

DESCRIPTION

COMPOSITE SHEET FOR FORMING PROTECTIVE FILM

5

TECHNICAL FIELD

[0001]

The present invention relates to a composite sheet for forming a protective film which is adhered to workpieces such as semiconductor wafers, allows the workpieces to be processed (for example, diced) while being adhered to the workpieces, and is capable of forming a protective film on the workpieces or articles obtained by processing the workpieces (for example, semiconductor chips).

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Priority is claimed on Japanese Patent Application No. 2014-138087, filed on July 3, 2014, and Japanese Patent Application No. 2015-127417, filed on June 25, 2015, the contents of which are incorporated herein by reference.

15

BACKGROUND ART

[0002]

In recent years, semiconductor devices have been manufactured using a mounting method called a face down method. In this method, when a semiconductor chip having a circuit surface on which an electrode such as a bump is formed is mounted, the circuit surface side of the semiconductor chip is joined to a chip-mounted portion such as a lead frame. Therefore, the rear surface side of the semiconductor chip on which no circuits are formed is exposed.

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[0003]

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Therefore, it is common to form a protective film made of a hard organic material on the rear surface side of the semiconductor chip in order to protect the

semiconductor chip. Therefore, Patent Document 1 discloses a sheet for forming a protective film and dicing having a thermosetting protective film-forming layer which is capable of forming the above-described protective film. According to this sheet for forming a protective film and dicing, it is possible to dice semiconductor wafers and form protective films on the semiconductor chips at the same time and obtain protective film-attached semiconductor chips.

[0004]

In a case in which the sheet for forming a protective film and dicing is used, the circumferential edge portion of the sheet is attached to a ring frame, the protective film-forming layer is attached to a semiconductor wafer, and the sheet is heated and cooled in this state. By means of the above-described steps, the protective film-forming layer is thermally cured, thereby forming a protective film.

[0005]

However, in a case in which the sheet for forming a protective film and dicing of the related art is used, when the sheet for forming a protective film and dicing is subjected to the above-described heating step while being supported by the ring frame, there are cases in which a problem of the sheet for forming a protective film and dicing becoming loose due to the weight of the semiconductor wafer and not returning to the original state even after the cooling step is caused. The sheet for forming a protective film and dicing becoming loose as described above causes a disadvantage when the sheet is stored in a cassette for transportation, causes a disadvantage of hindering smooth vacuum-adsorption of the sheet to an adsorption table at a portion outside a portion corresponding to the wafer and thus puckering the sheet, or causes a disadvantage due to the sheet which has been already stretched when expansion is carried out.

[0006]

In addition, Patent Document 1 discloses, as the sheet for forming a protective film and dicing, a constitution in which the protective film-forming layer is directly laminated on a supporting film (FIG. 1). However, the absence of a pressure sensitive adhesive layer between the supporting film and the protective film-forming layer causes the adhesive strength between the supporting film and the protective film-forming layer to be excessive and thus does not allow chips to be picked up or, conversely, excessively weakens the adhesive strength between the supporting film and the protective film-forming layer and thus causes a problem of chips being dropped during dicing.

[0007]

Patent Document 2 discloses a protective film-forming layer-attached dicing sheet having the same constitution as that of the sheet for forming a protective film and dicing of Patent Document 1. Patent Document 2 describes loosening occurring during thermal curing, but does not consider returning of the sheet in the cooling step.

[0008]

Patent Document 3 discloses a method for manufacturing a semiconductor device in which a film for a semiconductor rear surface as a protective film-forming layer and dicing tape are separately used. In this method of Patent Document 3, the film for a semiconductor rear surface is diced in a non-cured state and is thermally cured after chips are picked up, and thus there is no problem of loosening described above.

CITATION LIST

PATENT DOCUMENTS

[0009]

[Patent Document 1] Japanese Unexamined Patent Application, First

Publication No. 2006-140348

[Patent Document 2] PCT International Publication No. WO2013/047674

[Patent Document 3] Japanese Unexamined Patent Application, First
Publication No. 2012-156377

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SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0010]

The present invention has been made in consideration of the above-described
circumstances, and an object of the present invention is to provide a composite sheet for
10 forming a protective film which effectively suppresses loosening of the sheet which has
been subjected to a heating step and a cooling step and allows chips to be favorably
picked up.

MEANS TO SOLVE THE PROBLEMS

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[0011]

In order to achieve the above-described object, the present invention includes
the following aspects.

(1) A composite sheet for forming a protective film including: a pressure
sensitive adhesive sheet formed by laminating a pressure sensitive adhesive layer on one
20 surface side of a base material; and a protective film-forming film laminated on the
pressure sensitive adhesive layer side of the pressure sensitive adhesive sheet, in which,
in a case in which the base material is heated at 130°C for two hours under a load of 0.1
g/mm applied to the base material and cooled to 23°C, ratios of expansion and
contraction of the base material in an MD direction and a CD direction between before
25 the heating and after the heating are both in a range of 95% to 103%, and tensile moduli

of elasticity of the base material in the MD direction and the CD direction at 23°C are both in a range of 100 to 700 MPa.

Meanwhile, in the present specification, the concept of “sheets” includes tape.

In an aspect of the present invention, the composite sheet for forming a
5 protective film includes the base material, the pressure sensitive adhesive layer, and the
protective film-forming film, the base material, the pressure sensitive adhesive layer, and
the protective film-forming film are laminated in this order, and, in a case in which the
base material is heated at 130°C for two hours under a load of 0.1 g/mm applied to the
base material and cooled to 23°C, the ratios of expansion and contraction of the base
10 material in the MD direction and the CD direction between before the heating and after
the heating are both in a range of 95% to 103%, and the tensile moduli of elasticity of the
base material in the MD direction and the CD direction at 23°C are both in a range of 100
to 700 MPa.

In another aspect of the present invention, the pressure sensitive adhesive sheet
15 is a laminate having the pressure sensitive adhesive layer laminated on one surface of the
base material.

[0012]

According to the aspect (1), since the base material has a property regarding the
above-described ratios of expansion and contraction, it is possible to effectively suppress
20 loosening of the composite sheet for forming a protective film which has been subjected
to a heating step and a cooling step. In addition, since the base material has a property
regarding the above-described tensile modulus of elasticity, the pressure sensitive
adhesive sheet becomes appropriately flexible, and it is possible to favorably expand (if
necessary) the sheet and pick up chips after dicing.

[0013]

(2) In the aspect (1), the base material is preferably a polypropylene film.

[0014]

(3) In the aspect (1) or (2), a thickness of the base material is preferably in a
5 range of 50 to 200 μm .

[0015]

(4) In the aspect of any one of (1) to (3), the composite sheet for forming a
protective film preferably includes a pressure sensitive adhesive layer for a jig laminated
at a circumferential edge portion on a side opposite to the pressure sensitive adhesive
10 sheet side of the protective film-forming film.

[0016]

(5) In the aspect of any one of (1) to (4), a release sheet laminated on the
protective film-forming film is preferably provided.

[0017]

15 (6) In the aspect of any one of (1) to (5), the protective film-forming film is
preferably a layer forming a protective film on a semiconductor wafer or a semiconductor
chip obtained by dicing a semiconductor wafer.

(7) In the aspect of any one of (1) to (6), when the base material is heated to
130°C at a temperature-increase rate of 10°C/minute and held at that temperature for two
20 hours, a weight decrease ratio of the base material is 0.01% to 2%, more preferably lower
than 0.9%, and still more preferably 0.5% or lower.

(8) In the aspect of any one of (1) to (4), (6), and (7), when the composite sheet
for forming a protective film is heated to 130°C at a temperature-increase rate of
10°C/minute and held at that temperature for two hours, a weight decrease ratio of the

composite sheet for forming a protective film is 0.01% to 6.0%, more preferably 3.0% or lower, still more preferably 2.5% or lower, and particularly preferably 1.2% or lower.

(9) In the aspect of any one of (1) to (8), a melting point of the base material is preferably 130°C or higher, more preferably in a range of 130°C to 170°C, still more preferably in a range of 130°C to 160°C, and particularly preferably in a range of 131°C to 156°C.

EFFECTS OF THE INVENTION

[0018]

10 According to the composite sheet for forming a protective film of the present invention, it is possible to effectively suppress loosening of the sheet which has been subjected to a heating step and a cooling step and allows chips to be favorably picked up.

BRIEF DESCRIPTION OF DRAWINGS

15 [0019]

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

FIG. 2 is a plan view of the composite sheet for forming a protective film in a state of being attached to a workpiece.

20 FIG. 3 is a cross-sectional view showing an example of the composite sheet for forming a protective film according to an embodiment of the present invention being used.

FIG. 4 is a cross-sectional view of the composite sheet for forming a protective film according to the embodiment of the present invention.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0020]

Hereinafter, an embodiment of the present invention will be described.

FIG. 1 is a cross-sectional view of a composite sheet for forming a protective
5 film according to an embodiment of the present invention. FIG. 2 is a plan view of the
composite sheet for forming a protective film in a state of being attached to a workpiece.
As shown in FIG. 1, a composite sheet for forming a protective film 1 according to the
present embodiment is constituted by providing a pressure sensitive adhesive sheet 2
formed by laminating a pressure sensitive adhesive layer 22 on one surface of a base
10 material 21, a protective film-forming film 3 laminated on the pressure sensitive adhesive
layer 22 side of the pressure sensitive adhesive sheet 2, and a pressure sensitive adhesive
layer for a jig 4 laminated at the circumferential edge portion of the protective
film-forming film 3 on a side opposite to the pressure sensitive adhesive sheet 2 side.
Meanwhile, the composite sheet for forming a protective film 1 according to the present
15 embodiment refers to a composite sheet for forming a protective film of which the
protective film-forming film 3 is not yet attached to the workpiece.

[0021]

In the present embodiment, as shown in FIGS. 1 and 2, the base material 21 and
the pressure sensitive adhesive layer 22 in the pressure sensitive adhesive sheet 2 and the
20 protective film-forming film 3 are formed in the same size and shape and have a circular
shape in a planar view, but the present invention is not limited thereto. For example, the
pressure sensitive adhesive sheet 2 and the protective film-forming film 3 may have
different sizes or shapes and all may have a polygonal shape or a shape formed of a
combination of an arc and a straight line in a planar view.

25 [0022]

In addition, in the present embodiment, as shown in FIGS. 1 and 2, the pressure sensitive adhesive layer for a jig 4 is formed in a ring shape, and the outer circumferential edge thereof is located at the same position as the outer circumferential edges of the pressure sensitive adhesive sheet 2 and the protective film-forming film 3 in a planar view, but the present invention is not limited thereto. For example, the pressure sensitive adhesive layer for a jig 4 may not have a ring shape, may be slivered in the middle, and may have an outer circumferential edge that is located at a different position from the outer circumferential edges of the pressure sensitive adhesive sheet 2 and the protective film-forming film 3 in a planar view.

10 [0023]

When a workpiece is processed, the composite sheet for forming a protective film 1 according to the present embodiment is used to hold the workpiece in a state of being attached to the workpiece and form a protective film on the workpiece or a chip obtained from the workpiece. In the present embodiment, this protective film is formed by thermally curing the protective film-forming film 3. As an example, the composite sheet for forming a protective film 1 according to the present embodiment is used to hold a semiconductor wafer as the workpiece during the dicing of the semiconductor wafer and form a protective film on a semiconductor chip obtained by means of the dicing, but the present invention is not limited thereto.

20 [0024]

1. Pressure sensitive adhesive sheet

The pressure sensitive adhesive sheet 2 in the composite sheet for forming a protective film 1 according to the present embodiment is constituted by providing the base material 21 and the pressure sensitive adhesive layer 22 laminated on one surface of the base material 21.

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[0025]

1-1. Base material

The base material 21 in the composite sheet for forming a protective film 1 according to the present embodiment has a property that, in a case in which the base material is heated at 130°C for two hours under a load of 0.1 g/mm applied to the base material 21 and cooled to 23°C, the ratios of expansion and contraction of the base material in the machine direction (MD) and the cross direction (CD) between before the heating and after the heating (hereinafter, in some cases, referred to as the “ratio of expansion and contraction under load”) are both in a range of 95% to 103%. In the present specification, “a property” means a chemical or physicochemical property. The method for measuring the ratio of expansion and contraction under load will be described in testing examples below. Here, the MD direction refers to the line direction for the manufacturing of the base material 21, and the CD direction refers to the direction perpendicular to the MD direction, that is, the width direction for the manufacturing of the base material 21.

[0026]

When the base material 21 has the above-described property, it is possible to effectively suppress loosening of the composite sheet for forming a protective film 1 which has been subjected to a heating step and a cooling step. Therefore, the composite sheet for forming a protective film 1 according to the present embodiment has a low likelihood of causing troubles in steps subsequent to the heating and cooling step.

[0027]

When the ratio of expansion and contraction under load is lower than 95%, the shrinkage amount of the composite sheet for forming a protective film 1 is great, there is a concern that the workpiece may break due to a large internal stress being generated in

the workpiece, and there is another concern that the composite sheet for forming a protective film 1 may be separated from a jig such as a ring frame. On the other hand, when the ratio of expansion and contraction under load exceeds 103%, the composite sheet for forming a protective film 1 becomes significantly loose, and there is a significant concern that the loose composite sheet for forming a protective film may cause troubles in individual steps. From such a viewpoint, the ratio of expansion and contraction under load is preferably in a range of 96% to 101% and particularly preferably in a range of 97% to 100%.

[0028]

Here, in a case in which the base material is heated at 130°C for two hours with no loads applied to the base material 21 and cooled to 23°C, the ratios of expansion and contraction of the base material in the MD direction and the CD direction between before the heating and after the heating (hereinafter, in some cases, referred to as the “ratio of expansion and contraction without load”) are both preferably in a range of 93% to 100%, more preferably in a range of 95% to 100%, still more preferably in a range of 97% to 100%, and particularly preferably in a range of 98% to 100%. The method for measuring the ratio of expansion and contraction without load will be described in testing examples below.

[0029]

In a case in which the workpiece (the semiconductor wafer) becomes extremely thin and lightweight in actual processes, when the ratio of expansion and contraction without load is 93% or higher, the shrinkage amount of the composite sheet for forming a protective film 1 is small, and it is possible to limit workpiece breaking due to a large internal stress being generated in the workpiece. In addition, it is also possible to suppress the composite sheet for forming a protective film 1 being separated from a jig

such as a ring frame. On the other hand, when the ratio of expansion and contraction without load is 100% or lower, the loosening of the composite sheet for forming a protective film 1 becomes small, and it is possible to decrease the likelihood of troubles being caused due to the loosening of the composite sheet for forming a protective film in individual steps.

[0030]

In addition, in the base material 21 in the composite sheet for forming a protective film 1 according to the present embodiment, the tensile moduli of elasticity (Young's moduli) in the MD direction and the CD direction at 23°C are both in a range of 100 to 700 MPa. The method for measuring the tensile moduli of elasticity will be described in testing examples below.

[0031]

When the base material 21 has the above-described property, the pressure sensitive adhesive sheet 2 becomes appropriately flexible, and it is possible to favorably expand (if necessary) the sheet and pick up chips after dicing. In ordinary pickup steps, the pressure sensitive adhesive sheet 2 holding chips obtained by means of dicing is struck with upthrust pins, but the pressure sensitive adhesive sheet 2 is flexible, and thus the pressure sensitive adhesive sheet 2 struck with upthrust pins pushes chips up. Therefore, it becomes easy to release chips from the pressure sensitive adhesive sheet 2, and the pickup property becomes favorable. The pickup strength (the measurement method will be described in testing examples below) is preferably 5 N or lower, particularly preferably 4 N or lower, and still more preferably 3 N or lower.

[0032]

When the tensile moduli of elasticity exceed 700 MPa, the flexibility of the pressure sensitive adhesive sheet 2 degrades, and the above-described excellent effects

cannot be obtained. On the other hand, when the tensile moduli of elasticity are lower than 100 MPa, the pressure sensitive adhesive sheet 2 becomes too soft, and it becomes impossible to favorably dice the sheet. From such a viewpoint, the tensile moduli of elasticity are preferably in a range of 120 to 600 MPa and particularly preferably in a range of 150 to 500 MPa.

[0033]

When a single base material is heated to 130°C at a temperature-increase rate of 10°C/minute and held at that temperature for two hours, the base material 21 preferably has a property that the weight decrease ratio (the measurement method will be described in testing examples below) is 0.01% to 2%, more preferably lower than 0.9%, and still more preferably 0.5% or lower. That is, the weight decrease ratio of the single base material constituting the base material 21 is preferably 0.01% to 2%, more preferably 0.01% to 0.9%, and still more preferably 0.01% to 0.5%. When the weight decrease ratio of the single base material constituting the base material 21 is in the above-described range, the base material 21 does not easily deform when heated, and the base material 21 has excellent heat resistance suitable for the intended use of the composite sheet for forming a protective film according to the embodiment of the present invention. In addition, when the weight decrease ratio of the single base material constituting the base material 21 is in the above-described range, gas is rarely generated from the base material 21 when the composite sheet for forming a protective film according to the embodiment of the present invention is heated, and it is possible to suppress the deterioration of the composite sheet for forming a protective film.

[0034]

The melting point of the base material 21 is preferably 130°C or higher, particularly preferably in a range of 130°C to 170°C, still more preferably in a range of

130°C to 160°C, and, more specifically, preferably in a range of 131°C to 156°C. When the melting point of the base material 21 is in the above-described range, the base material becomes capable of easily satisfying the above-described ratio of expansion and contraction under load and tensile moduli of elasticity.

5 In the present specification, “thickness” refers to the average value of thicknesses measured at arbitrary five positions using a contact-type thickness meter on a slivered surface obtained by arbitrarily slivering a subject in the thickness direction.

[0035]

10 The thickness of the base material 21 is preferably in a range of 50 to 200 μm , particularly preferably in a range of 50 to 120 μm , and still more preferably in a range of 60 to 100 μm . When the thickness is thinner than 50 μm , there is a tendency for the ratio of expansion and contraction under load of the base material 21 to increase. On the other hand, when the thickness exceeds 200 μm , there is a concern that the pickup property may degrade.

15 [0036]

A material constituting the base material 21 needs to have the above-described properties and, for example, can be appropriately selected from resin films described below.

[0037]

20 Specific examples of the resin films include polyethylene films such as low-density polyethylene (LDPE) films, linear low-density polyethylene (LLDPE) films, and high-density polyethylene (HDPE) films, polyolefin-based films such as polypropylene films, polybutene films, polybutadiene films, polymethylpentene films, ethylene-norbornene copolymer films, and norbornene resin films; ethylene-based

copolymer films such as ethylene-vinyl acetate copolymer films, ethylene-(meth)acrylate copolymer films, and ethylene-(meth)acrylic acid ester copolymer films; polyvinyl chloride-based films such as polyvinyl chloride films and vinyl chloride copolymer films; polyester-based films such as polyethylene terephthalate films and polybutylene terephthalate films; polyurethane films; polyimide films; polystyrene films; polycarbonate films; fluororesin films; and the like. In addition, modified films such as crosslinked films and ionomer films thereof can also be used. The base material 21 may be a film made of one of the above-described films or a laminate film made of a combination of two or more of the above-described films. Meanwhile, in the present specification, “(meth)acrylic acid” refers to both acrylic acid and methacrylic acid. The above-described manner of expression shall also apply to other analogous terminologies.

[0038]

Among these, polypropylene films are preferred. Some kinds of polypropylene films have appropriate heat resistance and flexibility and easily satisfy the above-described ratio of expansion and contraction under load and tensile moduli of elasticity.

[0039]

In order to improve close adhesiveness between the resin film and the pressure sensitive adhesive layer 22 laminated on the surface of the resin film, it is possible to carry out a surface treatment or a primer treatment using an oxidation method or an unevenness-forming method on either or both surfaces as desired. Examples of the oxidation method include a corona discharge treatment, a plasma discharge treatment, a (wet-type) chromium oxidation treatment, a flame treatment, a hot air treatment, an ozone or ultraviolet ray irradiation treatment, and the like, and examples of the unevenness-forming method include a sand blast method, a thermal spraying treatment

method, and the like.

[0040]

The base material 21 may include a variety of additives such as a coloring agent, a flame retardant, a plasticizer, an antistatic agent, a lubricant, and a filler in the resin
5 film.

[0041]

1-2. Pressure sensitive adhesive layer

The pressure sensitive adhesive sheet 2 in the composite sheet for forming a protective film 1 according to the present embodiment includes the pressure sensitive
10 adhesive layer 22 on one surface of the base material 21. Due to the presence of the pressure sensitive adhesive layer 22, the protective film-forming film 3 can be strongly fixed during dicing by controlling the peel strength of the pressure sensitive adhesive layer 22, and it is possible to exhibit an appropriate release property allowing chips obtained by means of dicing to be easily picked up. When the pressure sensitive
15 adhesive layer 22 is not provided, the adhesive strength between the base material 21 and the protective film-forming film 3 becomes excessive and thus it becomes impossible to pick up chips or, conversely, the adhesive strength between the base material 21 and the protective film-forming film 3 excessively weakens and thus there are cases in which a problem of chips being dropped during dicing is caused.

20 [0042]

The pressure sensitive adhesive layer 22 may be made of a single layer or two or more multiple layers, and, in the case of multiple layers, the pressure sensitive adhesive layer may be made of the same material (pressure sensitive adhesive) or different materials (pressure sensitive adhesives).

25 [0043]

A pressure sensitive adhesive constituting the pressure sensitive adhesive layer 22 may be a non-curable pressure sensitive adhesive or a curable pressure sensitive adhesive. In addition, the curable pressure sensitive adhesive may be in a to-be-cured state or in a cured state. In a case in which the pressure sensitive adhesive layer 22 is made of multiple layers, the pressure sensitive adhesive layer may be a combination of a non-curable pressure sensitive adhesive and a curable pressure sensitive adhesive. Examples of the non-curable pressure sensitive adhesive include acrylic pressure sensitive adhesives, rubber pressure sensitive adhesives, silicone pressure sensitive adhesives, urethane-based pressure sensitive adhesives, polyester-based pressure sensitive adhesives, polyvinyl ether-based pressure sensitive adhesives, and the like, and, among these, acrylic pressure sensitive adhesives are preferred. Examples of the curable pressure sensitive adhesives include energy-ray-curable pressure sensitive adhesives, thermosetting pressure sensitive adhesives, and the like, and, among these, energy-ray-curable pressure sensitive adhesives are preferred, and acrylic energy-ray-curable pressure sensitive adhesives are particularly preferred.

[0044]

In a case in which the pressure sensitive adhesive layer 22 is constituted of an energy-ray-curable pressure sensitive adhesive, the energy-ray-curable pressure sensitive adhesive may be in a non-cured state or in a cured when the composite sheet for forming a protective film 1 is attached to an adherend.

As the energy rays, generally, ultraviolet rays, electron beams, or the like are used. The irradiance of the energy rays varies depending on the kind of the energy rays; however, in the case of ultraviolet rays, the irradiance is preferably in a range of 50 to 1,000 mJ/cm² and particularly preferably in a range of 100 to 500 mJ/cm² in terms of light intensity. In addition, in the case of electron beams, the irradiance is preferably in

a range of approximately 10 to 1,000 krad.

[0045]

The energy-ray-curable pressure sensitive adhesive constituting the pressure sensitive adhesive layer 22 may include an energy-ray-curable polymer as the main component or may include a mixture of an energy-ray-non-curable pressure sensitive adhesive and an energy-ray-curable polyfunctional monomer and/or oligomer as the main component.

[0046]

A case in which the energy-ray-curable pressure sensitive adhesive includes an energy-ray-curable polymer as the main component will be described below.

Meanwhile, the “main component” mentioned herein means that the content is 60% by mass or higher of the total mass of the energy-ray-curable pressure sensitive adhesive.

[0047]

The energy-ray-curable polymer is preferably a (meth)acrylic acid ester (co)polymer (A) in which an energy-ray-curable functional group (that is, an energy-ray-curable group) is introduced into a side chain (hereinafter, in some cases, referred to as “energy-ray-curable polymer (A)”). This energy-ray-curable polymer (A) is preferably obtained by reacting a (meth)acrylic copolymer (a1) having a functional group-containing monomer unit and an unsaturated group-containing compound (a2) having a substituent that is bonded to the above-described functional group.

[0048]

The acrylic copolymer (a1) is made up of at least a constituent unit derived from a functional group-containing monomer and a constituent unit derived from a (meth)acrylic acid ester monomer or a derivative thereof.

[0049]

The functional group-containing monomer forming the constituent unit derived from the functional group-containing monomer is preferably a monomer having a polymerizable double bond and a functional group such as a hydroxy group, an amino group, a substituted amino group, an epoxy group, or a carboxyl group in the molecule.

[0050]

Additional specific examples of the functional group-containing monomer include 2-hydroxyethyl (meth)acrylates, 2-hydroxypropyl (meth)acrylates, 3-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylates, glycidyl (meth)acrylates, acrylic acid, and the like, and these monomers may be used singly or in a combined form.

[0051]

As the (meth)acrylic acid ester monomer, alkyl (meth)acrylate having 1 to 20 carbon atoms in an alkyl group, cycloalkyl (meth)acrylate having 3 to 11 carbon atoms in an alkyl group, or benzyl (meth)acrylate is used. Among these, alkyl (meth)acrylate having 1 to 18 carbon atoms in an alkyl group is particularly preferred, and examples thereof include methyl (meth)acrylates, ethyl (meth)acrylates, propyl (meth)acrylates, n-butyl (meth)acrylates, 2-ethylhexyl (meth)acrylates, and the like.

[0052]

In the acrylic copolymer (a1), with respect to the total mass of the acrylic copolymer (a1), the content of the constituent unit derived from the functional group-containing monomer is generally in a range of 3% to 100% by mass and preferably in a range of 5% to 40% by mass, and the amount of the constituent unit derived from the (meth)acrylic acid ester monomer or a derivative thereof is generally in a range of 0% to 97% by mass and preferably in a range of 60% to 95% by mass.

That is, in the acrylic copolymer (a1), with respect to the total mass of the acrylic copolymer (a1), it is preferable that the content of the constituent unit derived from the functional group-containing monomer is in a range of 3% to 100% by mass and the content of the constituent unit derived from the (meth)acrylic acid ester monomer or a derivative thereof is generally in a range of 0% to 97% by mass; it is more preferable that the amount of the constituent unit derived from the functional group-containing monomer is in a range of 5% to 40% by mass and the content of the constituent unit derived from the (meth)acrylic acid ester monomer or a derivative thereof is in a range of 60% to 95% by mass.

Meanwhile, the total mass of the constituent unit derived from the functional group-containing monomer and the constituent unit derived from the (meth)acrylic acid ester monomer or a derivative thereof may not exceed 100% by mass.

[0053]

The acrylic copolymer (a1) is obtained by copolymerizing the functional group-containing monomer and the (meth)acrylic acid ester monomer or a derivative thereof using an ordinary method; however, in addition to the above-described monomers, dimethylacrylamide, vinyl formate, vinyl acetate, styrene, and the like may be copolymerized.

[0054]

When the acrylic copolymer (a1) having the function group-containing monomer unit (that is, the constituent unit derived from a functional group-containing monomer) is reacted with the unsaturated group-containing compound (a2) having a substituent that is bonded to the above-described functional group, the energy-ray-curable polymer (A) is obtained.

[0055]

The substituent in the unsaturated group-containing compound (a2) can be appropriately selected depending on the kind of the function group in the functional group-containing monomer unit in the acrylic copolymer (a1). For example, in a case in which the functional group is a hydroxy group, an amino group, or a substituted amino group, the substituent is preferably an isocyanate group or an epoxy group, in a case in which the functional group is an epoxy group, the substituent is preferably an amino group, a carboxyl group, or an aziridinyl group, and in a case in which the functional group is a carboxyl group, the substituent is preferably an epoxy group.

[0056]

In addition, the number of energy-ray-polymerizable carbon-carbon double bonds in a single molecule of the unsaturated group-containing compound (a2) is in a range of 1 to 5 and preferably 1 or 2. Specific examples of the above-described unsaturated group-containing compound (a2) include 2-methacryloyloxyethyl isocyanate, meta-isopropenyl- α,α -dimethylbenzyl isocyanate, methacryloyl isocyanate, allyl isocyanate, 1,1-(bisacryloyloxymethyl)ethyl isocyanate; acryloyl monoisocyanate compounds obtained from a reaction between a diisocyanate compound or a polyisocyanate compound and hydroxyethyl (meth)acrylates; acryloyl monoisocyanate compounds obtained from a reaction among a diisocyanate compound or a polyisocyanate compound, a polyol compound, and hydroxyethyl (meth)acrylates; glycidyl (meth)acrylates; (meth)acrylic acids, 2-(1-aziridinyl)ethyl (meth)acrylates; alkenyloxazoline compounds such as 2-vinyl-2-oxazoline and 2-isopropenyl-2-oxazoline; and the like.

Among these, 2-methacryloyloxyethyl isocyanate is preferred.

[0057]

The amount of the unsaturated group-containing compound (a2) is generally in a

range of 10 to 100 equivalents and preferably in a range of 20 to 95 equivalents per 100 equivalents of the functional group-containing monomer in the acrylic copolymer (a1).

[0058]

In the reaction between the acrylic copolymer (a1) and the unsaturated
5 group-containing compound (a2), the reaction temperature, the pressure, the solvent, the duration, the presence or absence of a catalyst, and the kind of the catalyst can be appropriately selected depending on the combination of the functional group and the substituent. Therefore, the functional group in the acrylic copolymer (a1) and the substituent in the unsaturated group-containing compound (a2) are reacted together, and
10 the unsaturated group is introduced into a side chain in the acrylic copolymer (a1), thereby obtaining the energy-ray-curable polymer (A).

[0059]

The weight-average molecular weight of the energy-ray-curable polymer (A) obtained as described above is preferably 10,000 or higher, particularly preferably in a
15 range of 150,000 to 1,500,000, and still more preferably in a range of 200,000 to 1,000,000. Meanwhile, in the present specification, the weight-average molecular weight (Mw) refers to a polystyrene-equivalent value measured by means of gel permeation chromatography (GPC).

[0060]

20 Even in a case in which the energy-ray-curable pressure sensitive adhesive includes an energy-ray-curable polymer as the main component, the energy-ray-curable pressure sensitive adhesive may further include an energy-ray-curable monomer and/or oligomer (B).

[0061]

25 As the energy-ray-curable monomer and/or oligomer (B), for example, an ester

of a polyvalent alcohol and (meth)acrylic acid, or the like can be used.

[0062]

Examples of the energy-ray-curable monomer and/or oligomer (B) include monofunctional acrylic acid esters such as cyclohexyl (meth)acrylates and isobornyl (meth)acrylates, polyfunctional acrylic acid esters such as trimethylolpropane tri(meth)acrylates, pentaerythritol tri(meth)acrylates, pentaerythritol tetra(meth)acrylates, dipentaerythritol hexa(meth)acrylates, 1,4-butanediol di(meth)acrylates, 1,6-hexanediol di(meth)acrylates, polyethylene glycol di(meth)acrylates, and dimethyloltricyclodecane di(meth)acrylates, polyester oligo (meth)acrylates, polyurethane oligo (meth)acrylates, and the like.

Among these, polyfunctional acrylic acid esters and polyurethane oligo (meth)acrylates are preferred.

[0063]

In a case in which the energy-ray-curable monomer and/or oligomer (B) is blended, the content of the energy-ray-curable monomer and/or oligomer (B) in the energy-ray-curable pressure sensitive adhesive is preferably in a range of 5% to 80% by mass and particularly preferably in a range of 20% to 60% by mass of the total mass of the energy-ray-curable pressure sensitive adhesive.

[0064]

Here, in a case in which ultraviolet rays are used as the energy rays for curing an energy-ray-curable resin composition, a photopolymerization initiator (C) is preferably added thereto, and the use of this photopolymerization initiator (C) enables the polymerization cure time and the light-ray irradiance to be decreased.

[0065]

Specific examples of the photopolymerization initiator (C) include

benzophenone, acetophenone, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin benzoic acid, methyl benzoin benzoate, benzoin dimethyl ketal, 2,4-diethyl thioxanethone, 1-hydroxycyclohexyl phenyl ketone, benzyl diphenyl sulfide, tetramethylthiuram monosulfide,

5 azobisisobutyronitrile, benzyl, dibenzyl, diacetyl, β -chloroanthraquinone, (2,4,6-trimethyl benzyl diphenyl) phosphine oxide, 2-benzothiazole-N,N-diethyldithiocarbamate, oligo {2-hydroxy-2-methyl-1-[4-(1-propenyl) phenyl] propanone}, 2,2-dimethoxy-1,2-diphenylethane-1-one, and the like. These photopolymerization

10 initiators may be used singly or jointly.

[0066]

When the amount of an energy-ray-curable copolymer (A) is set to 100 parts by mass (in a case in which the energy-ray-curable monomer and/or oligomer (B) is blended, the total amount of the energy-ray-curable copolymer (A) and the energy-ray-curable

15 monomer and/or oligomer (B) is set to 100 parts by mass), the amount of the photopolymerization initiator (C) being used is preferably in a range of 0.1 to 10 parts by mass and particularly preferably in a range of 0.5 to 6 parts by mass.

[0067]

In addition to the above-described components, other components may be

20 appropriately blended into the energy-ray-curable pressure sensitive adhesive. Examples of the other components include a non-energy-ray-curable polymer component or oligomer component (D) and the like.

[0068]

Examples of the non-energy-ray-curable polymer component or oligomer

25 component (D) include polyacrylic acid esters, polyesters, polyurethane, polycarbonate,

polyolefin, and the like, and polymers or oligomers having a weight-average molecular weight (Mw) in a range of 3,000 to 2,500,000 are preferred.

[0069]

In addition, in the energy-ray-curable pressure sensitive adhesive, a cross-link
5 structure may be formed using a cross-linking agent (E).

That is, an aspect of the energy-ray-curable pressure sensitive adhesive includes
the energy-ray-curable copolymer (A) and, if desired, at least one component selected
from the group consisting of at least one component (B) selected from the group
consisting of energy-ray-curable monomers and oligomers, the photopolymerization
10 initiator (C), the non-energy-ray-curable polymer component or oligomer component (D),
and the cross-linking agent (E).

As the cross-linking agent (E), it is possible to use a polyfunctional compound
that is reactive to the functional group in the energy-ray-curable copolymer (A) or the
like. Examples of the above-described polyfunctional compound include isocyanate
15 compounds, epoxy compounds, amine compounds, melamine compounds, aziridine
compounds, hydrazine compounds, aldehyde compounds, oxazoline compounds, metallic
alkoxide compounds, metallic chelate compounds, metallic salts, ammonium salts,
reactive phenol resins, and the like.

[0070]

20 When the above-described other components (D) and (E) are used, it is possible
to improve a pressure sensitive adhesion property and a release property before curing,
strength after curing, adhesiveness to other layers, preservation stability, and the like.
The amount of these components used is not particularly limited and is appropriately
determined in a range of 0 to 40 parts by mass with respect to 100 parts by mass of the
25 energy-ray-curable copolymer (A).

[0071]

Next, a case in which the energy-ray-curable pressure sensitive adhesive includes a mixture of a non-energy-ray-curable polymer component and an energy-ray-curable polyfunctional monomer and/or oligomer as the main component will be described below.

[0072]

As the non-energy-ray-curable polymer component, it is possible to use, for example, a component that is the same as the above-described acrylic copolymer (a1), an acrylic copolymer including a (meth)acrylic acid ester monomer or a derivative thereof as the constituent unit instead of the functional group-containing monomer, or the like. The amount of the non-energy-ray-curable polymer component in the energy-ray-curable resin composition is preferably in a range of 20% to 99.9% by mass and particularly preferably in a range of 30% to 80% by mass of the total mass of the energy-ray-curable resin composition.

[0073]

As the energy-ray-curable polyfunctional monomer and/or oligomer, a monomer and/or oligomer that is the same as the above-described component (B) is selected. Regarding the blending ratio between the non-energy-ray-curable polymer component and the energy-ray-curable polyfunctional monomer and/or oligomer, the amount of the polyfunctional monomer and/or oligomer is preferably in a range of 10 to 150 parts by mass and particularly preferably in a range of 25 to 100 parts by mass with respect to 100 parts by mass of the non-energy-ray-curable polymer component.

[0074]

Even in this case, similar to the above-described case, the photopolymerization initiator (C) or the cross-linking agent (E) can be appropriately used.

That is, an aspect of the energy-ray-curable pressure sensitive adhesive includes the non-energy-ray-curable polymer component, at least one component selected from the group consisting of energy-ray-curable polyfunctional monomers and oligomers, and, if desired, at least one component selected from the group consisting of the photopolymerization initiator (C) and the cross-linking agent (E).

[0075]

Meanwhile, in a case in which an acrylic pressure sensitive adhesive is used as the pressure sensitive adhesive constituting the pressure sensitive adhesive layer 22, as the acrylic pressure sensitive adhesive, it is possible to use, for example, a component that is the same as the above-described acrylic copolymer (a1), an acrylic copolymer including a (meth)acrylic acid ester monomer or a derivative thereof as the constituent unit instead of the functional group-containing monomer, or the like. In addition, in this case, a cross-link structure may be formed in the acrylic pressure sensitive adhesive using the same cross-linking agent as the above-described cross-linking agent (E).

[0076]

In a case in which an acrylic pressure sensitive adhesive is used as the pressure sensitive adhesive constituting the pressure sensitive adhesive layer 22, the pressure sensitive adhesive layer 22 may further include an epoxy resin. In a case in which the pressure sensitive adhesive layer 22 is constituted using an acrylic pressure sensitive adhesive, there are cases in which a curable adhesive constituting the protective film-forming film 3 that is adjacent to the pressure sensitive adhesive layer 22 migrates to the pressure sensitive adhesive layer 22 and the properties of the pressure sensitive adhesive layer 22 change. However, when the pressure sensitive adhesive layer 22 includes an epoxy resin, it becomes possible to prevent the properties from being changed due to the above-described migration of the curable adhesive.

[0077]

In the above-described case, the content of the epoxy resin in the pressure sensitive adhesive layer 22 is preferably higher than 0 parts by mass and 20 parts by mass or lower and particularly preferably in a range of 1 to 17 parts by mass with respect to
5 100 parts by mass of the acrylic copolymer.

[0078]

The thickness of the pressure sensitive adhesive layer 22 in the present embodiment is preferably in a range of 2 to 50 μm , particularly preferably in a range of 2 to 40 μm , and still more preferably in a range of 3 to 30 μm . When the thickness of the
10 pressure sensitive adhesive layer 22 is 2 μm or thicker, excellent peel strength is sufficiently exhibited, and, when the thickness of the pressure sensitive adhesive layer 22 is 50 μm or thinner, workability becomes favorable.

[0079]

2. Protective film-forming film

15 The protective film-forming film 3 may have the same size and shape as those of workpieces such as semiconductor wafers, may have slightly smaller size and shape as those of workpieces, and may have slightly larger size and shape as those of workpieces.

[0080]

The protective film-forming film 3 is preferably made of a non-cured curable
20 adhesive. In this case, when a workpiece such as a semiconductor wafer is superimposed on the protective film-forming film 3, and then the protective film-forming film 3 is cured, it is possible to strongly adhere a protective film to the workpiece and form a durable protective film on chips and the like. On the protective film-forming film 3, favorable printing can be carried out by means of laser light irradiation regardless

of whether or not the curable adhesive is cured.

That is, in an aspect of the present invention, the composite sheet for forming a protective film includes a protective film-forming film made of a non-cured curable material.

5 [0081]

The protective film-forming film 3 preferably has a pressure sensitive adhesion property at room temperature and exhibits the pressure sensitive adhesion property when heated. In such a case, when a workpiece such as a semiconductor wafer is superimposed on the protective film-forming film 3 as described above, the workpiece and the protective film-forming film can be attached together. Therefore, it is possible to reliably determine the position of the protective film-forming film 3 before being cured, and it becomes easy to handle the composite sheet for forming a protective film 1.

[0082]

The curable adhesive constituting the protective film-forming film 3 having the above-described characteristics preferably includes a curable component and a binder polymer component. As the curable component, a thermosetting component, an energy-ray-curable component, or a mixture thereof can be used; however, when a method for curing the protective film-forming film 3 or the heat resistance of the cured protective film-forming film is taken into account, a thermosetting component is particularly preferably used.

[0083]

Examples of the thermosetting component include an epoxy resin, a phenol resin (a resin having a low molecular weight), a melamine resin, an urea resin, a polyester resin, an urethane resin, an acrylic resin, a polyimide resin, a benzoxazine resin, and the like, and mixture thereof. Among these, an epoxy resin, a phenol resin, and mixtures

thereof are preferably used. The molecular weight of the thermosetting component being used is generally in a range of approximately 300 to 10,000.

[0084]

The epoxy resin has a property of forming a three-dimensional net shape when heated and forming a robust coating. As the above-described epoxy resin, a variety of epoxy resins that have been known in the related art can be used; however, generally, epoxy resins having a molecular weight in a range of approximately 300 to 2,500 are preferred. Furthermore, epoxy resins obtained by blending an epoxy resin having a molecular weight in a range of 300 to 500 which is liquid in a normal state and an epoxy resin having a molecular weight in a range of 400 to 2,500 and particularly in a range of 500 to 2,000 which is solid at normal temperature are preferably used. In addition, the epoxy equivalent of the epoxy resin is preferably in a range of 50 to 5,000 g/eq.

[0085]

Specific examples of the above-described epoxy resin include glycidyl ethers of phenols such as bisphenol A, bisphenol F, resorcinol, phenyl novolac, and cresol novolac; glycidyl ethers of alcohols such as butanediol, polyethylene glycol, and polypropylene glycol; glycidyl ethers of carboxylic acid such as phthalic acid, isophthalic acid, and tetrahydrophthalic acid; glycidyl-type or alkyl glycidyl-type epoxy resins obtained by substituting active hydrogen bonded to a nitrogen atom with a glycidyl group such as aniline isocyanurate; so-called alicyclic epoxides into which an epoxy is introduced by, for example, oxidizing a carbon-carbon double bond in the molecule such as vinyl cyclohexane diepoxide, 3,4-epoxycyclohexylmethyl-3,4-dicyclohexane carboxylate, and 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane. Additionally, epoxy resins having a biphenyl skeleton, a dicyclohexadiene skeleton, a naphthalene skeleton, or the like can also be used.

[0086]

Among these, bisphenol-based glycidyl-type epoxy resins, o-cresol novolac-type epoxy resins, and phenol novolac-type epoxy resins are preferably used. These epoxy resins can be used singly or in a combined form.

5 [0087]

In a case in which the epoxy resin is used, a thermal activation-type latent epoxy resin-curing agent is preferably jointly used as an aid. The “thermal activation-type latent epoxy resin-curing agent” refers to a curing agent which does not react with the epoxy resin at room temperature, is activated when heated to a certain temperature or
10 higher, and reacts with the epoxy resin. Examples of a method for activating the thermal activation-type latent epoxy resin-curing agent include a method in which active species (anions and cations) are generated by a chemical reaction caused by heating; a method in which the thermal activation-type latent epoxy resin-curing agent is stably dispersed in the epoxy resin at near room temperature and is dissolved at a high
15 temperature together with the epoxy resin and a curing reaction is initiated; a method in which the thermal activation-type latent epoxy resin-curing agent is eluted at a high temperature using a molecular sieve sealing-type curing agent and a curing reaction is initiated; a method in which a microcapsule is used, and the like.

[0088]

20 Specific examples of the thermal activation-type latent epoxy resin-curing agent include a variety of onium salts, dibasic acid dihydrazide, dicyandiamide, amine adduct curing-agents, high-melting point active hydrogen compounds such as imidazole compounds, and the like. These thermal activation-type latent epoxy resin-curing agents can be used singly or in a combined form. The amount of the above-described
25 thermal activation-type latent epoxy resin-curing agent is preferably in a range of 0.1 to

20 parts by mass, particularly preferably in a range of 0.2 to 10 parts by mass, and still more preferably in a range of 0.3 to 5 parts by mass with respect to 100 parts by mass of the epoxy resin.

[0089]

5 As the phenol-based resin, polymers having a phenolic hydroxyl group such as condensates of a phenol and an aldehyde such as alkyl phenol, polyvalent phenol, and naphthol can be used without any particular limitations. Specifically, phenol novolac resins, o-cresol novolac resins, p-cresol novolac resins, t-butylphenol novolac resins, dicyclopentadiene cresol resins, polyparavinyl phenol resins, bisphenol A-type novolac
10 resins, modified substances thereof, and the like can be used.

[0090]

 The phenolic hydroxyl group in these phenol-based resins is capable of forming cured substances having high impact resistance by being easily addition-reacted with the epoxy group in the epoxy resin when heated. Therefore, the epoxy resin and the
15 phenol-based resin may be jointly used.

 Examples of the energy-ray-curable component include the components exemplified as the energy-ray-curable polymer or at least one component (B) selected from the group consisting of energy-ray-curable monomers and oligomers in the section of the pressure sensitive adhesive layer 22.

[0091]

20 The binder polymer component is blended in order to impart appropriate tack to the protective film-forming film 3 or improve the operability of the composite sheet for forming a protective film 1. The weight-average molecular weight of the binder polymer is generally in a range of 30,000 to 2,000,000, preferably in a range of 50,000 to
25 1,500,000, and particularly preferably in a range of 100,000 to 1,000,000. When the

molecular weight is 30,000 or higher, the protective film-forming film 3 is sufficiently formed, and, when the molecular weight is 2,000,000 or lower, the compatibility with other components is maintained favorable, and it is possible to uniformly form the protective film-forming film 3. As the above-described binder polymer, for example, an acrylic polymer, a polyester resin, a phenoxy resin, an urethane resin, a silicone resin, a rubber-based polymer, or the like can be used, and an acrylic polymer is particularly preferably used.

[0092]

Examples of the acrylic polymer include (meth)acrylic acid ester copolymers made up of a (meth)acrylic acid ester monomer and a constituent unit derived from a (meth)acrylic acid derivative. Here, the (meth)acrylic acid ester monomer is preferably an alkyl (meth)acrylate ester having 1 to 18 carbon atoms in an alkyl group, and more specific examples thereof include methyl (meth)acrylates, ethyl (meth)acrylates, propyl (meth)acrylates, butyl (meth)acrylates, and the like. In addition, examples of the (meth)acrylic acid derivative include (meth)acrylic acids, glycidyl (meth)acrylates, hydroxyethyl (meth)acrylates, and the like.

[0093]

Among these, when a glycidyl group is introduced into an acrylic polymer using glycidyl methacrylate or the like as a constituent unit, the compatibility with the epoxy resin as the above-described thermosetting component improves, the glass transition temperature (T_g) of the cured protective film-forming film 3 increases, and the heat resistance improves. In addition, among these, when a hydroxyl group is introduced into an acrylic polymer using hydroxyethyl acrylate or the like as a constituent unit, it is possible to control close adhesiveness or a pressure sensitive adhesion property to workpieces. Meanwhile, in a case in which a glycidyl group is introduced into an

acrylic polymer using glycidyl methacrylate or the like as a constituent unit, the acrylic polymer or the phenoxy resin having the epoxy group has a thermosetting property.

However, the above-described thermosetting polymer is also considered as the binder polymer component, not as the thermosetting component in the present embodiment.

5 [0094]

In a case in which an acrylic polymer is used as the binder polymer, the weight-average molecular weight of the polymer is preferably 100,000 or higher and particularly preferably in a range of 150,000 to 1,000,000. The glass transition temperature of the acrylic polymer is generally 20°C or lower and preferably in a range of approximately -70°C to 0°C, and the acrylic polymer has a pressure sensitive adhesion property at room temperature (23°C).

[0095]

Regarding the blending ratio between the thermosetting component and the binder polymer component, when amount of the binder polymer component is set to 100 parts by weight, the amount of the thermosetting component blended is preferably in a range of 50 to 1,500 parts by weight, more preferably in a range of 70 to 1,000 parts by weight, and still more preferably in a range of 80 to 800 parts by weight. When the thermosetting component and the binder polymer component are blended together at the above-described ratio, the thermosetting component exhibits appropriate tack before being cured, it is possible to stably carry out attachment operations, and protective films having an excellent coating strength can be obtained after the thermosetting component is cured.

[0096]

The protective film-forming film 3 preferably includes a filler and/or a coloring agent. When the protective film-forming film 3 includes a filler, it is possible to

maintain the hardness of cured protective films at a high level and improve moisture resistance. In addition, it is also possible to adjust the glossiness of the surface of protective films to be formed to a desired value. Furthermore, it is possible to approximate the thermal expansion coefficient of cured protective films to the thermal expansion coefficient of semiconductor wafers and thus alleviate semiconductor wafers being warped in the middle of processes. On the other hand, when the protective film-forming film 3 includes a filler and/or a coloring agent, it is also possible to enable laser printing having excellent visibility.

[0097]

Examples of the filler include silica such as crystalline silica, molten silica, and synthetic silica and inorganic fillers such as alumina and glass balloons. Among these, synthetic silica is preferred, and, particularly, synthetic silica from which a radiation source of an α ray which causes malfunction of semiconductor devices is extremely removed is optimal. The shape of the filler may be any one of a spherical shape, a needle shape, or an irregular shape.

[0098]

In addition, as the filler that is added to the protective film-forming film 3, in addition to the above-described inorganic filler, a functional filler may be blended.

Examples of the functional filler include gold, silver, copper, nickel, aluminum, stainless steel, carbon, or ceramic conductive fillers, conductive fillers in which nickel, aluminum, or the like is coated with silver, all of which are intended to impart an antistatic property, thermal conductive fillers of a metallic material such as gold, silver, copper, nickel, aluminum, stainless steel, silicon, or germanium, an alloy thereof, or the like which are intended to impart a thermal conductive property, and the like.

[0099]

As the coloring agent, it is possible to use a well-known coloring agent such as an inorganic pigment, an organic pigment, or an organic dye.

[0100]

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

[0101]

10 Examples of the organic pigment and the organic dye include aluminum-based
 colorants, cyanine-based colorants, merocyanine-based colorants, croconium-based
 colorants, squarylium-based colorants, azulenium-based colorants, polymethine-based
 colorants, naphthoquinone-based colorants, pyrylium-based colorants,
 phthalocyanine-based colorants, naphthalocyanine-based colorants, naphtholactam-based
 15 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
 20 phenol-based colorants, triarylmethane-based colorants, anthraquinone-based colorants,
 dioxazine-based colorants, naphthol-based colorants, azomethine-based colorants,
 benzimidazolone-based colorants, pyranthrone-based colorants, threne-based color, and
 the like. These pigments or dyes can be used in an appropriate mixed form in order to
 adjust the light transmittance to a target value.

25 [0102]

Among these, pigments, particularly, inorganic pigments are preferably used from the viewpoint of a printing property by means of laser light irradiation. Among inorganic pigments, carbon black is particularly preferred. Carbon black is generally black, but portions from which carbon black is scraped by means of laser light irradiation exhibit white, and the contrast difference becomes large, and thus the visibility of laser-printed portions is extremely excellent.

[0103]

The amount of the filler and the coloring agent blended into the protective film-forming film 3 may be appropriated adjusted so as to exhibit desired operations.

Specifically, the amount of the filler blended is, generally, preferably in a range of 40% to 80% by mass and particularly preferably in a range of 50% to 70% by mass of the total mass of the protective film-forming film. In addition, the amount of the coloring agent blended is, generally, preferably in a range of 0.001% to 5% by mass, particularly preferably in a range of 0.01% to 3% by mass, and still more preferably in a range of 0.1% to 2.5% by mass of the total mass of the protective film-forming film.

[0104]

The protective film-forming film 3 may include a coupling agent. When the protective film-forming film includes a coupling agent, it is possible to improve adhesiveness and close adhesiveness between protective films and workpieces without impairing the heat resistance of the protective films after the protective film-forming film 3 is cured and improve water resistance (moisture-heat resistance). The coupling agent is preferably a silane coupling agent in terms of the general versatility, cost merit, and the like thereof.

[0105]

Examples of the silane coupling agent include

γ -glycidoxypentyltrimethoxysilane, γ -glycidoxypentylmethyldiethoxysilane,
 β -(3,4-epoxycyclohexyl) ethyl trimethoxy silane, γ -(methacryloxypropyl)
 trimethoxysilane, γ -amino propyl trimethoxy silane,
 N-6-(aminoethyl)- γ -aminopentyltrimethoxysilane, N-6-(aminoethyl)- γ -aminopentyl
 5 methyl diethoxy silane, N-phenyl- γ -aminopentyl trimethoxy silane,
 γ -ureidopentyltriethoxysilane, γ -mercaptopentyltrimethoxysilane, γ -mercaptopentyl
 methyl dimethoxy silane, bis(3-triethoxysilylpropyl) tetrasulfane,
 methyltrimethoxysilane, methyltriethoxysilane, vinyl trimethoxysilane,
 vinyltriacetoxysilane, imidazole silane, and the like. These silane coupling agents can
 10 be used singly or in a mixed form.

[0106]

In order to adjust the cohesive strength of the protective film-forming film 3 to
 be cured, the protective film-forming film 3 may include a cross-linking agent such as an
 organic polyvalent isocyanate compound, an organic polyvalent imine compound, or an
 15 organic metallic chelate compound. In addition, in order to limit static electricity and
 improve the reliability of chips, the protective film-forming film 3 may include an
 antistatic agent. Furthermore, in order to enhance the flame-retardant performance of
 protective films and improve the reliability as packages, the protective film-forming film
 3 may include a flame retardant such as a phosphoric acid compound, a bromine
 20 compound, or a phosphorus-based compound.

That is, an aspect of the protective film-forming film 3 includes the curable
 component, the binder polymer component, and, if desired, at least one component
 selected from the group consisting of the coloring agent, the filler, the coupling agent, the
 cross-linking agent, the antistatic agent, and the flame retardant.

[0107]

In order to effectively exhibit functions as protective films, the thickness of the protective film-forming film 3 is preferably in a range of 3 to 300 μm , particularly preferably in a range of 5 to 250 μm , and still more preferably in a range of 7 to 200 μm .

5 [0108]

Here, in a case in which a protective film is formed by curing the protective film-forming film 3 in a state of being in contact with the pressure sensitive adhesive layer 22 in the pressure sensitive adhesive sheet 2, the glossiness value of the surface of the protective film on the pressure sensitive adhesive sheet 2 side is preferably 25 or
10 higher and particularly preferably 30 or higher. Meanwhile, in the present specification, the glossiness value refers to a value measured using a glossimeter at a measurement angle of 60° according to JIS Z8741. When the glossiness value of the surface of a protective film formed on chips is in the above-described range, the appearance is excellent, and the visibility of prints formed by means of laser printing is also excellent.

15 [0109]

3. Pressure sensitive adhesive layer for jig

The composite sheet for forming a protective film 1 according to the present embodiment includes the pressure sensitive adhesive layer for a jig 4 at the circumferential edge portion on a side opposite to the pressure sensitive adhesive sheet 2
20 side of the protective film-forming film 3. When the composite sheet for forming a protective film includes the pressure sensitive adhesive layer for a jig 4 as described above, it is possible to reliably attach and fix the composite sheet for forming a protective film 1 to a jig such as a ring frame regardless of the peel strength of the protective film-forming film 3.

25 [0110]

In the present embodiment, the pressure sensitive adhesive layer for a jig 4 is formed in a ring shape and may be made up of a single layer or two or more multiple layers, and, in a case in which the pressure sensitive adhesive layer for a jig is made up of multiple layers, a constitution in which a core material is interposed between layers is preferred.

[0111]

A pressure sensitive adhesive constituting the pressure sensitive adhesive layer for a jig 4 is preferably constituted of a non-energy-ray-curable pressure sensitive adhesive from the viewpoint of the peel strength to the jig such as the ring frame. The non-energy-ray-curable pressure sensitive adhesive preferably has a desired peel strength and desired removability, for example, an acrylic pressure sensitive adhesive, a rubber pressure sensitive adhesive, a silicone pressure sensitive adhesive, an urethane-based pressure sensitive adhesive, a polyester-based pressures sensitive adhesive, a polyvinyl ether-based pressure sensitive adhesive, or the like can be used, and, among these, an acrylic pressure sensitive adhesive of which the peel strength and the removability can be easily controlled is preferred.

[0112]

As the core material, generally, resin films can be used, and, among these, polyvinyl chloride-based films such as polyvinyl chloride films and vinyl chloride copolymer films are preferred, and polyvinyl chloride films are particularly preferred. Polyvinyl chloride films have a property of being easily returned to the original state when cooled even in the case of being softened by means of heating. The thickness of the core material is preferably in a range of 2 to 200 μm and particularly preferably in a range of 5 to 100 μm .

[0113]

The thickness of the pressure sensitive adhesive layer for a jig 4 is preferably in a range of 5 to 200 μm and particularly preferably in a range of 10 to 100 μm from the viewpoint of adhesiveness to the jig such as the ring frame.

[0114]

5 4. Release sheet

The composite sheet for forming a protective film 1 may include a release sheet on the protective film-forming film 3 and pressure sensitive adhesive layer for a jig 4 side thereof (the upper side in FIG. 1). A composite sheet for forming a protective film 10 which is an embodiment of the present invention is shown in FIG. 4. According to such a release sheet 7, it is possible to protect the protective film-forming film 3 and the pressure sensitive adhesive layer for a jig 4 until the composite sheet for forming a protective film 1 is used.

[0115]

The release sheet 7 has an arbitrary constitution, and a constitution in which a plastic film is released using a release agent or the like is exemplified. Specific examples of the plastic film include polyester films such as polyethylene terephthalate, polybutylene terephthalate, and polyethylene naphthalate and polyolefin films such as polypropylene and polyethylene. As the release agent, a silicone-based release agent, a fluorine-based release agent, a long-chain alkyl-based release agent, or the like can be used, and, among these, a silicone-based release agent which is inexpensive and capable of providing stable performance is preferred. The thickness of the release sheet is not particularly limited, but is generally in a range of approximately 20 to 250 μm .

[0116]

When the composite sheet for forming a protective film is heated to 130°C at a temperature-increase rate of 10°C/minute and held at that temperature for two hours, the

weight decrease ratio (the measurement method will be described in testing examples below) of the composite sheet for forming a protective film is 0.01% or higher and 6.0% or lower, more preferably 3.0% or lower, still more preferably 2.5% or lower, and particularly 1.2% or lower. That is, the weight decrease ratio of the composite sheet for forming a protective film is preferably 0.01% to 6.0%, more preferably 0.01% to 3.0%, still more preferably 0.01% to 2.5%, and particularly 0.01% to 1.2%. Here, the composite sheet for forming a protective film refers to a composite sheet for forming a protective film which includes the base material, the pressure sensitive adhesive layer, and the protective film-forming film, in which the base material, the pressure sensitive adhesive layer, and the protective film-forming film are laminated in this order, and which does not include the release sheet and the pressure sensitive adhesive layer for a jig. When the weight decrease ratio of the composite sheet for forming a protective film is in the above-described range, the composite sheet for forming a protective film does not easily deform when heated and has excellent heat resistance suitable for the intended use thereof. In addition, when the weight decrease ratio of the composite sheet for forming a protective film is in the above-described range, gas is rarely generated from the composite sheet for forming a protective film during heating of the composite sheet for forming a protective film, and it is possible to limit deterioration of the composite sheet for forming a protective film. Furthermore, when the weight decrease ratio of the composite sheet for forming a protective film is in the above-described range, the peel strength between the composite sheet for forming a protective film and workpieces does not easily decrease.

[0117]

5. Method for manufacturing composite sheet for forming a protective film

The composite sheet for forming a protective film 1 can be manufactured by,

preferably, respectively producing a first laminate including the protective film-forming film 3, a second laminate including the pressure sensitive adhesive sheet 2, and a third laminate including the pressure sensitive adhesive layer for a jig 4, then, laminating the protective film-forming film 3 and the pressure sensitive adhesive sheet 2 using the first
5 laminate and the second laminate, and, furthermore, laminating the pressure sensitive adhesive layer for a jig 4 using the third laminate, but the manufacturing method is not limited thereto.

[0118]

In order to manufacture the first laminate, the protective film-forming film 3 is
10 formed on a release surface (a surface having a release property; generally, a surface on which a release treatment is carried out, but the release surface is not limited thereto) of a first release sheet. Specifically, a coating agent for the protective film-forming film which includes a curable adhesive constituting the protective film-forming film 3 and, furthermore, a solvent, if desired, is prepared, and the coating agent is applied and dried
15 on the release surface of the first release sheet using a coater such as a roll coater, a knife coater, a roll knife coater, an air knife coater, a die coater, a bar coater, a gravure coater, or a curtain coater, thereby forming the protective film-forming film 3 on the release surface of the first release sheet. Next, a release surface of a second release sheet is superimposed on and pressed to the exposed surface of the protective film-forming film 3,
20 thereby obtaining a laminate (first laminate) in which the protective film-forming film 3 is sandwiched by two release sheets.

[0119]

In order to manufacture the second laminate, a coating agent for the pressure sensitive adhesive layer which includes a pressure sensitive adhesive constituting the
25 pressure sensitive adhesive layer 22 and, furthermore, a solvent, if desired, is applied and

dried on a release surface of a third release sheet, thereby forming the pressure sensitive adhesive layer 22 on the release surface of the third release sheet. After that, the base material 21 is pressed to the exposed surface of the pressure sensitive adhesive layer 22, thereby obtaining a laminate (second laminate) made up of the pressure sensitive adhesive sheet 2 made up of the base material 21 and the pressure sensitive adhesive layer 22 and the release sheet.

[0120]

Here, in a case in which the pressure sensitive adhesive layer 22 is made of an energy-ray-curable pressure sensitive adhesive, the energy-ray-curable pressure sensitive adhesive may be cured by irradiating the pressure sensitive adhesive layer 22 with energy rays. In addition, in a case in which the pressure sensitive adhesive layer 22 is made up of multiple layers, and a layer in contact with the protective film-forming film 3 is made of an energy-ray-curable pressure sensitive adhesive, the energy-ray-curable pressure sensitive adhesive may be cured by irradiating the layer in contact with the pressure sensitive adhesive layer 22 with energy rays.

[0121]

As the energy rays, generally, ultraviolet rays, electron beams, or the like are used. The irradiance of the energy rays varies depending on the kind of the energy rays; however, in the case of ultraviolet rays, the irradiance is preferably in a range of 50 to 1,000 mJ/cm² and particularly preferably in a range of 100 to 500 mJ/cm² in terms of light intensity. In addition, in the case of electron beams, the irradiance is preferably in a range of approximately 10 to 1,000 krad.

[0122]

In order to manufacture the third laminate in a case in which the pressure sensitive adhesive layer for a jig 4 is a single layer, the pressure sensitive adhesive layer

for a jig 4 is formed on the release surface of the first release sheet. Specifically, a coating agent for the pressure sensitive adhesive layer for a jig which includes a pressure sensitive adhesive constituting the pressure sensitive adhesive layer for a jig 4 and, furthermore, a solvent, if desired, is prepared, and the coating agent is applied and dried on the release surface of the first release sheet, thereby forming the pressure sensitive adhesive layer for a jig 4. Next, the release surface of the second release sheet is superimposed on and pressed to the exposed surface of the pressure sensitive adhesive layer for a jig 4, thereby obtaining a laminate (third laminate) in which the pressure sensitive adhesive layer for a jig 4 is sandwiched by two release sheets.

[0123]

In order to manufacture the third laminate in a case in which the pressure sensitive adhesive layer for a jig 4 includes a core material, for example, a first pressure sensitive adhesive layer for a jig is formed on the release surface of the first release sheet, and the core material is laminated on the first pressure sensitive adhesive layer for a jig. In addition, a second pressure sensitive adhesive layer for a jig is formed on the release surface of the second release sheet. In addition, the second pressure sensitive adhesive layer for a jig and the core material on the first pressure sensitive adhesive layer for a jig are superimposed together, and both laminates are pressed to each other. Therefore, a laminate (third laminate) in which the pressure sensitive adhesive layer for a jig 4 including the core material is sandwiched by two release sheets is obtained.

[0124]

Once the first laminate, the second laminate, and the third laminate are obtained as described above, the second release sheet in the first laminate is released, the release sheet in the second laminate is released, and the protective film-forming film 3 exposed in the first laminate and the pressure sensitive adhesive layer 22 in the pressure sensitive

adhesive sheet 2 exposed in the second laminate are superimposed and pressed together (fourth laminate).

[0125]

Meanwhile, in the third laminate, the second release sheet and the inner
5 circumferential edge of the pressure sensitive adhesive layer for a jig 4 are half-cut while the first release sheet remains untouched. The second release sheet and a surplus portion (round portion) of the pressure sensitive adhesive layer for a jig 4 which is generated by means of the half-cutting need to be appropriately removed. In addition, the first release sheet is released from the fourth laminate, and the exposed protective
10 film-forming film 3 and the pressure sensitive adhesive layer for a jig 4 exposed in the third laminate are superimposed and pressed together. After that, the outer circumferential edge of the composite sheet for forming a protective film 1 is half-cut while the first release sheet in the third laminate remains untouched.

[0126]

15 In the above-described manner, the composite sheet for forming a protective film 10 in which the release sheet 7 is laminated on the composite sheet for forming a protective film 1 made up of the pressure sensitive adhesive sheet 2 including the pressure sensitive adhesive layer 22 laminated on the base material 21, the protective film-forming film 3 laminated on the pressure sensitive adhesive layer 22 side of the
20 pressure sensitive adhesive sheet 2, and the pressure sensitive adhesive layer for a jig 4 laminated on the circumferential edge portion of the protective film-forming film 3 on a side opposite to the pressure sensitive adhesive sheet 2 is obtained. In this case, the release sheet 7 is laminated on a side of the pressure sensitive adhesive layer for a jig 4 opposite to the protective film-forming film 3.

25 [0127]

The composite sheet for forming a protective film 1 having the above-described constitution may be provided with the same size and shape as those of the protective film-forming film 3 and the pressure sensitive adhesive sheet 2, and thus, compared with composite sheets for forming a protective film having a different size or shape, the half-cutting step is simple, and the composite sheet for forming a protective film can be easily manufactured.

[0128]

In addition, in the above-described composite sheet for forming a protective film 1, the protruding outer circumferential edge of the pressure sensitive adhesive layer for a jig 4 may be located at the same location as the outer circumferential edge of the entire composite sheet for forming a protective film 1, and thus, when a long release sheet (casting film) carrying a plurality of the composite sheets for forming a protective film 1 according to the present embodiment is wound, there is an advantage that a so-called winding mark is not easily generated.

[0129]

6. Method for using composite sheet for forming protective film

A method for manufacturing a protective film-attached chip from a semiconductor wafer, which is an example of a workpiece, using the composite sheet for forming a protective film 1 according to the present embodiment will be described below. In the beginning, as shown in FIG. 3, the protective film-forming film 3 is attached to a semiconductor wafer 5, and the pressure sensitive adhesive layer for a jig 4 is attached to a ring frame 6. When the protective film-forming film 3 is attached to the semiconductor wafer 5, a pressure sensitive adhesion property may be exhibited by heating the protective film-forming film 3 if desired.

[0130]

Next, the protective film-forming film 3 is cured, thereby forming a protective film. In a case in which the protective film-forming film 3 is a thermosetting adhesive, the protective film-forming film 3 is heated at a predetermined temperature for an appropriate duration and then is cooled. At this time, since the loosening of the composite sheet for forming a protective film 1 according to the present embodiment is effectively suppressed, no troubles are caused in the subsequent steps.

[0131]

If desired, laser printing may be carried out on the protective film-forming film 3 to be cured or the cured protective film-forming film 3 (protective film). After that, the semiconductor wafer 5 is diced using an ordinary method, and a chip having the protective film (protective film-attached chip) is obtained. In addition, the pressure sensitive adhesive sheet 2 is expanded in a planar direction if desired, and the protective film-attached chip is picked up from the pressure sensitive adhesive sheet 2. The composite sheet for forming a protective film 1 according to the present embodiment includes the pressure sensitive adhesive layer 22, and thus the scattering of the chip during the dicing is suppressed. In addition, since the pressure sensitive adhesive sheet 2 in the composite sheet for forming a protective film 1 according to the present embodiment is appropriately flexible, it is possible to favorably expand the sheet and pick up the chip.

[0132]

The above-described embodiment is a description for easy understanding of the present invention and does not intend to limit the present invention. Therefore, all design changes or equivalents in the technical scope of the present invention may be considered as the respective elements disclosed in the present embodiment.

[0133]

For example, the pressure sensitive adhesive layer for a jig 4 may be a bilayer constitution made up of a base material and a pressure sensitive adhesive layer. In this case, the pressure sensitive adhesive layer for a jig is preferably constituted so that the base material is adhered to the protective film-forming film 3 exhibiting the pressure sensitive adhesion property and the pressure sensitive adhesive layer is attached to the jig such as the ring frame. In addition, the pressure sensitive adhesive layer for a jig 4 may not be provided in the composite sheet for forming a protective film 1. In this case, it is preferable that the protective film-forming film 3 is formed in a diameter smaller than that of the pressure sensitive adhesive sheet 2 so that the pressure sensitive adhesive layer 22 in the pressure sensitive adhesive sheet 2 is exposed and the exposed pressure sensitive adhesive layer 22 is attached to the jig such as the ring frame.

EXAMPLES

[0134]

Hereinafter, the present invention will be more specifically described using examples and the like, but the scope of the present invention is not limited to these examples and the like.

[0135]

[Example 1]

In Example 1, the composite sheet for forming a protective film 1 as shown in FIG. 1 was manufactured in the following manner.

(1) Production of first laminate including protective film-forming film

The following components (a) to (g) were mixed together and were diluted using methyl ethyl ketone so that the concentration of solid contents reached 50% by mass, thereby preparing a coating agent for a protective film-forming film.

(a) Binder polymer: a (meth)acrylic acid ester copolymer (a copolymer obtained by copolymerizing n-butyl acrylate (10 parts by mass), methyl acrylate (70 parts by mass), glycidyl methacrylate (5 parts by mass), and 2-hydroxyethyl acrylate (15 parts by mass), weight-average molecular weight: 800,000, glass transition temperature: -1°C) 150 parts by mass (in terms of solid contents, which shall apply below), (b-1) thermosetting component: a bisphenol A-type epoxy resin (manufactured by Mitsubishi Chemical Corporation, trade name “jER828”, epoxy equivalent in a range of 184 to 194 g/eq) (60 parts by mass), (b-2) thermosetting component: a bisphenol A-type epoxy resin (manufactured by Mitsubishi Chemical Corporation, trade name “jER1055”, epoxy 10 equivalent in a range of 800 to 900 g/eq) (10 parts by mass), (b-3) thermosetting component: a dicyclopentadiene-type epoxy resin (manufactured by DIC Corporation, trade name “EPICLON-HP7200HH”, epoxy equivalent in a range of 255 to 260 g/eq) (30 parts by mass), (c) thermal activation latent epoxy resin-curing agent: dicyandiamide (manufactured by ADEKA Corporation, trade name, ADEKA HARDNER EH3636AS, 15 amount of active hydrogen of 21 g/eq) (2 parts by mass), (d) curing accelerator: 2-phenyl-4,5-dihydroxymethylimidazole (manufactured by Shikoku chemicals Corporation, trade name “CURESOL 2PHZ”) (2 parts by mass), (e) filler: a silica filler (manufactured by Admatechs., trade name “SC2050MA”, average particle diameter: 0.5 μm) (320 parts by mass), (f) coloring agent: carbon black (manufactured by Mitsubishi 20 Chemical Corporation, trade name “#MA650”, average particle diameter: 28 nm) (1.2 parts by mass), and (g) silane coupling agent: (manufactured by Shin-Etsu Chemical Co., Ltd., trade name “KBM-403”) (2 parts by mass)

[0136]

A first release sheet obtained by forming a silicone-based release agent layer on 25 a single surface of a 38 μm-thick polyethylene terephthalate (PET) film (manufactured

by Lintec Corporation, trade name “SP-PET381031”) and a second release sheet obtained by forming a silicone-based release agent layer on a single surface of a 38 μm -thick PET film (manufactured by Lintec Corporation, trade name “SP-PET381130”) were prepared.

5 [0137]

In the beginning, the coating agent for a protective film-forming film was applied using a knife coater onto the release surface of the first release sheet so that the thickness of the finally-obtained protective film-forming film reached 25 μm and was dried, thereby forming a protective film-forming film. After that, the release surface of
10 a second release sheet was superimposed on the protective film-forming film and the release sheet and the film are attached together, thereby obtaining a laminate made up of the first release sheet, the protective film-forming film (thickness: 25 μm), and the second release sheet. This laminate had a long length and was wound so as to produce a wound body.

15 [0138]

(2) Production of second laminate including pressure sensitive adhesive sheet

The following components (h) and (i) were mixed together and were diluted using methyl ethyl ketone so that the concentration of solid contents reached 25% by mass, thereby preparing a coating agent for a pressure sensitive adhesive layer.

20 (h) Pressure sensitive adhesive: a (meth)acrylic acid ester copolymer (a copolymer obtained by copolymerizing 2-ethylhexyl acrylate (60 parts by mass), methyl methacrylate (30 parts by mass), and 2-hydroxyethyl acrylate (10 parts by mass), weight-average molecular weight: 600,000) 100 parts by mass and (i) cross-linking agent: a xylene diisocyanate adduct of trimethylolpropane (manufactured by Mitsui
25 Takeda Chemicals, Inc., trade name “TAKENATE D110N”) (20 parts by mass)

[0139]

As a release sheet, a release sheet obtained by forming a silicone-based release agent layer on a single surface of a 38 μm -thick PET film (manufactured by Lintec Corporation, trade name "SP-PET381031") was prepared.

5 [0140]

In addition, as a base material, a polypropylene film (thickness: 80 μm) having ratios of expansion and contraction under load of 98.6% in the MD direction and 99.1% in the CD direction, ratios of expansion and contraction without load of 99.0% in the MD direction and 98.8% in the CD direction, tensile moduli of elasticity of 320 MPa in the MD direction and 290 MPa in the CD direction, and a melting point of 156°C was prepared. Meanwhile, the methods for measuring the ratio of expansion and contraction under load, the ratio of expansion and contraction without load, the tensile modulus of elasticity, and the melting point are as described in testing examples below (which shall apply below).

15 [0141]

In the beginning, the coating agent for a pressure sensitive adhesive layer was applied using a knife coater onto the release surface of the release sheet so that the thickness of the finally-obtained pressure sensitive adhesive layer reached 5 μm and was dried, thereby forming a pressure sensitive adhesive layer. After that, the base material was attached to the pressure sensitive adhesive layer, and a second laminate made up of a pressure sensitive adhesive sheet made up of the base material and the pressure sensitive adhesive layer and the release sheet was obtained. This laminate had a long length. After that, the laminate was wound so as to produce a wound body.

[0142]

(3) Production of third laminate including pressure sensitive adhesive layer for
jig 4

The following components (j) and (k) were mixed together and were diluted
using toluene so that the concentration of solid contents reached 15% by mass, thereby
5 preparing a coating agent for a pressure sensitive adhesive layer. (j) Pressure sensitive
adhesive: a (meth)acrylic acid ester copolymer (a copolymer obtained by copolymerizing
butyl acrylate (69.5 parts by mass), methyl methacrylate (30 parts by mass), and
2-hydroxyethyl acrylate (0.5 parts by mass), weight-average molecular weight: 500,000)
100 parts by mass and (k) cross-linking agent: a tolylene diisocyanate-based
10 cross-linking agent (manufactured by Toyochem Co., Ltd., trade name "BHS8515") (5
parts by mass)

[0143]

First and second release sheets obtained by forming a silicone-based release
agent layer on a single surface of a 38 μm -thick PET film (manufactured by Lintec
15 Corporation, trade name "SP-PET381031") and a polyvinyl chloride film (manufactured
by Okamoto Industries, Inc., thickness: 50 μm) as a core material were prepared.

[0144]

In the beginning, the coating agent for a pressure sensitive adhesive layer was
applied using a knife coater onto the release surface of the first release sheet so that the
20 thickness of the finally-obtained pressure sensitive adhesive layer reached 5 μm and was
dried, thereby forming a first pressure sensitive adhesive layer. After that, the core
material was attached to the first pressure sensitive adhesive layer, and a laminate A
made up of the core material, the first pressure sensitive adhesive layer, and the first
release sheet was obtained. This laminate A had a long length and was wound so as to
25 produce a wound body.

[0145]

Next, the coating agent for a pressure sensitive adhesive layer was applied using a knife coater onto the release surface of the second release sheet so that the thickness of the finally-obtained pressure sensitive adhesive layer reached 5 μm and was dried, thereby forming a second pressure sensitive adhesive layer. After that, the surface of the laminate A on which the core material was exposed was attached to the second pressure sensitive adhesive layer, and a third laminate made up of the first release sheet/ the first pressure sensitive adhesive layer/ the core material/ the second pressure sensitive adhesive layer/ the second release sheet was obtained. This laminate had a long length and was wound so as to produce a wound body.

[0146]

(4) Production of fourth laminate

The second release sheet was released from the first laminate obtained in the above-described (1), thereby exposing the protective film-forming film. Meanwhile, the release sheet was released from the second laminate obtained in the above-described (2), thereby exposing the pressure sensitive adhesive layer. The first laminate and the second laminate were attached together so that the protective film-forming film came into contact with the pressure sensitive adhesive layer, thereby obtaining a fourth laminate in which the pressure sensitive adhesive sheet made up of the base material and the pressure sensitive adhesive layer, the protective film-forming film, and the first release sheet were laminated.

[0147]

(5) Production of composite sheet for forming a protective film

The second release sheet was released from the third laminate obtained in the above-described (3), the inner circumferential edge of the pressure sensitive adhesive

layer for a jig was half-cut while the first release sheet remained untouched, and the inside round portion was removed. At this time, the diameter of the inner circumferential edge of the pressure sensitive adhesive layer for a jig was set to 170 mm.

[0148]

5 The first release sheet was released from the fourth laminate obtained in the above-described (4), and the exposed protective film-forming film and the pressure sensitive adhesive layer for a jig exposed in the third laminate were superimposed and pressed together. After that, the outer circumferential edge of the composite sheet for forming a protective film was half-cut while the first release sheet in the third laminate
10 remained untouched. At this time, the diameter of the outer circumferential edge of the pressure sensitive adhesive layer for a jig was set to 205 mm.

[0149]

In the above-described manner, a composite sheet for forming a protective film made up of the pressure sensitive adhesive sheet obtained by laminating the pressure
15 sensitive adhesive layer (thickness: 5 μ m) on the base material, the protective film-forming film laminated on the pressure sensitive adhesive layer side of the pressure sensitive adhesive sheet, the pressure sensitive adhesive layer for a jig laminated on the circumferential edge portion of the protective film-forming film on a side opposite to the pressure sensitive adhesive sheet, and the release sheet laminated on a side of the
20 pressure sensitive adhesive layer for a jig opposite to the protective film-forming film was obtained.

[0150]

[Example 2]

A composite sheet for forming a protective film was manufactured in the same
25 manner as in Example 1 except for the fact that, as the base material, a polypropylene

film (thickness: 80 μm) having ratios of expansion and contraction under load of 96.3% in the MD direction and 99.6% in the CD direction, ratios of expansion and contraction without load of 98.8% in the MD direction and 99.0% in the CD direction, tensile moduli of elasticity of 190 MPa in the MD direction and 170 MPa in the CD direction, and a melting point of 154°C was used.

[0151]

[Example 3]

A composite sheet for forming a protective film was manufactured in the same manner as in Example 1 except for the fact that, as the base material, a polypropylene film (thickness: 80 μm) having ratios of expansion and contraction under load of 99.7% in the MD direction and 102.8% in the CD direction, ratios of expansion and contraction without load of 99.3% in the MD direction and 99.4% in the CD direction, tensile moduli of elasticity of 490 MPa in the MD direction and 450 MPa in the CD direction, and a melting point of 131°C was used.

[0152]

[Example 4]

A composite sheet for forming a protective film was manufactured in the same manner as in Example 1 except for the fact that, as the base material, a polypropylene film (thickness: 80 μm) having ratios of expansion and contraction under load of 101.4% in the MD direction and 100.4% in the CD direction, ratios of expansion and contraction without load of 99.6% in the MD direction and 99.6% in the CD direction, tensile moduli of elasticity of 630 MPa in the MD direction and 620 MPa in the CD direction, and a melting point of 163°C was used.

[0153]

[Comparative Example 1]

A composite sheet for forming a protective film was manufactured in the same manner as in Example 1 except for the fact that, as the base material, a polypropylene film (thickness: 80 μm) having ratios of expansion and contraction under load of 155.0% in the MD direction and 195.0% in the CD direction, ratios of expansion and contraction without load of 97.0% in the MD direction and 97.8% in the CD direction, tensile moduli of elasticity of 220 MPa in the MD direction and 210 MPa in the CD direction, and a melting point of 118°C was used.

[0154]

[Comparative Example 2]

A composite sheet for forming a protective film was manufactured in the same manner as in Example 1 except for the fact that, as the base material, a polypropylene film (thickness: 80 μm) having ratios of expansion and contraction under load of 93.9% in the MD direction and 129.8% in the CD direction, ratios of expansion and contraction without load of 94.0% in the MD direction and 97.3% in the CD direction, tensile moduli of elasticity of 130 MPa in the MD direction and 120 MPa in the CD direction, and a melting point of 124°C was used.

[0155]

[Testing Example 1] <Measurement of ratio of expansion and contraction under

load>

The base materials used in the examples and the comparative examples were slivered so as to have a 22 mm-long short side in the CD direction and a 110 mm-long long side in the MD direction and were used as test specimens in the MD direction. Among the length of 110 mm, 100 mm in the central portion of the test specimen in the

longitudinal direction was marked as a measurement distance, and clips having a mass of 2.2 g were respectively mounted on both end portions (5 mm portions at the end portions) of the test specimen in the longitudinal direction.

[0156]

5 The test specimen was hung in an oven using one clip. At this time, the load on the test specimen was the mass of the lower side clip, that is, 0.1 g/mm. The test specimen was heated at 130°C and 30%RH for two hours in the oven, was removed from the oven, and was cooled to 23°C. After that, the measurement distance marked on the test specimen was measured again, and the ratio of expansion and contraction under load
10 (%) of the base material was computed on the basis of the following equation. The results are shown in Table 1.

The ratio of expansion and contraction under load (%)=(the measurement distance after heating/the measurement distance before heating)×100

[0157]

15 In addition, the base materials used in the examples and the comparative examples were slivered so as to have a 22 mm-long short side in the MD direction and a 110 mm-long long side in the CD direction and were used as test specimens in the CD direction. The ratios of expansion and contraction under load (%) of the test specimens in the CD direction were computed in the same manner as described above. The results
20 are shown in Table 1.

[0158]

[Testing Example 2] <Measurement of ratio of expansion and contraction without load>

25 The ratios of expansion and contraction (%) were computed in the same manner as in Testing Example 1 except for the fact that, in the measurement of the ratio of

expansion and contraction under load (Testing Example 1), the lower side clip was not mounted in the test specimen and were used as the ratios of expansion and contraction without load. The results are shown in Table 1.

[0159]

5 [Testing Example 3] <Measurement of tensile modulus of elasticity>

The base materials used in the examples and the comparative examples were slivered to 15 mm×140 mm test specimens, and the tensile moduli of elasticity (Young's moduli) at 23°C were measured according to JIS K7127:1999. Specifically, the test specimen was set to an interchuck distance of 100 mm in a tensile tester (manufactured
10 by Shimadzu Corporation, trade name: "AUTOGRAPH AG-IS 500N"), a tensile test was carried out at a rate of 200 mm/min, and the tensile modulus of elasticity (MPa) was measured. Meanwhile, the tensile moduli of elasticity were measured both in the MD direction and in the CD direction of the base material. The results are shown in Table 1.

[0160]

15 [Testing Example 4] <Measurement of melting point>

The melting points of the base materials used in the examples and the comparative examples were measured using a thermogravimetric analyzer (manufactured by PerkinElmer Inc., trade name: "Pyris1"). Specifically, the base material was heated every 10°C/minute from 50°C to 250°C, differential scanning calorimetry (DSC) was
20 carried out, and temperatures at which an endothermic peak was observed were considered as melting points. The results are shown in Table 1.

[0161]

[Testing Example 5] <Evaluation of loosening>

The release sheets was released from the composite sheets for forming a
25 protective film manufactured in the examples and the comparative examples, and the

obtained composite sheet for forming a protective film was attached to a silicone wafer (#2000 polishing, the diameter of the outer circumferential edge: 6 inches, thickness: 350 μm , and mass: 14 g) and a ring frame (stainless steel, inner diameter: 195 mm) as shown in FIG. 3. The protective film-forming film was cured by being heated in an environment of 130°C for two hours in the above-described state and then was cooled to room temperature.

[0162]

In addition, the distance (the subduction amount; mm) between the height of the lower end surface of the composite sheet for forming a protective film located on the lower side of the ring frame and the height of the lower end surface of the composite sheet for forming a protective film located on the lower side of the semiconductor wafer was measured and evaluated as loosening. The evaluation standards are as described below. The results are shown in Table 1.

A: Shorter than 0.5 mm

B: 0.5 mm or longer and shorter than 2.0 mm

C: 2.0 mm or longer

[0163]

As a result, the composite sheets for forming a protective film of Comparative Examples 1 and 2 were evaluated as B or C and were significantly loosened, and thus the pickup strengths thereof were not evaluated.

[0164]

[Testing Example 6] <Evaluation of dicing device aptitude>

The silicone wafer and the ring frame-attached composite sheet for forming a protective film (after the curing step) which had been produced in Testing Example 5 were adsorbed to an adsorption table in a dicing device (manufactured by DISCO

Corporation, trade name “DFD651”). At this time, whether or not poor adsorption was caused by the loosening of the composite sheet for forming a protective film was determined, and the dicing device aptitude was evaluated using the following standards. The results are shown in Table 1.

5 A: The composite sheet for forming a protective film was adsorbed without any problems and was sufficiently fixed for dicing.

 B: The composite sheet for forming a protective film was poorly adsorbed and could not be diced.

[0165]

10 [Testing Example 7] <Evaluation of pickup strength>

 The silicone wafer which had been evaluated as A in Testing Example 5 and the silicone wafer in the ring frame-attached composite sheet for forming a protective film were diced to a chip size of 5 mm×5 mm, thereby obtaining protective film-attached chips. Next, the composite sheet for forming a protective film was upthrust using a
15 needle from the base material side, and the protective film-attached chips were picked up. At this time, the strengths (N) necessary to pick up the chips were measured using a push-pull gauge (manufactured by Aikoh Engineering Co., Ltd., trade name “RX-1”). The average value of the measurement values of 20 chips was considered as the pickup strength (N), and the pickup strength was evaluated using the following standards. The
20 results are shown in Table 1.

 A: 4.0 N or lower

 B: More than 4.0 N and 5.0 N or lower

 C: More than 5.0 N

[0166]

25 [Testing Example 8] <Evaluation of weight decrease ratio of base material>

The base materials used in the examples and the comparative examples were heated to 130°C at a temperature-increase rate of 10°C/minute and held at that temperature for two hours, and then the weight decrease ratios at this time were measured using a thermogravimetric analyzer (manufactured by Shimadzu Corporation, trade name: DTG-60). Such a weight decrease ratio can be obtained using the following calculation equation.

Weight decrease ratio [%]=[(weight before heating-weight after heating)/weight before heating]×100

The results are shown in Table 1.

[0167]

[Testing Example 9] <Evaluation of weight decrease ratio of composite sheet for forming protective film >

According to the examples and the comparative examples, a composite sheet for forming a protective film which included the base material, the pressure sensitive adhesive layer, and the protective film-forming film, in which the base material, the pressure sensitive adhesive layer, and the protective film-forming film were laminated in this order, and which did not include the release sheet and the pressure sensitive adhesive layer for a jig was produced. Using a thermogravimetric analyzer (manufactured by Shimadzu Corporation, trade name: DTG-60), the composite sheet for forming a protective film was heated to 130°C at a temperature-increase rate of 10°C/minute and held at that temperature for two hours, and then the weight decrease ratio at this time was measured. Such a weight decrease ratio can be obtained using the following calculation equation.

Weight decrease ratio [%]=[(weight before heating-weight after heating)/weight before heating]×100

The results are shown in Table 1.

[0168]

[Table 1]

	Base material						Composite sheet for forming protective film							
	Ratio of expansion and contraction				Tensile modulus of elasticity		Melting point	Weight decrease ratio of base material	Weight decrease ratio of composite sheet for forming protective film	Evaluation of loosening		Evaluation of dicing device aptitude	Evaluation of pickup strength	
	Under load		Without load											
					MD	CD	MD	CD	MD	CD				
	%	%	%	%	MPa	MPa	°C	%	%	Numerical value	Determination	Numerical value	Determination	
Example 1	98.6	99.1	99.0	98.8	320	290	156	0.4	1.2	0.0	A	2.9	A	
Example 2	96.3	99.6	98.8	99.0	190	170	154	0.5	1.0	0.0	A	2.5	A	
Example 3	99.7	102.8	99.3	99.4	490	450	131	0.5	2.5	0.2	A	3.5	A	
Example 4	101.4	100.4	99.6	99.6	630	620	163	1.0	3.0	0.4	A	4.5	B	
Comparative Example 1	155.0	195.0	97.0	97.8	220	210	118	1.1	2.9	2.0	C	-	-	
Comparative Example 2	93.9	129.8	94.0	97.3	130	120	124	0.9	3.3	1.0	B	-	-	

[0169]

As is clear from Table 1, the composite sheets for forming a protective film manufactured in the examples rarely loosened after the heating and cooling step and could be favorably diced and picked up.

5

INDUSTRIAL APPLICABILITY

[0170]

The composite sheet for forming a protective film according to the present invention is preferably used to manufacture chips having a protective film from

10 semiconductor wafers.

DESCRIPTION OF THE REFERENCE SYMBOLS

[0171]

1, 10 ... composite sheet for forming protective film

15 2 ... pressure sensitive adhesive sheet

21 ... base material

22 ... pressure sensitive adhesive layer

3 ... protective film-forming film

4 ... pressure sensitive adhesive layer for jig

20 5 ... semiconductor wafer

6 ... ring frame

7 ... release sheet

CLAIMS

1. A composite sheet for forming a protective film comprising:
a pressure sensitive adhesive sheet formed by laminating a pressure sensitive
5 adhesive layer on one surface side of a base material; and
a protective film-forming film laminated on the pressure sensitive adhesive layer
side of the pressure sensitive adhesive sheet,
wherein, in a case in which the base material is heated at 130°C for two hours
under a load of 0.1 g/mm applied to the base material and cooled to 23°C, ratios of
10 expansion and contraction of the base material in an MD direction and a CD direction
between before the heating and after the heating are both in a range of 95% to 103%, and
tensile moduli of elasticity of the base material in the MD direction and the CD
direction at 23°C are both in a range of 100 to 700 MPa.
- 15 2. The composite sheet for forming a protective film according to Claim 1,
wherein the base material is a polypropylene film.
3. The composite sheet for forming a protective film according to Claim 1 or
2,
20 wherein a thickness of the base material is in a range of 50 to 200 μm .
4. The composite sheet for forming a protective film according to any one of
Claims 1 to 3, further comprising:
a pressure sensitive adhesive layer for a jig laminated at a circumferential edge

portion on a side opposite to the pressure sensitive adhesive sheet side of the protective film-forming film.

5. The composite sheet for forming a protective film according to any one of

5 Claims 1 to 4, further comprising:

a release sheet laminated on the protective film-forming film.

6. The composite sheet for forming a protective film according to any one of Claims 1 to 5,

10 wherein the protective film-forming film is a layer forming a protective film on a semiconductor wafer or a semiconductor chip obtained by dicing a semiconductor wafer.