the release film, laminated in that order through the thickness direction, wherein the surface of the substrate Bm12 on the side on which the adhesive layer Ad1 was provided was the smooth surface, and the surface (exposed surface) of the substrate Bm11 on the opposite side from the side on which the adhesive layer Ad1 was provided was the uneven surface. The composition of this composite sheet for protective film formation is shown in Table 3.

[0274]

<Evaluation of Composite Sheets for Protective Film Formation>

For each of the composite sheets for protective film formation obtained above, the laser printability, the infrared examination characteristics, the blocking resistance, the filling and coatability of the substrate surface by the adhesive layer, and the chipping resistance were evaluated using the methods described below. The results are shown in Table 1 to Table 3 (in the tables, the abbreviation "filling and coatability" is used.)

[0275]

[Laser Printability]

The release film was removed from the composite sheet for protective film formation, and a mounting apparatus (RAD-2700F/12, manufactured by Lintec Corporation) was used to affix the composite sheet for protective film formation to a stainless steel ring frame, and to affix the film for protective film formation in the composite sheet for protective film formation to the back surface of a silicon wafer (diameter: 8 inches, thickness: 100 μm) that had been heated to 70°C.

Next, in those cases where the film for protective film formation was heat-curable, the film was cured by heating at 130°C for 2 hours, whereas in those cases

where the film for protective film formation was energy ray-curable, the film was cured by two repetitions of irradiation with ultraviolet rays under conditions including an illuminance of 145 mW/cm^2 and an irradiation dose of 230 mJ/cm^2 , thus forming a protective film.

Subsequently, using a printing apparatus (MD-S9910A manufactured by Keyence Corporation), laser light with a wavelength of 532 nm was irradiated onto the protective film from the substrate side under conditions including an output of 4.8 W, a frequency of 80 kHz, and a scan speed of 500 mm/sec, thereby laser printing the two patterns described below (pattern 1, pattern 2) onto the protective film.

(Patterns)

Pattern 1: character size: $0.30 \text{ mm} \times 0.5 \text{ mm}$, character spacing: 0.05 mm, number of characters: 20

Pattern 2: character size: $0.15 \text{ mm} \times 0.3 \text{ mm}$, character spacing: 0.05 mm, number of characters: 20

[0276]

Subsequently, the characters formed on the protective film by the laser printing described above were inspected through the supporting sheet, and the laser printability was evaluated against the following criteria. If the gas generated from the protective film by laser printing accumulates between the adhesive layer and the protective film, then this can cause chipping during dicing, and therefore samples in which gas accumulation had not occurred were used for the evaluation.

(Evaluation criteria)

A: all the characters in pattern 1 and pattern 2 were printed distinctly.

B: in pattern 2, a portion of the characters were blurred and printed indistinctly, but all of the characters in pattern 1 were printed distinctly.

C: in both pattern 1 and pattern 2, a portion of the characters were printed indistinctly.

[0277]

[Infrared Examination Characteristics]

The release film was removed from the composite sheet for protective film formation, and a mounting apparatus (RAD-2700F/12, manufactured by Lintec Corporation) was used to affix the composite sheet for protective film formation to a stainless steel ring frame, and to affix the film for protective film formation in the composite sheet for protective film formation to the #2000 ground back surface of a silicon wafer (diameter: 8 inches, thickness: 100 μm) that had been heated to 70°C.

Next, in those cases where the film for protective film formation was heat-curable, the film was cured by heating at 130°C for 2 hours, whereas in those cases where the film for protective film formation was energy ray-curable, the film was cured by two repetitions of irradiation with ultraviolet rays under conditions including an illuminance of 145 mW/cm^2 and an irradiation dose of 230 mJ/cm^2 , thus forming a protective film.

Subsequently, a dicing apparatus (DFD6361, manufactured by DISCO Corporation) was used to perform blade dicing under conditions including a feed rate of 30 mm/sec and a rotational rate of 30,000 rpm, thereby dicing the silicon wafer and obtaining chips having a size 2 mm $\times$ 2 mm.

[0278]

The obtained silicon chips were examined using an infrared microscope (BX-IR, manufactured by Olympus Corporation), by inspecting the ground surface (the back surface of the silicon chip) through the supporting sheet and also examining the diced

surfaces (the side surfaces of the silicon chip), and the infrared examination characteristics were evaluated against the following criteria.

(Evaluation criteria)

A: grinding traces on the ground surface were clearly visible. Further, chipping of a size of at least 2 μm but less than 5 μm that was formed inward from the diced surfaces of the silicon chip toward the interior of the silicon chip could be clearly confirmed.

B: grinding traces on the ground surface were clearly visible. However, chipping of a size of at least 2 μm but less than 5 μm that was formed inward from the diced surfaces of the silicon chip toward the interior of the silicon chip could not be clearly confirmed.

C: grinding traces on the ground surface were either not visible, or were not clearly visible, and chipping was either completely unconfirmed, or could not be clearly confirmed, regardless of size.

[0279]

[Blocking Resistance]

A length of 10 m of the composite sheet for protective film formation was wound around an ABS resin core with a diameter of 3 inches, and then stored in this state for 3 days at room temperature.

Subsequently, the stored roll of the composite sheet for protective film formation was fed from the roll, the release film was removed, and using a mounting apparatus (RAD-2700F/12, manufactured by Lintec Corporation), an attempt was made to perform the process of affixing the fed composite sheet for protective film formation to a stainless steel ring frame and affixing the film for protective film formation in the composite sheet for protective film formation to the back surface of a silicon wafer (diameter: 8 inches,

thickness: 100 μm) being heated at 70°C for 10 consecutive silicon wafers. Based on the operability of this process, the blocking resistance was evaluated against the following criteria.

(Evaluation criteria)

A: absolutely no blocking occurred, and the above operation was able to be performed with no problems.

B: the film for protective film formation was able to be affixed to the silicon wafer, but in the roll composed of the wound composite sheet for protective film formation, some adhesion occurred at the contact surfaces between the substrate and the release film, so that when the composite sheet for protective film formation was fed from the roll, partial detachment was observed, either between the substrate and the adhesive layer, or between the adhesive layer and the film for protective film formation.

C: in the roll composed of the wound composite sheet for protective film formation, some adhesion occurred at the contact surfaces between the substrate and the release film, clear blocking occurred, and when the composite sheet for protective film formation was fed from the roll, partial detachment occurred between the adhesive layer and the film for protective film formation, with either the supporting sheet (the laminated sheet of the substrate and the adhesive layer) being transferred to the release film, or actual feeding of the composite sheet for protective film formation becoming impossible.

[0280]

[Filling and Coatability of the Substrate Surface by the Adhesive Layer]

The supporting sheets obtained above were inspected using a digital microscope (VHS-1000, manufactured by Keyence Corporation), and the ability of the adhesive layer to fill and coat the substrate surface was evaluated against the following criteria.

○: no air bubbles were observed between the substrate and the adhesive layer.

×: air bubbles were visible between the substrate and the adhesive layer.

[0281]

[Chipping Resistance]

The four diced surfaces (the side surfaces) of 10 of the silicon chips of size 2 mm × 2 mm used in the above evaluation of the infrared examination characteristics were inspected using an optical microscope, and the chipping resistance was evaluated against the following criteria.

○: the number of chipping locations in which chipping having a size of at least 30 μm was formed inward from the diced surface of the silicon chip toward the interior of the silicon chip was, on average, less than one location per silicon chip.

×: the number of chipping locations in which chipping having a size of at least 30 μm was formed inward from the diced surface of the silicon chip toward the interior of the silicon chip was, on average, at least one location per silicon chip.

[0282]

[Table 1]

				Example						
				1	2	3	4	5	6	7
Composition of composite sheet for protective film formation	Supporting sheet	Substrate	Type	Bm1	Bm1	Bm1	Bm2	Bm3	Bm4	Bm3
			Thickness (μm)	80	80	80	80	80	80	80
			Tensile modulus of elasticity (MPa)	360	360	360	360	360	500	360
			Surface roughness Ra of adhesive layer formation surface (first surface) (μm)	0.05	0.05	0.05	0.05	0.05	0.05	0.05
			Surface roughness Ra of exposed surface (second surface) (μm)	0.1	0.1	0.1	0.2	0.3	0.3	0.3
	Adhesive layer	Type	Ad1	Ad2	Ad3	Ad3	Ad3	Ad3	Ad3	
		Thickness (μm)	5	20	5	5	5	5	5	
	Film for protective film formation	Type	Pf1	Pf1	Pf1	Pf1	Pf1	Pf1	Pf2	
		Thickness (μm)	25	25	25	25	25	25	25	
Evaluation results	Laser printability			A	A	A	A	B	B	B
	Infrared examination characteristics			A	A	A	A	B	B	B
	Blocking resistance			B	B	B	A	A	A	A
	Filling and coatability			○	○	○	○	○	○	○
	Chipping resistance			○	○	○	○	○	○	○

[0283]

[Table 2]

				Example				
				8	9	10	11	12
Composition of composite sheet for protective film formation	Supporting sheet	Substrate	Type	Bm7	Bm8	Bm9	Bm10	Bm11
			Thickness (μm)	80	80	80	80	80
			Tensile modulus of elasticity (MPa)	360	360	360	360	360
			Surface roughness Ra of adhesive layer formation surface (first surface) (μm)	0.05	0.03	0.03	0.35	0.37
			Surface roughness Ra of exposed surface (second surface) (μm)	0.055	0.4	0.47	0.4	0.47
	Adhesive layer	Type	Ad1	Ad1	Ad1	Ad1	Ad1	
		Thickness (μm)	5	5	5	5	5	
	Film for protective film formation	Type	Pf1	Pf1	Pf1	Pf1	Pf1	
		Thickness (μm)	25	25	25	25	25	
Evaluation results	Laser printability			A	B	B	B	B
	Infrared examination characteristics			A	B	B	B	B
	Blocking resistance			B	A	A	A	A
	Filling and coatability			○	○	○	○	○
	Chipping resistance			○	○	○	○	○

[0284]

[Table 3]

				Reference Example	Comparative Example			
				1	1	2	3	4
Composition of composite sheet for protective film formation	Supporting sheet	Substrate	Type	Bm2	Bm5	Bm6	Bm6	Bm12
			Thickness (μm)	80	80	80	80	80
			Tensile modulus of elasticity (MPa)	360	360	360	360	360
			Surface roughness Ra of adhesive layer formation surface (first surface) (μm)	0.05	0.05	0.5	0.05	0.43
			Surface roughness Ra of exposed surface (second surface) (μm)	0.2	0.05	0.05	0.5	0.47
	Adhesive layer	Type	Ad4	Ad1	Ad2	Ad1	Ad1	
		Thickness (μm)	20	5	20	5	5	
	Film for protective film formation	Type	Pf1	Pf1	Pf1	Pf1	Pf1	
		Thickness (μm)	25	25	25	25	25	
Evaluation results	Laser printability			A	A	C	C	C
	Infrared examination characteristics			A	A	C	C	C
	Blocking resistance			A	C	C	A	A
	Filling and coatability			○	○	×	○	×
	Chipping resistance			×	○	○	○	○

[0285]

As is evident from the above results, in the composite sheets for protective film formation of Examples 1 to 12, by ensuring that the surface roughness of the first surface of the substrate is $0.37\ \mu\text{m}$ or less, and that the surface roughness of the second surface of the substrate is greater than the surface roughness of the surface of the first surface, and is from 0.055 to $0.47\ \mu\text{m}$, the blocking resistance, the laser printability and the infrared examination characteristics were all excellent. Moreover, in each of the examples, the chipping resistance and the filling and coatability were also excellent. Among the

examples, the composite sheets for protective film formation of Examples 1 to 3 and Example 8 had comparatively small values for the surface roughness of the second surface of the substrate, and therefore the laser printability and the infrared examination characteristics were particularly superior. In contrast, the composite sheets for protective film formation of Examples 5 to 7 and Examples 9 to 12 had comparatively large values for the surface roughness of the second surface of the substrate, and therefore the blocking resistance was particularly superior. Further, the composite sheet for protective film formation of Example 4 had a mid-range value for the surface roughness of the second surface of the substrate, and therefore the blocking resistance, the laser printability and the infrared examination characteristics were all particularly superior.

[0286]

In comparison, in the composite sheet for protective film formation of Comparative Example 1, the surface roughness of the second surface of the substrate was too small, and therefore the blocking resistance was poor.

Further, in the composite sheet for protective film formation of Comparative Example 2, the surface roughness of the first surface of the substrate was too large and the surface roughness of the second surface of the substrate was too small, and therefore the blocking resistance, the laser printability and the infrared examination characteristics were all inferior. Further, in the composite sheet for protective film formation of Comparative Example 2, the surface roughness of the first surface of the substrate was too large, and therefore the filling and coatability was also poor.

Further, in the composite sheet for protective film formation of Comparative Example 3, the surface roughness of the second surface of the substrate was too large, and therefore the laser printability and the infrared examination characteristics were both poor.

Furthermore, in the composite sheet for protective film formation of Comparative Example 4, the surface roughness of the first surface of the substrate was too large, and therefore the laser printability, the infrared examination characteristics, and the filling and coatability were all poor.

[0287]

The composite sheet for protective film formation of Reference Example 1 satisfies the requirements for a surface roughness of the first surface of the substrate of $0.4\text{ }\mu\text{m}$ or less, and a surface roughness for the second surface of the substrate of 0.053 to $0.48\text{ }\mu\text{m}$, and therefore the blocking resistance, the laser printability and the infrared examination characteristics were all excellent. However, because the adhesive layer was too thick, the chipping resistance was poor.

INDUSTRIAL APPLICABILITY

[0288]

The present invention can be used in the production of semiconductor devices.

DESCRIPTION OF THE REFERENCE SIGNS

[0289]

1: Supporting sheet

11: Substrate

11a: One surface (first surface) of substrate

11b: Other surface (second surface) of substrate

12: Adhesive layer

13, 23: Film for protective film formation

101, 102, 103: Composite sheet for protective film formation

CLAIMS

1. A composite sheet for protective film formation comprising a supporting sheet and a film for protective film formation provided on the supporting sheet, wherein

the supporting sheet comprising a substrate, and an adhesive layer laminated to the substrate,

a surface roughness (Ra) of a surface of the substrate on a side on which the adhesive layer is provided is 0.4 μm or less,

a surface roughness (Ra) of a surface of the substrate on an opposite side from the side on which the adhesive layer is provided is greater than the surface roughness of the surface on the side on which the adhesive layer is provided, and is from 0.053 to 0.48 μm ,

the substrate and the adhesive layer exhibit both of transmittance to light having a wavelength of 532 nm and light having a wavelength of 1,600 nm,

the storage modulus of the adhesive layer is at least 30 kPa,

the film for protective film formation is for protecting a semiconductor wafer or a semiconductor chip, and

the film for protective film formation is provided on the adhesive layer in the supporting sheet.

2. The composite sheet for protective film formation according to Claim 1, wherein

the surface roughness (Ra) of the surface of the substrate on the opposite side from the side on which the adhesive layer is provided is 0.15 to 0.48 μm .

3. The composite sheet for protective film formation according to Claim 1 or 2, wherein a thickness of the adhesive layer is 15 μm or less.
4. The composite sheet for protective film formation according to any one of Claims 1 to 3, wherein the adhesive layer is non-energy-curable.