

DESCRIPTION

Title of Invention

COMPOSITE SHEET FOR FORMING PROTECTIVE FILM

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Technical Field

[0001]

The present invention relates to a composite sheet for forming a protective film adapted to form a protective film on a workpiece such as a semiconductor wafer or a machined product (for example, semiconductor chip) obtained by machining the workpiece.

Priority is claimed on Japanese Patent Application No. 2014-106757, filed May 23, 2014, the content of which is incorporated herein by reference.

15 Background Art

[0002]

In recent years, semiconductor devices have been manufactured through a called face-down-mounting method. In this method, when a semiconductor chip having a circuit surface having electrodes such as bumps formed thereon is mounted, the circuit surface side of the semiconductor chip contacts a chip-mounting portion such as a lead frame. Accordingly, the rear surface side of the semiconductor chip, on which no circuit is formed, is exposed.

[0003]

Accordingly, in many cases, a protective film made of a thermosetting organic material is formed on the rear surface side of the semiconductor chip in order to protect

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the semiconductor chip. Printing is usually performed on this protective film in order to display a part number and the like of the semiconductor chip. In this case, as a printing method, a laser marking method (laser printing) for irradiating the protective film with laser light is generally used.

5 [0004]

PTLs 1 to 3 disclose a protective film-forming/dicing integrated sheet (a composite sheet for forming a protective film) in which a protective film-forming layer (protective film-forming film) adapted to form the above-described protective film is formed on an adhesive sheet. In these protective film-forming/dicing integrated sheets,
10 the protective film-forming film is cured by a heating treatment and forms the above-described protective film. That is, according to the protective film-forming/dicing integrated sheet, it is possible to perform both of the dicing of a semiconductor wafer and the formation of a protective film for a semiconductor chip, and thus it is possible to obtain a semiconductor chip with a protective film.

15 [0005]

In the past, in the manufacturing of a machined product formed of a flaky body such as a semiconductor chip from a workpiece such as a semiconductor wafer, blade dicing for obtaining a flaky body by cutting the workpiece with a rotary blade while spraying a liquid for washing or the like onto the workpiece has been generally
20 performed. However, in recent years, Stealth Dicing (registered trademark: the same hereinafter) enabling dry division into flaky bodies has been employed (PTL 3).

[0006]

For example, PTL 4 discloses a Stealth Dicing method in which a laminated adhesive sheet (a laminate of two adhesive sheets each formed of a base material and an
25 adhesive layer) is adhered to an extremely thin semiconductor wafer, the semiconductor

wafer is irradiated with laser light through the laminated adhesive sheet to form a modified portion inside the semiconductor wafer, and then the adhesive sheet is expanded to divide the semiconductor wafer along a dicing line, thereby producing a semiconductor chip.

5 Citation List

Patent Literature

[0007]

[PTL 1] Japanese Unexamined Patent Application, First Publication No.

2006-140348

10 [PTL 2] Japanese Unexamined Patent Application, First Publication No.

2012-33637

[PTL 3] Japanese Unexamined Patent Application, First Publication No.

2011-151362

[PTL 4] Japanese Patent No. 3762409

15 [PTL 5] Japanese Unexamined Patent Application, First Publication No.

2007-123404

Summary of Invention

Technical Problem

20 [0008]

As described above, in a case in which the workpiece is irradiated with laser light, it is necessary for the laser light to pass through the adhesive sheet and reach the protective film or the workpiece, and thus the adhesive sheet is required to have laser light transparency.

25 [0009]

In many cases, a release sheet is laminated on the protective film-forming film on the side opposite to the adhesive sheet in the composite sheet for forming a protective film in order to protect the protective film-forming film. When such a composite sheet for forming a protective film is unwound from a rolled state, a surface of the wound adhesive sheet on the side opposite to the protective film-forming film may be tightly adhered to a surface of the release sheet on the side opposite to the protective film-forming film, and thus blocking may occur and failure may thus occur in the unwinding from the roll, or the adhesive sheet may be transferred onto the wound release sheet, and thus the workpiece may not be adhered.

10 [0010]

The invention is contrived in view of the above-described actual situation, and an object thereof is to provide a composite sheet for forming a protective film in which it is possible to suppress the occurrence of blocking when the composite sheet for forming a protective film is unwound from a state of being wound in a roll shape, and excellent laser light transparency is thus exhibited when laser light irradiation is performed.

Solution to Problem

[0011]

In order to achieve the object, first, the invention provides a composite sheet for forming a protective film including a support sheet and a protective film-forming film which is laminated on the first surface side of the support sheet, in which an arithmetic mean roughness (Ra1) of a second surface of the support sheet is 0.2 μm or greater, and an arithmetic mean roughness (Ra2) of the second surface of the support sheet after the support sheet is heated for 2 hours at 130°C is 0.25 μm or less (Invention 1). In this description, the term “sheet” includes, for example, the concept of a long tape.

25 [0012]

According to the invention (Invention 1), when the composite sheet for forming a protective film is wound in a roll shape, the second surface of the support sheet is unlikely to be tightly adhered to a member coming into contact with the second surface of the support sheet (for example, a release sheet in a case in which the release sheet is provided on the protective film-forming film, or the protective film-forming film in a case in which the release sheet is not provided). Accordingly, when the composite sheet for forming a protective film wound in a roll shape is unwound, blocking rarely occurs. In addition, when laser light irradiation is performed from the second surface side of the support sheet, laser light passes through the support sheet without being scattered by irregularities of the second surface of the support sheet, and efficiently reaches the protective film obtained by curing the protective film-forming film or the workpiece (semiconductor wafer), and excellent laser light transparency is exhibited.

[0013]

In the invention (Invention 1), the arithmetic mean roughness (Ra2) of the second surface of the support sheet after the heating is preferably less than the arithmetic mean roughness (Ra1) (Invention 2).

[0014]

In the invention (Inventions 1 and 2), the support sheet is preferably formed of a base material and an adhesive layer laminated on one surface of the base material and on the first surface side of the support sheet, or formed of a base material (Invention 3).

[0015]

In the invention (Invention 3), the base material preferably has a melting point of 90°C to 180°C (Invention 4).

[0016]

In the invention (Inventions 3 and 4), the base material preferably has a storage

elastic modulus of 1 to 100 MPa at 130°C (Invention 5).

[0017]

In the invention (Inventions 3 to 5), the light transmittance of the base material at a wavelength of 1064 nm after the heating is preferably 40% or greater (Invention 6).

5 [0018]

In the invention (Inventions 3 to 6), the light transmittance of the base material at a wavelength of 532 nm after the heating is preferably 40% or greater (Invention 7).

[0019]

In the invention (Inventions 3 to 7), the base material is preferably a film formed
10 of a copolymer of ethylene and propylene (Invention 8).

[0020]

In the invention (Inventions 1 to 8), the composite sheet for forming a protective film preferably further includes an adhesive layer for a tool which is laminated on a peripheral portion of the protective film-forming film on the side opposite to the support
15 sheet (Invention 9).

[0021]

In the invention (Inventions 1 to 9), the composite sheet for forming a protective film preferably further includes a release sheet which is laminated on the protective film-forming film (Invention 10).

20 [0022]

In the invention (Inventions 1 to 10), the protective film-forming film is preferably a layer for forming a protective film for a semiconductor wafer or a semiconductor chip obtained by subjecting the semiconductor wafer to dicing (Invention 11).

25 Advantageous Effects of Invention

[0023]

According to a composite sheet for forming a protective film according to the invention, it is possible to suppress the occurrence of blocking when the composite sheet for forming a protective film is unwound from a state of being wound in a roll shape, and
5 thus excellent laser light transparency is exhibited when laser light irradiation is performed.

Brief Description of Drawings

[0024]

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

FIG. 2 is a cross-sectional view illustrating an example of use of a composite sheet for forming a protective film according to an embodiment of the invention, specifically a laminate structure.

15 FIG. 3 is a cross-sectional view of a composite sheet for forming a protective film according to another embodiment of the invention.

FIG. 4 is a plan view of a composite sheet for forming a protective film produced in an example.

20 Description of Embodiments

[0025]

Hereinafter, embodiments of the invention will be described.

FIG. 1 is a cross-sectional view of a composite sheet for forming a protective film according to an embodiment of the invention. As illustrated in FIG. 1, a composite
25 sheet 3 for forming a protective film according to this embodiment is provided with a

support sheet 4, a protective film-forming film 1 laminated on one surface (“first surface” to be described later: upper surface in FIG. 1) of the support sheet 4, and an adhesive layer 5 for a tool laminated on a peripheral portion of the protective film-forming film 1 on the side opposite to the support sheet 4. The adhesive layer 5 for a tool is a layer for adhering the composite sheet 3 for forming a protective film to a tool such as a ring frame. In addition, the composite sheet 3 for forming a protective film according to this embodiment is provided with a release sheet 6 on the protective film-forming film 1 and the adhesive layer 5 for a tool (on the side opposite to the support sheet 4). This release sheet 6 is removed by being released when using the composite sheet 3 for forming a protective film, and is not an essential constitution element of the composite sheet 3 for forming a protective film.

[0026]

The composite sheet 3 for forming a protective film according to this embodiment is used to hold a workpiece by being adhered to the workpiece when machining the workpiece, and to form a protective film on the workpiece or a machined product obtained by machining the workpiece. This protective film is formed of the protective film-forming film 1, and is preferably formed of the cured protective film-forming film 1.

[0027]

For example, the composite sheet 3 for forming a protective film according to this embodiment is used to hold a semiconductor wafer when subjecting the semiconductor wafer as a workpiece to dicing, and to form a protective film on a semiconductor chip obtained by dicing, but the use thereof is not limited thereto. In this case, the support sheet 4 of the composite sheet 3 for forming a protective film is usually called a dicing sheet.

[0028]

Usually, the composite sheet 3 for forming a protective film according to this embodiment is formed to be long and wound in a roll shape to be used in a roll-to-roll manner.

5 [0029]

1. Support Sheet

The support sheet 4 of the composite sheet 3 for forming a protective film according to this embodiment is provided with a base material 41 and an adhesive layer 42 laminated on one surface (on the side of the protective film-forming film 1; upper side in FIG. 1) of the base material 41. In this description, a surface of the support sheet 4 on the side of the protective film-forming film 1 is referred to as “first surface”, and a surface on the opposite side (lower surface in FIG. 1) is referred to as “second surface”. In the support sheet 4, the adhesive layer 42 is laminated on the first surface side of the support sheet 4, and the base material 41 is laminated on the second surface side of the support sheet 4.

[0030]

1-1. Base Material

A surface of the base material 41 on the side opposite to the adhesive layer 42 (hereinafter, may be referred to as “rear surface of the base material 41”, the rear surface of this base material 41 corresponding to the second surface of the support sheet 4) has an arithmetic mean roughness (Ra1) of 0.2 μm or greater. After the base material 41 is heated for 2 hours at 130°C and cooled to room temperature (hereinafter, may be simply referred to as “after heating”), the rear surface of the base material 41 has an arithmetic mean roughness (Ra2) of 0.25 μm or less. The arithmetic mean roughness (Ra1) of the rear surface of the base material 41 is an arithmetic mean roughness of the rear surface of

the base material 41 before heating for 2 hours at 130°C, and hereinafter, may be referred to as “arithmetic mean roughness (Ra1) before heating”. The arithmetic mean roughness (Ra1) before heating and the arithmetic mean roughness (Ra2) after heating are measured based on JIS B0601: 2001, and details of the measuring method are as shown in test examples to be described later.

[0031]

Usually, conditions of the heating treatment (130°C, 2 hours) are conditions of a heating treatment for thermally curing the protective film-forming film 1. The composite sheet 3 for forming a protective film wound in a roll shape is unwound before heating, and laser light irradiation of laser printing or Stealth Dicing is performed after heating. The heating treatment is not required to be a treatment for thermally curing the protective film-forming film 1. For example, in a case in which the protective film-forming film 1 is an energy ray-curable film, a separate heating treatment may be performed.

[0032]

When the arithmetic mean roughness (Ra1) of the rear surface of the base material 41 before heating is 0.2 μm or greater, the rear surface of the base material 41 is unlikely to be tightly adhered to a surface of the release sheet 6 on the side opposite to the protective film-forming film 1 when the composite sheet 3 for forming a protective film is in a wound state. Accordingly, when the composite sheet 3 for forming a protective film wound in a roll shape is unwound, blocking rarely occurs. Accordingly, it is possible to suppress the occurrence of failure in the unwinding due to the blocking, or failure in the adhesion of the workpiece due to the transfer of the support sheet 4 onto the wound release sheet 6.

[0033]

From the above-described viewpoint, the arithmetic mean roughness (Ra1) of the rear surface of the base material 41 before heating is preferably 0.25 μm or greater, and particularly preferably 0.30 μm or greater.

[0034]

5 Here, the upper limit of the arithmetic mean roughness (Ra1) of the rear surface of the base material 41 before heating is preferably 1.0 μm or less, particularly preferably 0.8 μm or less, and even more preferably 0.7 μm or less. When the arithmetic mean roughness (Ra1) before heating is greater than 1.0 μm , there is a concern that it may be difficult to satisfy the above-described arithmetic mean roughness (Ra2) after heating.

10 That is, the arithmetic mean roughness (Ra1) of the rear surface of the base material 41 before heating is preferably in a range of 0.25 to 1.0 μm , and more preferably in a range of 0.30 to 0.7 μm .

[0035]

When the arithmetic mean roughness (Ra2) of the rear surface of the base
15 material 41 after heating depending on the conditions is 0.25 μm or less, laser light passes through the support sheet 4 without being scattered by irregularities of the rear surface of the base material 41, and efficiently reaches the protective film obtained by curing the protective film-forming film 1 or the workpiece (semiconductor wafer) when laser light irradiation is performed from the rear surface side of the base material 41, and
20 excellent laser light transparency is exhibited. Accordingly, it is possible to form a print with excellent laser printing properties and high visibility, and excellent workpiece divisibility by Stealth Dicing is exhibited.

[0036]

From the above-described viewpoint, the arithmetic mean roughness (Ra2) of

the rear surface of the base material 41 after heating is preferably $0.20\text{ }\mu\text{m}$ or less, and particularly preferably $0.10\text{ }\mu\text{m}$ or less.

[0037]

Here, the lower limit of the arithmetic mean roughness (Ra2) of the rear surface
5 of the base material 41 after heating is not particularly limited as long as the arithmetic mean roughness (Ra1) before heating is satisfied. The lower limit is usually $0.001\text{ }\mu\text{m}$ or greater, and preferably $0.01\text{ }\mu\text{m}$ or greater.

That is, the arithmetic mean roughness (Ra2) of the rear surface of the base material 41 after heating is preferably in a range of 0.001 to $0.20\text{ }\mu\text{m}$, and more
10 preferably in a range of 0.01 to $0.10\text{ }\mu\text{m}$.

[0038]

In addition, in the base material 41, the arithmetic mean roughness (Ra2) of the rear surface of the base material 41 after heating depending on the conditions is preferably less than the arithmetic mean roughness (Ra1) before heating. Due to such a
15 setting, it is possible to improve both of the effect of suppressing the blocking before heating and the laser light transparency after heating.

[0039]

The method of adjusting the arithmetic mean roughness (Ra1) of the rear surface of the base material 41 before heating is not particularly limited. In general, the
20 adjustment can be performed by changing the surface roughness of the surface of the roll which is used in the preparation of the resin film constituting the base material 41, or by blending a filler which becomes flat by sandblasting or melting through heating.

[0040]

As a method of adjusting the arithmetic mean roughness (Ra2) of the rear

surface of the base material 41 after heating, the base material 41 is preferably formed of a resin film (a film containing a resin-based material as a main material) having a melting point in a predetermined range, and particularly preferably formed of a resin film having a melting point in a predetermined range and a storage elastic modulus at 130°C in a
5 predetermined range.

[0041]

The melting point of the base material 41 is preferably 90°C to 180°C, particularly preferably 100°C to 160°C, and even more preferably 110°C to 150°C. When the melting point of the base material 41 is in the above range, the arithmetic mean
10 roughness (Ra2) of the rear surface of the base material 41 after heating is easily adjusted in the above range. When the melting point of the base material 41 is lower than 90°C, there is a concern that the base material 41 may be completely melted during curing by heating. When the melting point of the base material 41 is higher than 180°C, there is a concern that the arithmetic mean roughness of the rear surface of the base material 41
15 may not be changed by heating for 2 hours at 130°C. The melting point is measured based on JIS K7121 (ISO3146), and details of the measuring method are as shown in test examples to be described later.

[0042]

The method of adjusting the melting point of the base material 41 is not
20 particularly limited. In general, the melting point can be adjusted according to a melting point of the resin material to be used. In addition, the melting point of the base material 41 can be adjusted to an arbitrary melting point by mixing a plurality of resin materials having different melting points or by copolymerizing a plurality of monomers.

[0043]

The storage elastic modulus of the base material 41 at 130°C is preferably 1 to 100 MPa, particularly preferably 2 to 80 MPa, and even more preferably 5 to 50 MPa. When the storage elastic modulus of the base material 41 at 130°C is in the above range, the arithmetic mean roughness (Ra2) of the rear surface of the base material 41 after heating is easily adjusted in the above range. When the storage elastic modulus of the base material 41 at 130°C is less than 1 MPa, there is a concern that the base material 41 may be greatly deformed during heating, and thus the workpiece may not be held. When the storage elastic modulus of the base material 41 at 130°C is greater than 100 MPa, there is a concern that the arithmetic mean roughness of the rear surface of the base material 41 may not be changed even by heating for 2 hours at 130°C. The method of measuring the storage elastic modulus is as shown in test examples to be described later.

[0044]

The method of adjusting the storage elastic modulus of the base material 41 at 130°C is not particularly limited. In general, the storage elastic modulus can be adjusted mainly according to a storage elastic modulus of the resin material to be used. In addition, in general, the storage elastic modulus tends to increase when the molecular weight is high even with the same chemical structure, and the storage elastic modulus also tends to increase by crosslinking or a narrow molecular weight distribution. Based on these tendencies, the storage elastic modulus of the base material 41 can be adjusted to an arbitrary storage elastic modulus.

[0045]

In a case in which laser light with a wavelength of 1064 nm is used in Stealth Dicing or the like, the light transmittance of the base material 41 at a wavelength of 1064 nm after heating is preferably 40% or greater, particularly preferably 50% or greater, and

even more preferably 60% or greater. When the light transmittance of the base material 41 at a wavelength of 1064 nm after heating is in the above range, excellent workpiece divisibility by Stealth Dicing is exhibited. In this embodiment, the above-described light transmittance can be realized by adjusting the arithmetic mean roughness (Ra2) of the rear surface of the base material 41 after heating in the above range. As for the light transmittance of the base material 41 at a wavelength of 1064 nm after heating, the higher, the better. The maximum feasible light transmittance is about 99%.

[0046]

In a case in which laser light with a wavelength of 532 nm is used in laser marking on the protective film, the light transmittance of the base material 41 at a wavelength of 532 nm after heating is preferably 40% or greater, particularly preferably 50% or greater, and even more preferably 60% or greater. When the light transmittance of the base material 41 at a wavelength of 532 nm after heating is in the above range, excellent laser printing properties are exhibited. In this embodiment, the above-described light transmittance can be realized by adjusting the arithmetic mean roughness (Ra2) of the rear surface of the base material 41 after heating in the above range. As for the light transmittance of the base material 41 at a wavelength of 532 nm after heating, the higher, the better as in the above description. The maximum feasible light transmittance is about 99%.

[0047]

Specific example of the resin film constituting the base material 41 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, ethylene-propylene copolymer 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)acrylic acid 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
5 films such as polyethylene terephthalate films and polybutylene terephthalate films; polyurethane films; polyimide films; polystyrene films; polycarbonate films; and fluoro resin films. Modified films such as crosslinked films and ionomer films thereof are also used. Laminated films in which the films are laminated may also be used. In this description, the term “(meth)acrylic acid” means both of an acrylic acid and a
10 methacrylic acid. The same applies to other similar terms.

[0048]

In the case of a laminated film, for example, a film in which the arithmetic mean roughness is changed before or after heating is preferably disposed on the rear surface side of the base material 41, and a heat-resistant film which is not deformed even at a
15 high temperature is preferably disposed on the base material 41 on the side of the adhesive layer 42.

[0049]

Among the films, polyolefin-based films are preferred, polyethylene films, polypropylene films, and ethylene-propylene copolymer films are particularly preferred,
20 and ethylene-propylene copolymer films are even more preferred. According to these resin films, the above-described physical properties are easily satisfied, and particularly, in the case of ethylene-propylene copolymer films, the above-described physical properties are easily satisfied by adjusting a copolymerization ratio between an ethylene monomer and a propylene monomer. In addition, these resin films are also preferred
25 from the viewpoint of workpiece adhesiveness and chip releasability.

[0050]

If desired, one or both surfaces of the resin film can be subjected to a surface treatment by an oxidation method, a roughening method, or the like, or a primer treatment in order to improve adhesion to the adhesive layer 42 to be laminated on a surface of the resin film. Examples of the oxidation method include a corona discharge treatment, a plasma discharge treatment, a chromium oxidation treatment (wet type), a flame treatment, a hot air treatment, ozone treatment, and an ultraviolet irradiation treatment. Examples of the roughening method include a sandblasting method and a spray treatment method.

[0051]

The base material 41 may contain various additives such as a colorant, a flame retardant, a plasticizer, an antistatic agent, a lubricant, and a filler in the resin film.

[0052]

The thickness of the base material 41 is not particularly limited as long as the composite sheet 3 for forming a protective film can appropriately function in each process in which the composite sheet 3 for forming a protective film is used. The thickness is preferably 20 to 450 μm , particularly preferably 25 to 400 μm , and even more preferably 50 to 350 μm .

[0053]

1-2. Adhesive Layer

The adhesive layer 42 included in the support sheet 4 of the composite sheet 3 for forming a protective film according to this embodiment may be formed of a non-energy ray-curable adhesive or an energy ray-curable adhesive. The non-energy ray-curable adhesive preferably has desired adhesive power and re-releasability, and for example, acrylic adhesives, rubber-based adhesives, silicone-based adhesives,

urethane-based adhesives, polyester-based adhesives, polyvinyl ether-based adhesives, and the like can be used. Among these, acrylic adhesives are preferred which have high adhesion to the protective film-forming film 1 and can effectively suppress falling of the workpiece or the machined product in a dicing process and the like.

5 [0054]

Regarding the energy ray-curable adhesive, the adhesive power thereof is reduced by energy ray irradiation, and thus when the support sheet 4 is separated from the workpiece or the machined product, these can be easily separated from each other by energy ray irradiation.

10 [0055]

In a case in which the adhesive layer 42 is formed of an energy ray-curable adhesive, the adhesive layer 42 in the composite sheet 3 for forming a protective film is preferably cured. The material obtained by curing the energy ray-curable adhesive usually has high elastic modulus and high surface smoothness. Accordingly, when the protective film-forming film 1 coming into contact with the cured portion formed of such a material is cured and a protective film is thus formed, a surface coming into contact with the cured portion in the protective film has high smoothness (gloss), and thus the protective film has excellent appearance as a protective film of a chip. In addition, when laser printing is performed on the protective film having high surface smoothness, visibility of the printing is improved.

[0056]

The energy ray-curable adhesive constituting the adhesive layer 42 may mainly contain an energy ray-curable polymer, or a mixture of a polymer which is not energy ray-curable and an energy ray-curable polyfunctional monomer and/or oligomer.

25 [0057]

A case in which the energy ray-curable adhesive mainly contains an energy ray-curable polymer will be described below.

[0058]

The energy ray-curable polymer is preferably a (meth)acrylic acid ester
5 (co)polymer (A) (hereinafter, may be referred to as “energy ray-curable polymer (A)”) with an energy ray-curable functional group (energy ray-curable group) introduced to a side chain thereof. This energy ray-curable polymer (A) is preferably obtained by reacting a (meth)acrylic copolymer (a1) having a functional group-containing monomer unit with an unsaturated group-containing compound (a2) having a substituent which is
10 bonded to the functional group of the (meth)acrylic copolymer (a1).

[0059]

The acrylic copolymer (a1) includes 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.

15 [0060]

The functional group-containing monomer as a constituent unit of the acrylic copolymer (a1) preferably has a polymerizable double bond and a functional group such as a hydroxyl group, an amino group, a substituted amino group, or an epoxy group in a molecule.

20 [0061]

Specific examples of the functional group-containing monomer include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, and 4-hydroxybutyl (meth)acrylate. These are used alone or in combination of two or more types thereof.

25 [0062]

As the (meth)acrylic acid ester monomer constituting the acrylic copolymer (a1), alkyl (meth)acrylate with an alkyl group having 1 to 20 carbon atoms, cycloalkyl (meth)acrylate, and benzyl (meth)acrylate are used. Among these, alkyl (meth)acrylate with an alkyl group having 1 to 18 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, and 2-ethylhexyl (meth)acrylate, is particularly preferably used.

[0063]

The acrylic copolymer (a1) contains the constituent unit derived from a functional group-containing monomer at a ratio of usually 3% to 100% by mass, preferably 4% to 80% by mass, and more preferably 5% to 40% by mass with respect to the total mass of the acrylic copolymer (a1), and contains the constituent unit derived from a (meth)acrylic acid ester monomer or a derivative thereof at a ratio of usually 0% to 97% by mass, and preferably 60% to 95% by mass with respect to the total mass of the acrylic copolymer (a1).

[0064]

The acrylic copolymer (a1) is obtained by copolymerizing the functional group-containing monomer and the (meth)acrylic acid ester monomer or a derivative thereof in the usual way as described above. Other than these monomers, dimethylacrylamide, vinyl formate, vinyl acetate, styrene, and the like may be copolymerized.

[0065]

The energy ray-curable polymer (A) is obtained by reacting the acrylic copolymer (a1) having a functional group-containing monomer unit with the unsaturated group-containing compound (a2) having a substituent which is bonded to the functional group of the acrylic copolymer (a1).

[0066]

The substituent of the unsaturated group-containing compound (a2) can be appropriately selected according to the type of the functional group of the functional group-containing monomer unit of the acrylic copolymer (a1). For example, in a case
 5 in which the functional group is a hydroxyl group, an amino group, or a substituted amino group, the substituent is preferably an isocyanate group or an epoxy group, and 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.

[0067]

10 The number of energy ray-polymerizable carbon-carbon double bonds contained in the unsaturated group-containing compound (a2) is 1 to 5, and preferably 1 or 2 per molecule. Specific examples of such an unsaturated group-containing compound (a2) include 2-methacryloyloxyethyl isocyanate, m-isopropenyl- α,α -dimethylbenzyl isocyanate, methacryloyl isocyanate, allyl isocyanate, 1,1-(bisacryloyloxymethyl)ethyl
 15 isocyanate; acryloyl monoisocyanate compounds each obtained by reacting a diisocyanate compound or a polyisocyanate compound with hydroxyethyl (meth)acrylate; acryloyl monoisocyanate compounds each obtained by reacting a diisocyanate compound or a polyisocyanate compound, a polyol compound, and hydroxyethyl (meth)acrylate; glycidyl (meth)acrylate; (meth)acrylic acid,
 20 2-(1-aziridinyl)ethyl (meth)acrylate, 2-vinyl-2-oxazoline, and 2-isopropenyl-2-oxazoline.

[0068]

The unsaturated group-containing compound (a2) is used usually in a proportion of 10 to 100 equivalents, and preferably 20 to 95 equivalents per 100 equivalents of the functional group-containing monomer of the acrylic copolymer (a1).

25 [0069]

In the reaction of the acrylic copolymer (a1) with the unsaturated group-containing compound (a2), the temperature, pressure, solvent, and time of the reaction, the presence or absence of a catalyst, and the type of the catalyst can be appropriately selected according to a combination of the functional group and the substituent. Accordingly, the functional group present in the acrylic copolymer (a1) reacts with the substituent in the unsaturated group-containing compound (a2), the unsaturated group is introduced to a side chain in the acrylic copolymer (a1), and thus the energy ray-curable polymer (A) is obtained.

[0070]

The weight-average molecular weight of the energy ray-curable polymer (A) obtained in this manner is preferably 10,000 or greater, particularly preferably 150,000 to 1,500,000, and even more preferably 200,000 to 1,000,000. In this description, the weight-average molecular weight (Mw) is a value measured by gel permeation chromatography (GPC) in terms of polystyrene.

[0071]

Even in a case in which the energy ray-curable adhesive mainly contains an energy ray-curable polymer, the energy ray-curable adhesive may further contain an energy ray-curable monomer and/or oligomer (B).

[0072]

As the energy ray-curable monomer and/or oligomer (B), for example, an ester of a polyhydric alcohol and a (meth)acrylic acid can be used.

[0073]

Examples of the energy ray-curable monomer and/or oligomer (B) include monofunctional acrylic acid esters such as cyclohexyl (meth)acrylate and isobornyl (meth)acrylate, polyfunctional acrylic acid esters such as trimethylolpropane

tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, polyethylene glycol di(meth)acrylate, and dimethylol tricyclodecane di(meth)acrylate, polyester oligo(meth)acrylates, and polyurethane oligo(meth)acrylates.

5 [0074]

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 adhesive is preferably 5% to 80% by mass, and particularly preferably 20% to 60% by mass with respect to the total mass of the energy ray-curable adhesive.

10 [0075]

Here, in a case in which ultraviolet rays are used as the energy rays for curing the energy ray-curable resin composition, it is preferable to add a photopolymerization initiator (C), and by the use of this photopolymerization initiator (C), it is possible to reduce the polymerization curing time and the amount of light irradiation.

15 [0076]

Specific examples of the photopolymerization initiator (C) include benzophenone, acetophenone, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin benzoate, benzoin methyl benzoate, benzoin dimethyl ketal, 2,4-diethylthioxanthone, 1-hydroxy cyclohexyl phenyl ketone, benzyl diphenyl sulfide, tetramethylthiuram monosulfide, azobisisobutyronitrile, benzyl, dibenzyl, diacetyl, β -chloroanthraquinone, (2,4,6-trimethylbenzyl diphenyl)phosphine oxide, 2-benzothiazole-N,N-diethyldithiocarbamate, oligo{2-hydroxy-2-methyl-1-[4-(1-propenyl)phenyl]propanone}, and 2,2-dimethoxy-1,2-diphenylethan-1-one. These may be used alone or in combination of

25 two or more types thereof.

[0077]

The photopolymerization initiator (C) is preferably used in an amount within a range of 0.1 to 10 parts by mass, and particularly preferably 0.5 to 6 parts by mass with respect to 100 parts by mass of the energy ray-curable copolymer (A) (with respect to
5 100 parts by mass of the total amount of the energy ray-curable copolymer (A) and the energy ray-curable monomer and/or oligomer (B) in a case in which the energy ray-curable monomer and/or oligomer (B) is blended).

[0078]

In the energy ray-curable adhesive, other components may be appropriately
10 blended other than the above-described components. Examples of other components include a polymer component or oligomer component (D) which is not energy ray-curable, and a crosslinking agent (E).

[0079]

Examples of the polymer component or oligomer component (D) which is not
15 energy ray-curable include polyacrylic esters, polyesters, polyurethanes, polycarbonates, and polyolefins, and a polymer or oligomer having a weight-average molecular weight (Mw) of 3,000 to 2,500,000 is preferred.

[0080]

As the crosslinking agent (E), a polyfunctional compound which is reactive with
20 the functional group of the energy ray-curable copolymer (A) or the like can be used. Examples of such a polyfunctional compound include isocyanate compounds, epoxy compounds, amine compounds, melamine compounds, aziridine compounds, hydrazine compounds, aldehyde compounds, oxazoline compounds, metal alkoxide compounds, metal chelate compounds, metal salts, ammonium salts, and reactive phenolic resins.

25 [0081]

By blending these other components (D) and (E) in the energy ray-curable adhesive, the adhesive properties and releasability before curing, the strength after curing, the adhesiveness to other layers, the storage stability, and the like can be improved in the adhesive layer 42. The amount of these other components to be blended 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 energy ray-curable copolymer (A).

[0082]

Next, a case in which the energy ray-curable adhesive mainly contains a mixture of a polymer component which is not energy ray-curable and an energy ray-curable polyfunctional monomer and/or oligomer will be described below.

[0083]

As the polymer component which is not energy ray-curable, for example, the same components as those of the above-described acrylic copolymer (a1) can be used. The content of the polymer component which is not energy ray-curable in the energy ray-curable resin composition is preferably 20% to 99.9% by mass, and particularly preferably 30% to 80% by mass with respect to the total mass of the energy ray-curable resin composition.

[0084]

As the energy ray-curable polyfunctional monomer and/or oligomer, the same material as the above-described component (B) is selected. Regarding the blending ratio between the polymer component which is not energy ray-curable and the energy ray-curable polyfunctional monomer and/or oligomer, the polyfunctional monomer and/or oligomer is preferably 10 to 150 parts by mass, and particularly preferably 25 to 100 parts by mass with respect to 100 parts by mass of the polymer component.

[0085]

Also in this case, as described above, the photopolymerization initiator (C) and the crosslinking agent (E) can be appropriately blended.

[0086]

The thickness of the adhesive layer 42 is not particularly limited as long as the composite sheet 3 for forming a protective film can appropriately function in each process in which the composite sheet 3 for forming a protective film is used.

Specifically, the thickness of the adhesive layer 42 is preferably 1 to 50 μm , particularly preferably 2 to 30 μm , and even more preferably 3 to 20 μm .

[0087]

2. Protective film-forming film

The protective film-forming film 1 is for forming a protective film for a workpiece or a machined product obtained by machining the workpiece. This protective film is formed of the protective film-forming film 1, and is preferably formed of the cured protective film-forming film 1. Examples of the workpiece include a semiconductor wafer, and examples of the machined product obtained by machining the workpiece include a semiconductor chip. However, the invention is not limited thereto. In a case in which the workpiece is a semiconductor wafer, the protective film is formed on the rear surface side (the side on which electrodes such as bumps are not formed) of the semiconductor wafer.

[0088]

The protective film-forming film 1 may be a single layer or formed of a plurality of layers. The protective film-forming film 1 is preferably formed of a single layer from the viewpoint of easy control of light transmittance and manufacturing cost.

[0089]

The protective film-forming film 1 is preferably formed of an uncured curable

adhesive. In this case, by curing the protective film-forming film 1 after superposing a workpiece such as a semiconductor wafer on the protective film-forming film 1, a protective film can be strongly adhered to the workpiece, and thus a durable protective film can be formed for a chip or the like.

5 [0090]

The protective film-forming film 1 preferably has adhesive properties at room temperature, or exhibits adhesive properties when being heated. Thus, when superposing a workpiece such as a semiconductor wafer on the protective film-forming film 1 as described above, these can be adhered to each other. Therefore, the positioning of the protective film-forming film 1 before curing can be securely performed.

[0091]

The curable adhesive constituting the protective film-forming film 1 having the above-described characteristics preferably contains 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, and it is particularly preferable to use a thermosetting component. That is, the protective film-forming film 1 is preferably formed of a thermosetting adhesive.

[0092]

20 Examples of the thermosetting component include epoxy resins, phenolic resins, melamine resins, urea resins, polyester resins, urethane resins, acrylic resins, polyimide resins, benzoxazine resins, and mixtures thereof. Among these, epoxy resins, phenolic resins, and mixtures thereof are preferably used as the thermosetting component.

[0093]

25 The epoxy resins have a property of forming a three-dimensional network when

being heated to form a solid coating film. As such an epoxy resin, various epoxy resins that have been conventionally known are used, and those having a number-average molecular weight of about 300 to 2,000 are usually preferred, and those having a number-average molecular weight of 300 to 500 are particularly preferred. Furthermore, an epoxy resin which has a liquid form in an ordinary state and has a number-average molecular weight of 330 to 400, and an epoxy resin which is solid at room temperature and has a number-average molecular weight of 400 to 2,500, preferably 500 to 2,000 are preferably used in the form of a mixture. In addition, the epoxy equivalent of the epoxy resin is preferably 50 to 5,000 g/eq. The number-average molecular weight of the epoxy resin can be obtained through a method using a GPC method.

[0094]

Specific examples of such an 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 acids, such as phthalic acid, isophthalic acid, and tetrahydrophthalic acid; glycidyl-type or alkyl glycidyl-type epoxy resins in which the active hydrogen bonded to the nitrogen atom of aniline isocyanurate and the like is substituted with a glycidyl group; and so-called alicyclic epoxides in which an epoxy moiety is introduced by, for example, oxidizing the carbon-carbon double bond in the molecule, such as vinylcyclohexane diepoxide, 3,4-epoxycyclohexylmethyl-3,4-dicyclohexanecarboxylate, and 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane. In addition, it is also possible to use an epoxy resin having a biphenyl skeleton, a dicyclohexadiene skeleton, a naphthalene skeleton, or the like.

[0095]

Among these, bisphenol-based glycidyl-type epoxy resins, o-cresol novolac-type epoxy resins, and phenol novolac-type epoxy resins are preferably used as the epoxy resin. These epoxy resins can be used alone or in combination of two or more types thereof.

5 [0096]

In a case in which an epoxy resin is used, as an auxiliary agent, a thermally active latent epoxy resin curing agent is preferably used in combination. The thermally active latent epoxy resin curing agent is a type of curing agent which does not react with an epoxy resin at room temperature, and is activated and reacts with the epoxy resin by heating to a certain temperature or higher. As a method of activating the thermally active latent epoxy resin curing agent, a method of generating active species (anions and cations) by a chemical reaction by heating; a method in which the curing agent is stably dispersed in the epoxy resin at around room temperature but is compatible with and dissolved in the epoxy resin at high temperatures to initiate a curing reaction; a method in which the curing agent is eluted at high temperatures using a type of curing agent which is enclosed in a molecular sieve to initiate a curing reaction; a method using a microcapsule, or the like is available.

10
15

[0097]

Specific examples of the thermally active latent epoxy resin curing agent include various onium salts and high-melting-point active hydrogen compounds such as dibasic acid dihydrazide compounds, dicyandiamides, amine adduct curing agents, and imidazole compounds. These thermally active latent epoxy resin curing agents can be used alone or in combination of two or more types thereof. The above-described thermally active latent epoxy resin curing agent is used in a proportion of, with respect to 100 parts by weight of the epoxy resin, preferably 0.1 to 20 parts by weight, particularly preferably

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0.2 to 10 parts by weight, and even more preferably 0.3 to 5 parts by weight.

[0098]

As the phenolic resins, condensates of phenols and aldehydes such as alkylphenols, polyhydric phenols, and naphthols are used without particular limitations.

5 Specifically, for example, phenol novolac resins, o-cresol novolac resins, p-cresol novolac resins, t-butylphenol novolac resins, dicyclopentadiene cresol resins, polyparavinylphenol resins, bisphenol A-type novolac resins, or modified products thereof are used.

[0099]

10 The phenolic hydroxyl group contained in these phenolic resins can be easily subjected to an addition reaction by heating with an epoxy group of the epoxy resin to form a cured product with high impact resistance. Therefore, an epoxy resin and a phenolic resin may be used in combination as the thermosetting component.

[0100]

15 The binder polymer component provides moderate tackiness for the protective film-forming film 1, thereby improving the operability of the composite sheet 3 for forming a protective film. The weight-average molecular weight of the binder polymer is usually in a range of 50,000 to 2,000,000, preferably in a range of 100,000 to 1,500,000, and particularly preferably in a range of 200,000 to 1,000,000. When the
20 molecular weight is too low, the film formation of the protective film-forming film 1 becomes insufficient, and when it is too high, the compatibility with other components becomes poor, and as a result, the formation of a uniform film is prevented. As the binder polymer, for example, acrylic polymers, polyester resins, phenoxy resins, urethane resins, silicone resins, rubber-based polymers, and the like are preferably used, and
25 acrylic polymers are particularly preferably used.

[0101]

Examples of the acrylic polymers include (meth)acrylic acid ester copolymers formed of constituent units derived from a (meth)acrylic acid ester monomer and a (meth)acrylic acid derivative. Here, as the (meth)acrylic acid ester monomer, (meth)acrylic acid alkyl esters, preferably with an alkyl group having 1 to 18 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, and butyl (meth)acrylate are used. In addition, examples of the (meth)acrylic acid derivative include (meth)acrylic acid, glycidyl (meth)acrylate, and hydroxyethyl (meth)acrylate.

10 [0102]

When a glycidyl group is introduced to an acrylic polymer using, as a constituent unit, glycidyl methacrylate or the like from the above-described examples, compatibility with an epoxy resin as the above-described thermosetting component is improved, the glass transition temperature (T_g) after the protective film-forming film 1 is cured is increased, and heat resistance is improved. When a hydroxyl group is introduced to an acrylic polymer using hydroxyethyl acrylate or the like as a constituent unit from the above-described examples, adhesion or adhesion properties to a workpiece can be controlled.

[0103]

20 The weight-average molecular weight of the polymer in a case of using an acrylic polymer as the binder polymer is preferably 100,000 or greater, and particularly preferably 150,000 to 1,000,000. The glass transition temperature of the acrylic polymer is usually 20°C or lower, and preferably about -70°C to 0°C. The acrylic polymer has adhesive properties at room temperature (23°C).

25 [0104]

Regarding the blending ratio between the thermosetting component and the binder polymer component, the thermosetting component is blended preferably in a range of 50 to 1,500 parts by weight, particularly preferably in a range of 70 to 1,000 parts by weight, and even more preferably in a range of 80 to 800 parts by weight with respect to 100 parts by weight of the binder polymer component. When the thermosetting component and the binder polymer component are blended at such a ratio, moderate tackiness is shown before curing and an adhesion operation can be stably performed, thereby obtaining a protective film having excellent coating film strength after curing.

[0105]

The protective film-forming film 1 preferably contains a colorant and/or a filler, and particularly preferably contains both of a colorant and a filler.

[0106]

As the colorant, known colorants such as inorganic pigments, organic pigments, and organic dyes can be used, and from the viewpoint of increasing light transmittance controllability, the colorant preferably used organic colorants. The colorant is preferably formed of a pigment from the viewpoint of increasing chemical stability (specifically, difficulty of elution, difficulty of occurrence of color transfer, and a small change with the passage of time are exemplified) of the colorant.

[0107]

Examples of the filler include silica such as crystalline silica, fused silica, and synthetic silica, and inorganic fillers such as alumina and glass balloon. Among these, silica is preferred, synthetic silica is more preferred, and particularly, synthetic silica in which radiation sources of α -rays which become a factor of malfunction of a semiconductor device are removed as much as possible is most suitable as the filler.

Examples of the shape of the filler include a spherical shape, a needle-like shape, and an

amorphous shape. A spherical shape is preferred, and a true spherical shape is particularly preferred. When particles of the filler have a spherical or true spherical shape, diffused reflection of light rays rarely occurs, and the profile of the spectrum of the light transmittance of the protective film-forming film 1 is easily controlled.

5 [0108]

The protective film-forming film 1 may contain a coupling agent. When a coupling agent is contained, the adhesiveness and adhesion between the protective film and the workpiece can be improved and the moisture resistance (moist-heat resistance) can be improved without damaging the heat resistance of the protective film after curing
10 of the protective film-forming film 1. As the coupling agent, a silane coupling agent is preferred because of versatility thereof, cost benefits, and the like.

[0109]

Examples of the silane coupling agent include

γ -glycidoxypentyltrimethoxysilane, γ -glycidoxypentylmethyldiethoxysilane,
15 β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -(methacryloxypropyl)trimethoxysilane,
 γ -aminopropyltrimethoxysilane, N-6-(aminoethyl)- γ -aminopropyltrimethoxysilane,
N-6-(aminoethyl)- γ -aminopentylmethyldiethoxysilane,
N-phenyl- γ -aminopropyltrimethoxysilane, γ -ureidopentyltriethoxysilane,
 γ -mercaptopropyltrimethoxysilane, γ -mercaptopentylmethyldimethoxysilane,
20 bis(3-triethoxysilylpropyl)tetrasulfane, methyltrimethoxysilane, methyltriethoxysilane,
vinyltrimethoxysilane, vinyltriacetoxysilane, and imidazolesilane. The silane coupling agents can be used alone or as a mixture of two or more types thereof.

[0110]

The protective film-forming film 1 may contain a crosslinking agent such as an

organic polyvalent isocyanato compound, an organic polyvalent imine compound, or an organic metal chelate compound in order to adjust the cohesive force before curing. In addition, the protective film-forming film 1 may contain an antistatic agent in order to suppress static electricity and to improve chip reliability. Furthermore, the protective film-forming film 1 may contain a flame retardant such as a phosphate compound, a bromine compound, or a phosphorus compound in order to increase flame retardancy of the protective film and to improve reliability as a package.

[0111]

The thickness of the protective film-forming film 1 is preferably 3 to 300 μm , particularly preferably 5 to 200 μm , and even more preferably 7 to 100 μm in order to effectively exhibit functions as a protective film.

[0112]

3. Adhesive Layer for Tool

The adhesive constituting the adhesive layer 5 for a tool preferably has desired adhesive power and re-releasability, and for example, acrylic adhesives, rubber-based adhesives, silicone-based adhesives, urethane-based adhesives, polyester-based adhesives, polyvinyl ether-based adhesives, and the like can be used. Among these, acrylic adhesives which have high adhesion to a tool such as a ring frame and can effectively suppress falling of the composite sheet 3 for forming a protective film from a ring frame or the like in a dicing process or the like are preferably used as the adhesive layer 5 for a tool. A base material as a core may be interposed inside the adhesive layer 5 for a tool in a thickness direction.

[0113]

The thickness of the adhesive layer 5 for a tool is preferably 5 to 200 μm , and particularly preferably 10 to 100 μm from the viewpoint of adhesiveness to a tool such as

a ring frame.

[0114]

4. Release Sheet

In this embodiment, the release sheet 6 protects the protective film-forming film 1 and the adhesive layer 5 for a tool until the composite sheet 3 for forming a protective film is used.

[0115]

The configuration of the release sheet 6 is optional, and one obtained by subjecting a plastic film to a release treatment 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, silicone-based agents, fluorine-based agents, long chain alkyl-based agents, and the like can be used. Among these, silicone-based agents with which stabilized performance is obtained at a low cost are preferred. The thickness of the release sheet 6 is not particularly limited, and is usually about 20 to 250 μm .

[0116]

5. Method of Manufacturing Composite Sheet for Forming Protective Film

The composite sheet 3 for forming a protective film can be preferably manufactured by separately preparing a first laminate including the protective film-forming film 1 and a second laminate including the support sheet 4, and then laminating the protective film-forming film 1 and the support sheet 4 by using the first laminate and the second laminate, although the process is not limited thereto.

[0117]

In order to manufacture the first laminate, the protective film-forming film 1 is

formed on a release surface of a first release sheet. Specifically, a coating agent for a protective film-forming film containing a curable adhesive constituting the protective film-forming film 1, and if desired, a solvent is prepared, and is then coated and dried on the release surface of the first release sheet using a coater such as a roll coater, a knife
5 coater, a roll knife coater, an air knife coater, a die coater, a bar coater, a gravure coater, or a curtain coater to form the protective film-forming film 1. Next, a release surface of a second release sheet is superposed on and pressure-bonded to the exposed surface of the protective film-forming film 1 to obtain a laminate (first laminate) in which the protective film-forming film 1 is sandwiched between the two release sheets.

10 [0118]

In the first laminate, if desired, the protective film-forming film 1 (and the second release sheet) may be subjected to cutting by a blade or half-cutting by laser irradiation from the side of the first release sheet or the second release sheet so as to be formed into a desired shape such as a circle. In this case, extra portions of the
15 protective film-forming film 1 and the second release sheet produced by half-cutting may be appropriately removed.

[0119]

In order to manufacture the second laminate, a coating agent for an adhesive layer containing an adhesive constituting the adhesive layer 42, and if desired, a solvent
20 is coated and dried on a release surface of a third release sheet to form the adhesive layer 42. Thereafter, the base material 41 is pressure-bonded to the exposed surface of the adhesive layer 42 to obtain a laminate (second laminate) formed of the third release sheet and the support sheet 4 formed of the base material 41 and the adhesive layer 42.

[0120]

25 Here, in a case in which the adhesive layer 42 is formed of an energy

ray-curable adhesive, the adhesive layer 42 may be cured by irradiating the adhesive layer 42 with energy rays in this step, or may be cured after lamination with the protective film-forming film 1. In addition, in a case in which the adhesive layer 42 is cured after lamination with the protective film-forming film 1, the adhesive layer 42 may
5 be cured before or after the dicing process.

[0121]

As the energy rays, typically, ultraviolet rays, electron rays, and the like are used. The amount of irradiation of energy rays varies depending on the type of energy rays. In a case in which the energy rays are ultraviolet rays, the amount of irradiation of the
10 energy rays is preferably 50 to 1,000 mJ/cm², and particularly preferably 100 to 500 mJ/cm² in terms of light quantity. In a case in which the energy rays are electron rays, the amount of irradiation of the energy rays is preferably about 10 to 1,000 krad.

[0122]

When the first laminate and the second laminate are obtained as described above,
15 the second release sheet in the first laminate is released while releasing the third release sheet in the second laminate, and the protective film-forming film 1 which is exposed in the first laminate and the adhesive layer 42 of the support sheet 4 which is exposed in the second laminate are superposed and pressure-bonded. If desired, the support sheet 4 may be subjected to half-cutting so as to be formed into a desired shape, for example, a
20 circle having a larger diameter than the protective film-forming film 1. In this case, extra portions of the support sheet 4 produced by half-cutting may be appropriately removed.

[0123]

In this manner, the composite sheet 3 for forming a protective film is obtained
25 which is formed of the support sheet 4 obtained by laminating the adhesive layer 42 on

the base material 41, the protective film-forming film 1 laminated on the support sheet 4 on the side of the adhesive layer 42, and the first release sheet laminated on the protective film-forming film 1 on the side opposite to the support sheet 4. Finally, after the first release sheet is released, the adhesive layer 5 for a tool is formed on a peripheral portion of the protective film-forming film 1 on the side opposite to the support sheet 4. The adhesive layer 5 for a tool can also be formed by coating through the same method as that for the adhesive layer 42.

[0124]

6. Method of Using Composite Sheet for Forming Protective Film

As an example using the composite sheet 3 for forming a protective film according to this embodiment, a method of manufacturing a chip with a protective film from a semiconductor wafer as a workpiece will be described below.

[0125]

First, a composite sheet 3 for forming a protective film wound in a roll shape is unwound to adhere the protective film-forming film 1 of the composite sheet 3 for forming a protective film to a semiconductor wafer 7 and to adhere the adhesive layer 5 for a tool to a ring frame 8 as illustrated in FIG. 2.

[0126]

In the composite sheet 3 for forming a protective film according to this embodiment, when the arithmetic mean roughness (Ra1) of the rear surface of the base material 41 before heating is 0.2 μm or greater, blocking rarely occurs at the time of unwinding, and thus failure in the unwinding or failure in the adhesion of the workpiece is suppressed.

[0127]

After that, the protective film-forming film 1 is cured to form a protective film,

and a laminate structure (hereinafter, may be referred to as “laminate structure L”) with a configuration in which the semiconductor wafer 7 with a protective film is laminated on the surface of the support sheet 4 functioning as an expandable dicing sheet on the side of the adhesive layer 42 is obtained. The laminate structure L illustrated in FIG. 2 is further provided with the adhesive layer 5 for a tool and the ring frame 8. In a case in which the protective film-forming film 1 is a thermosetting adhesive, the protective film-forming film 1 may be heated for an appropriate period of time at a predetermined temperature. In a case in which the protective film-forming film 1 is not a thermosetting adhesive, a separate heating treatment is performed.

10 [0128]

In the above description, the heating temperature is preferably 50°C to 200°C, and particularly preferably 90°C to 150°C. The heating time is preferably 0.1 to 10 hours, and particularly preferably 1 to 3 hours. In the composite sheet 3 for forming a protective film according to this embodiment, the arithmetic mean roughness (Ra2) of the rear surface of the base material 41 is 0.25 μm or less through such a heating treatment.

[0129]

When the laminate structure L provided with the semiconductor wafer 7 with a protective film is obtained as described above, the protective film is irradiated with laser light through the support sheet 4 to perform laser printing thereon, if desired.

20 [0130]

Next, the laminate structure L is subjected to a Stealth Dicing process. Specifically, the laminate structure L is installed in a laser irradiation apparatus for division, and a position of a surface of the semiconductor wafer 7 covered with the protective film 1 is detected. Then, the semiconductor wafer 7 is irradiated with laser light through the support sheet 4 to form a modified layer inside the semiconductor wafer

25

7. Thereafter, an expanding process is performed to expand the support sheet 4 functioning as a dicing sheet, and thus a force (tension in a principal plane direction) is applied to the semiconductor wafer 7 with a protective film. As a result, the semiconductor wafer 7 with a protective film adhered to the support sheet 4 is divided, and thus a chip having a protective film (a chip with a protective film) is obtained. Then, the chip with a protective film is picked up from the support sheet 4 using a pick-up device.

[0131]

The composite sheet 3 for forming a protective film according to this embodiment is excellent in laser light transparency since the arithmetic mean roughness (Ra2) of the rear surface of the base material 41 after heating is 0.25 μm or less. Accordingly, in the laser printing process, it is possible to form a print with excellent laser printing properties and high visibility. In addition, in the Stealth Dicing process, the composite sheet for forming a protective film is excellent in workpiece divisibility by Stealth Dicing.

[0132]

7. Another Embodiment of Composite Sheet for Forming Protective Film

FIG. 3 is a cross-sectional view of a composite sheet for forming a protective film according to another embodiment of the invention. As illustrated in FIG. 3, a composite sheet 3A for forming a protective film according to this embodiment is provided with a support sheet 4 in which an adhesive layer 42 is laminated on one surface of a base material 41, a protective film-forming film 1 laminated on the support sheet 4 on the side of the adhesive layer 42, and a release sheet 6 laminated on the protective film-forming film 1 on the side opposite to the support sheet 4. The protective film-forming film 1 according to this embodiment is formed to be substantially

the same as or slightly bigger than a workpiece in a plane direction, and be smaller than the support sheet 4 in the plane direction. The adhesive layer 42 on a portion on which the protective film-forming film 1 is not laminated can be adhered to a tool such as a ring frame.

5 [0133]

The materials and the thicknesses of the members in the composite sheet 3A for forming a protective film according to this embodiment are the same as those of the members of the above-described composite sheet 3 for forming a protective film. In a case in which the adhesive layer 42 is formed of an energy ray-curable adhesive, it is
10 preferable that the energy ray-curable adhesive in a portion coming into contact with the protective film-forming film 1 in the adhesive layer 42 be cured, and the energy ray-curable adhesive in the other portion not be cured. Accordingly, smoothness (gloss) of a protective film obtained by curing the protective film-forming film 1 can be increased, and a high adhesive force to a tool such as a ring frame can be maintained.

15 [0134]

An adhesive layer for a tool which is the same as the adhesive layer 5 for a tool of the above-described composite sheet 3 for forming a protective film may be separately provided on a peripheral portion of the adhesive layer 42 of the support sheet 4 of the composite sheet 3A for forming a protective film on the side opposite to the base material
20 41.

[0135]

In this embodiment, the support sheet 4 may not be provided with the adhesive layer 42, but may be formed (only) of the base material 41. In this case, a surface of the base material 41 on the side of the protective film-forming film 1 corresponds to the first
25 surface of the support sheet 4, and a surface of the base material 41 on the side opposite

to the protective film-forming film 1 corresponds to the second surface of the support sheet 4.

[0136]

In a case in which the support sheet 4 is formed of the base material 41, a
5 peripheral portion of the protective film-forming film 1 on the side opposite to the base material 41 (support sheet 4) is preferably provided with the adhesive layer 5 for a tool as illustrated in FIG. 1.

[0137]

The embodiments described above are described not to limit the invention but to
10 facilitate the understanding of the invention. Accordingly, the respective elements disclosed in the above-described embodiments are intended to include all design modifications or equivalents belonging to the technical scope of the invention.

[0138]

For example, other layers may be interposed between the base material 41 and
15 the adhesive layer 42 in the support sheet 4. Other layers may be laminated on the first surface of the support sheet 4 formed of the base material 41.

[0139]

In the composite sheet for forming a protective film according to the invention,
when the arithmetic mean roughness (Ra1) of the rear surface of the base material 41
20 before heating is about 0.51 to 0.65 μm , the arithmetic mean roughness (Ra2) after heating for 2 hours at 130°C is about 0.08 to 0.22 μm , the storage elastic modulus of the base material 41 at 130°C is about 13 to 20 MPa, the light transmittance after heating at 532 nm is about 73% to 91%, and the light transmittance after heating at 1064 nm is about 77% to 91%, the composite sheet for forming a protective film has more excellent
25 blocking resistance, laser printing properties, and dicing divisibility.

Examples

[0140]

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

5 [0141]

[Example 1]

In Example 1, a composite sheet 3 for forming a protective film was manufactured as follows as illustrated in FIGS. 3 and 4.

(1) Production of First Laminate Including Protective film-forming film

10 The following components were mixed at the following blending ratio (in terms of solid content) and diluted with methyl ethyl ketone such that the solid content concentration was 61% by mass, thereby preparing a coating agent for a protective film-forming film.

(A) Binder polymer: 100 parts by mass of a (meth)acrylic acid ester copolymer
15 obtained by copolymerizing 10 parts by mass of n-butyl acrylate, 70 parts by mass of methyl acrylate, 5 parts by mass of glycidyl methacrylate, and 15 parts by mass of 2-hydroxyethyl acrylate (weight-average molecular weight: 800,000, glass transition temperature: -1°C)

(B-1) 60 parts by mass of a bisphenol A-type epoxy resin (manufactured by
20 Mitsubishi Chemical Corporation, jER828, epoxy equivalent: 184 to 194 g/eq)

(B-2) 10 parts by mass of a bisphenol A-type epoxy resin (manufactured by Mitsubishi Chemical Corporation, jER1055, epoxy equivalent: 800 to 900 g/eq)

(B-3) 30 parts by mass of a dicyclopentadiene-based epoxy resin
(manufactured by DIC Corporation, EPICLON HP-7200HH, epoxy equivalent: 255 to
25 260 g/eq)

(C) Thermally active latent epoxy resin curing agent: 2 parts by mass of dicyandiamide (manufactured by ADEKA Corporation, ADEKA HARDENER EH-3636AS, active hydrogen amount: 21 g/eq)

(D) Curing promoter: 2 parts by mass of
 5 2-phenyl-4,5-dihydroxymethylimidazole (manufactured by Shikoku Chemicals Corporation, Curezol 2PHZ)

(E) 320 parts by mass of a silica filler (manufactured by Admatechs, SC2050MA, average particle diameter: 0.5 μm)

(F) Colorant: 0.6 parts by mass of carbon black (manufactured by Mitsubishi
 10 Chemical Corporation, #MA650, average particle diameter: 28 nm)

(G) Silane coupling agent: 0.4 parts by mass of γ -glycidoxypyrtrimethoxysilane (manufactured by Shin-Etsu Chemical Co., Ltd., KBM403, methoxy equivalent: 12.7 mmol/g, molecular weight: 236.3)

[0142]

15 First, a release surface of a first release sheet (manufactured by Lintec Corporation, SP-PET 3811, thickness: 38 μm) was coated with the above-described coating agent for a protective film-forming film using a knife coater and dried for 2 minutes at 120°C such that a protective film-forming film obtained finally had a thickness of 25 μm , and thus a protective film-forming film was formed. Thereafter, a
 20 release surface of a second release sheet (manufactured by Lintec Corporation, SP-PET 381031, thickness: 38 μm) was superposed on the protective film-forming film to adhere them to each other, and thus a laminate formed of the first release sheet (release sheet 6 in FIGS. 3 and 4), the protective film-forming film (protective film-forming film 1 in FIGS. 3 and 4), and the second release sheet was obtained. This laminate was long and

became a roll by being wound in a roll shape.

[0143]

The roll of the long laminate obtained in the above description was cut to be 300 mm in a width direction (shown by w_1 in FIG. 4). Next, a center portion of the laminate in the width direction was continuously half-cut into a circle (diameter d_1 : 220 mm; reference numeral 101 in FIG. 4) from the side of the second release sheet such that the second release sheet and the protective film-forming film were cut. Then, the second release sheet and the protective film-forming film present on the outside of the circle formed by half cutting were removed. Thus, a first laminate in which the circular protective film-forming film was laminated on the release surface of the first release sheet and the circular second release sheet was laminated thereon was obtained.

[0144]

(2) Production of Second Laminate Including Support Sheet

The following components (H) and (I) were mixed and diluted with methyl ethyl ketone such that the solid content concentration was 30% by mass, thereby preparing a coating agent for an adhesive layer.

(H) Main adhesive: 100 parts by mass of a (meth)acrylic acid ester copolymer (a copolymer obtained by copolymerizing 40 parts by mass of butyl acrylate, 55 parts by mass of 2-ethylhexyl acrylate, and 5 parts by mass of 2-hydroxyethyl acrylate, weight-average molecular weight: 600,000)

(I) Crosslinking agent: 10 parts by mass of an aromatic polyisocyanate compound (manufactured by Mitsui Chemicals, Inc., TAKENATE D110N)

[0145]

Next, an ethylene-propylene copolymer film with one surface (corresponding to a rear surface of a base material (second surface of support sheet)) with an arithmetic

mean roughness (Ra1) before heating, an arithmetic mean roughness (Ra2) after heating (130°C for 2 hours), a melting point, and a storage elastic modulus at 130°C adjusted as in the following Table 1 was produced, and the other surface of the film was subjected to a corona treatment to use the film as a base material. The arithmetic mean roughness (Ra1) before heating was adjusted by changing, in the preparation of the base material, the arithmetic surface roughness of a surface of the metal roll in which the rear surface side of the base material was wound. In addition, the arithmetic mean roughness (Ra2) after heating was adjusted by changing the copolymerization ratio between the ethylene and the propylene constituting the ethylene-propylene copolymer of the base material.

10 [0146]

A release sheet (manufactured by Lintec Corporation, SP-PET 381031) in which a silicone-based release agent layer was formed on one surface of a PET film having a thickness of 38 μm was prepared, a release surface of the release sheet was coated with the above-described coating agent for an adhesive layer using a knife coater and dried such that an adhesive layer obtained finally had a thickness of 10 μm , and thus an adhesive layer was formed. Thereafter, the above-described corona-treated surface of the base material was superposed on the adhesive layer to adhere them to each other, and thus a second laminate formed of: the support sheet (support sheet 4 in FIGS. 3 and 4) formed of the base material (base material 41 in FIG. 3) and the adhesive layer (adhesive layer 42 in FIG. 3); and the release sheet was obtained. This laminate was long, and after the laminate became a roll by being wound, it was cut to be 300 mm in a width direction (shown by w_1 in FIG. 4).

[0147]

(3) Production of Composite Sheet for Forming Protective Film

25 The circular second release sheet was released from the first laminate obtained

in the above-described (1) to expose the circular protective film-forming film.

Meanwhile, the release sheet was released from the second laminate obtained in the above-described (2) to expose the adhesive layer. The first laminate and the second laminate were adhered to the adhesive layer such that the protective film-forming film came into contact with the adhesive layer, and thus a third laminate in which the support sheet formed of the base material and the adhesive layer, the protective film-forming film, and the first release sheet were laminated was obtained.

[0148]

Next, the third laminate was half-cut from the side of the base material such that the support sheet (base material and adhesive layer) was cut. Specifically, as illustrated in FIG. 4, a concentric circle (diameter d_2 : 270 mm; reference numeral 401 in FIG. 4; circular support sheet) that was bigger than the circular protective film-forming film (diameter d_1 : 220 mm) was formed, and arcs (reference numeral 402 in FIG. 4) with an interval (shown by w_2 in FIG. 4) of 20 mm therebetween were formed on the outside of the circle. Two straight lines (reference numeral 403 in FIG. 4) parallel to an end portion in the width direction of the third laminate were formed between the circles adjacent to each other, and the circles adjacent to each other were connected by the straight lines.

[0149]

Thereafter, the portion between the circular support sheet and the arc and the portion sandwiched between the two straight lines were removed, and thus a composite sheet for forming a protective film illustrated in FIGS. 3 and 4 was obtained.

[0150]

[Examples 2 to 5 and Comparative Examples 1 to 3]

Composite sheets for forming a protective film of Examples 2 to 5 and

Comparative Examples 1 to 3 were manufactured in the same manner as in Example 1, except that the arithmetic mean roughness (Ra1) before heating and the arithmetic mean roughness (Ra2) after heating in the rear surface of the base material, the melting point, and the storage elastic modulus at 130°C were changed as shown in the following Table

5 1.

[0151]

[Test Example 1]

<Measurement of Arithmetic Mean Roughness of Base Material>

The arithmetic mean roughness (Ra1: μm) before heating and the arithmetic
10 mean roughness (Ra2: μm) after heating in the rear surface of the base material used in each of the examples and the comparative examples were measured based on JIS B0601: 2001 with a cut off value λ_c of 0.8 mm and an evaluation length L_n of 4 mm using a contact-type surface roughness meter (manufactured by Mitutoyo Corporation, SURFTEST SV-3000). The results thereof are shown in the following Table 1.

15 [0152]

Here, regarding the arithmetic mean roughness (Ra2) after heating, in a state in which the composite sheet for forming a protective film provided with the base material in each of the examples and the comparative examples was fixed to a ring frame, a value after the composite sheet for forming a protective film was heated for 2 hours at 130°C
20 under an air atmosphere in an oven, and then left to cool to room temperature was measured. In this heating treatment, the measurement surface (the rear surface of the base material) was prevented from coming into contact with an inner wall or a bottom portion in the oven.

[0153]

[Test Example 2]

<Measurement of Melting Point of Base Material>

Regarding the base material used in each of the examples and the comparative examples, a melt peak temperature was obtained based on JIS K7121 (ISO3146) using a differential scanning calorimeter (manufactured by TA Instruments, Q2000). Specifically, the base material was heated from 23°C to 200°C at 10°C/min to draw a DSC curve. A melt peak temperature (°C) was obtained from the obtained DSC curve during the temperature increase. The results thereof are shown in the following Table 1.

[0154]

10 [Test Example 3]

<Measurement of Storage Elastic Modulus of Base Material>

Regarding the base material used in each of the examples and the comparative examples, the storage elastic modulus at 130°C was measured using the following apparatus under the following conditions. The results thereof are shown in the following Table 1.

Measuring apparatus: manufactured by TA Instruments, dynamic modulus measuring apparatus “DMA Q800”

Test Start Temperature: 0°C

Test End Temperature: 200°C

20 Rate of Temperature Increase: 3°C/min

Frequency: 11 Hz

Amplitude: 20 μm

[0155]

[Test Example 4]

<Measurement of Light Transmittance>

The base material used in each of the examples and the comparative examples was heated for 2 hours at 130°C as in Test Example 1. Then, the light transmittance of the base material after heating at a wavelength of 200 to 1200 nm was measured using an ultraviolet visible light spectrophotometer (manufactured by Shimadzu Corporation, UV-3101PC, not using integrating spheres), and measurement values at a wavelength of 532 nm and a wavelength of 1064 nm were read. The results thereof are shown in the following Table 1.

[0156]

10 [Test Example 5]

<Blocking Resistance Evaluation>

The first release sheet was released from the composite sheet for forming a protective film manufactured in each of the examples and the comparative examples. The obtained composite sheet for forming a protective film was adhered to a silicon wafer (outside diameter: 8 inches, thickness: 100 μm) and a ring frame (made of stainless-steel) under an environment at 70°C in a roll-to-roll manner using an adhering apparatus (manufactured by Lintec Corporation, RAD-2700 F/12). In that case, 10 sheets were continuously subjected to the adhesion operation to evaluate blocking resistance based on the following standards. The results thereof are shown in the following Table 1.

A: Adhesion was possible without problems (without the occurrence of blocking).

B: Adhesion was possible, but the base material and the release sheet on the rear surface side of the base material were partially tightly adhered to each other, and thus the release sheet was partially released from the adhesive layer or the protective

film-forming film when the composite sheet for forming a protective film was unwound.

C: Adhesion failure occurred such as transfer of even one support sheet onto the release sheet on the rear surface side of the base material or failure in the unwinding of the composite sheet for forming a protective film (blocking occurred).

5 [0157]

[Test Example 6]

<Evaluation of Laser Printing Properties>

The first release sheet was released from the composite sheet for forming a protective film manufactured in each of the examples and the comparative examples.

10 The obtained composite sheet for forming a protective film was adhered to a silicon wafer (outside diameter: 8 inches, thickness: 100 μm) and a ring frame (made of stainless-steel) under an environment at 70°C using an adhering apparatus (manufactured by Lintec Corporation, RAD-2700 F/12). After that, a heating treatment was performed for 2 hours at 130°C to thermally cure the protective film-forming film, thereby forming
15 a protective film.

[0158]

Next, using a printing apparatus (manufactured by KEYENCE corporation, MD-T1000), the protective film was irradiated with laser light with a wavelength of 532 nm through the support sheet to perform laser printing on the protective film with the
20 following conditions.

Conditions 1: Letter Size: 0.4 mm $\times$ 0.5 mm, Space Between Letters: 0.3 mm,
Number of Letters: 20 letters

Conditions 2: Letter Size: 0.2 mm $\times$ 0.5 mm, Space Between Letters: 0.3 mm,
Number of Letters: 20 letters

[0159]

Of laser-printed letters formed on the protective film, visibility (laser printing properties) through the support sheet was evaluated based on the following standards. The results thereof are shown in the following Table 1.

5 A: It was possible to read all of the letters of Conditions 1 and 2 without problems.

 B: It was possible to read all of the letters of Conditions 1 without problems, although there were unclear portions in Conditions 2.

 C: There were unclear portions in Conditions 1 and 2.

10 [0160]

 [Test Example 7]

 <Evaluation of Dicing Divisibility>

 The first release sheet was released from the composite sheet for forming a protective film manufactured in each of the examples and the comparative examples.

15 The obtained composite sheet for forming a protective film was adhered to a silicon wafer (outside diameter: 8 inches, thickness: 100 μ m) and a ring frame (made of stainless-steel) under an environment at 70°C using an adhering apparatus (manufactured by Lintec Corporation, RAD-2700 F/12). After that, a heating treatment was performed for 2 hours at 130°C to thermally cure the protective film-forming film, thereby forming
20 a protective film.

 [0161]

 Next, using a laser saw (manufactured by DISCO Corporation, DFL7360), the obtained silicon wafer with a protective film was divided through Stealth Dicing including the following processes.

25 (Process 1) The silicon wafer and the ring frame to which the composite sheet

for forming a protective film of each of the examples and the comparative examples was adhered were installed at a predetermined position in a laser saw so as to be irradiated with laser light from the support sheet side (the rear surface side of the base material).

(Process 2) The position of the surface of the silicon wafer covered with the protective film was detected, and then a focal position of laser light of the laser saw was set, and along a scheduled cutting line set such that a chip body of 9 mm × 9 mm was formed on the silicon wafer with a protective film, irradiation of laser light with a wavelength of 1064 nm from the laser saw was performed 10 times from the protective film side to form a modified layer in the silicon wafer.

(Process 3) The silicon wafer and the ring frame to which the composite sheet for forming a protective film was adhered were installed in a die separator (manufactured by DISCO Corporation, DDS2300) to perform expanding with an expansion amount of 10 mm at a pulling-down rate of 100 mm/sec.

[0162]

Through the above processes, at least a part of the silicon wafer having the modified layer formed therein was divided along a scheduled division line, and a plurality of chips each with a protective film was obtained. Based on the division ratio ($= (\text{number of chips actually obtained by division} / \text{scheduled number of divided chips}) \times 100$) (%) at that time, dicing divisibility was evaluated according to the following standards. The results thereof are shown in Table 1.

A: Chip division ratio: 100% (good divisibility)

B: Chip division ratio: 90% to less than 100% (acceptable divisibility)

C: Chip division ratio: 80% to less than 90% (acceptable divisibility)

D: Chip division ratio: less than 80% (unacceptable divisibility)

[0163]

[Table 1]

	Base Material						Composite Sheet for Forming Protective Film		
	Arithmetic Mean Roughness		Melting Point	Storage Elastic Modulus at 130°C	Light Transmittance After Heating		Evaluation of Blocking Resistance	Evaluation of Laser Printing Properties	Evaluation of Dicing Divisibility
	Before Heating (Ra1)	After Heating (Ra2)			532 nm	1064 nm			
	μm				°C	MPa			
Example 1	0.58	0.15	117	20	75	79	A	A	B
Example 2	0.51	0.08	119	20	91	91	A	A	A
Example 3	0.47	0.22	121	22	66	68	A	B	C
Example 4	0.65	0.17	131	13	73	77	A	A	B
Example 5	0.53	0.22	112	37	66	68	A	B	C
Example 6	0.51	0.08	119	20	89	89	A	A	A
Comparative Example 1	0.53	0.52	181	19	25	32	A	C	D
Comparative Example 2	0.33	0.32	175	52	34	39	B	C	D
Comparative Example 3	0.08	0.08	181	19	91	91	C	A	A

[0164]

As seen from Table 1, the composite sheets for forming a protective film of the examples in which the arithmetic mean roughness (Ra1) of the rear surface of the base material before heating was 0.2 μm or greater, the arithmetic mean roughness (Ra2) of the rear surface of the base material after heating for 2 hours at 130°C was 0.25 μm or less had excellent blocking resistance, laser printing properties, and dicing divisibility.

Industrial Applicability

[0165]

A composite sheet for forming a protective film according to the invention is preferably used in a case in which a process of performing laser light irradiation so as to allow laser light to pass through a base material, such as laser printing or Stealth Dicing, is included.

Reference Signs List

[0166]

1: PROTECTIVE FILM-FORMING FILM

101: CIRCLE

3, 3A: COMPOSITE SHEET FOR FORMING PROTECTIVE FILM

4: SUPPORT SHEET

5 41: BASE MATERIAL

42: ADHESIVE LAYER

401: CIRCLE

402: ARC

403: STRAIGHT LINE

10 5: ADHESIVE LAYER FOR TOOL

6: RELEASE SHEET

7: SEMICONDUCTOR WAFER

8: RING FRAME

CLAIMS

1. A composite sheet for forming a protective film, comprising:
a support sheet; and
5 a protective film-forming film which is laminated on the first surface side of the support sheet,
wherein an arithmetic mean roughness (Ra1) of a second surface of the support sheet is 0.2 μm or greater, and
an arithmetic mean roughness (Ra2) of the second surface of the support sheet
10 after the support sheet is heated for 2 hours at 130°C is 0.25 μm or less.
2. The composite sheet for forming a protective film according to Claim 1,
wherein the arithmetic mean roughness (Ra2) of the second surface of the support sheet after the heating is less than the arithmetic mean roughness (Ra1).
15
3. The composite sheet for forming a protective film according to Claim 1 or 2,
wherein the support sheet is formed of a base material and an adhesive layer laminated on one surface of the base material and on the first surface side of the support
20 sheet, or formed of a base material.
4. The composite sheet for forming a protective film according to Claim 3,
wherein the base material has a melting point of 90°C to 180°C.
- 25 5. The composite sheet for forming a protective film according to Claim 3 or

4,

wherein the base material has a storage elastic modulus of 1 to 100 MPa at 130°C.

5 6. The composite sheet for forming a protective film according to any one of Claims 3 to 5,

wherein the light transmittance of the base material at a wavelength of 1064 nm after the heating is 40% or greater.

10 7. The composite sheet for forming a protective film according to any one of Claims 3 to 6,

wherein the light transmittance of the base material at a wavelength of 532 nm after the heating is 40% or greater.

15 8. The composite sheet for forming a protective film according to any one of Claims 3 to 7,

wherein the base material is a film formed of a copolymer of ethylene and propylene.

20 9. The composite sheet for forming a protective film according to any one of Claims 1 to 8, further comprising:

an adhesive layer for a tool which is laminated on a peripheral portion of the protective film-forming film on the side opposite to the support sheet.

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

Claims 1 to 9, further comprising:

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

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

5 Claims 1 to 10,

wherein the protective film-forming film is a layer for forming a protective film for a semiconductor wafer or a semiconductor chip obtained by subjecting the semiconductor wafer to dicing.