

DESCRIPTION

PROTECTIVE COATING-FORMING SHEET AND METHOD FOR
MANUFACTURING SEMICONDUCTOR CHIP PROVIDED WITH PROTECTIVE
COATING

TECHNICAL FIELD

[0001]

The present invention relates to a protective coating-forming sheet capable of forming a protective coating on a workpiece such as a semiconductor wafer or a processed product obtained by processing the workpiece (for example, a semiconductor chip).

Priority is claimed on Japanese Patent Application No. 2014-169266 and Japanese Patent Application No. 2014-169267, both filed on August 22, 2014, the contents of which are incorporated herein by reference.

BACKGROUND ART

[0002]

In recent years, many semiconductor devices have been produced by a mounting method known as the face-down method. In this method, during mounting of a semiconductor chip having a circuit surface on which electrodes such as bumps or the like have been formed, the circuit surface side of the semiconductor chip is affixed to a chip-mounting unit such as a lead frame. Accordingly, a structure is formed in which the back surface of the semiconductor chip on which no circuit is formed is exposed.

[0003]

Patent Documents 1 and 2 disclose protective coating-forming, dicing tape-integrated sheets (namely, protective coating-forming sheets) having a protective coating-forming layer (namely, a protective coating formation film) capable of forming an aforementioned protective coating formed on top of a pressure-sensitive adhesive sheet. In these protective coating-forming, dicing tape-integrated sheets, the protective coating formation film is cured by a heat treatment to form the above protective coating. In other words, by using such a protective coating-forming, dicing tape-integrated sheet, both dicing of the semiconductor wafer and formation of a protective coating on the semiconductor chips can be achieved, meaning semiconductor chips with an attached protective coating can be obtained.

[0004]

On the other hand, when manufacturing processed products composed of pieces such as semiconductor chips from a workpiece such as a semiconductor wafer, conventionally, a blade dicing process has generally been performed, in which a rotary cutting blade is used to cut the workpiece into pieces while a liquid is blown onto the workpiece for the purposes of cleaning and the like. However, in recent years, a stealth dicing (a registered trademark, this also applies to all subsequent mentions of the term) process which enables division of a workpiece into pieces using a dry method has increasingly been employed.

[0005]

For example, Patent Document 3 discloses a stealth dicing method in which by adhering a laminated pressure-sensitive adhesive sheet (a sheet obtained by laminating together two pressure-sensitive adhesive sheets each composed of a substrate and a pressure-sensitive adhesive layer) to an ultra-thin semiconductor wafer, irradiating the semiconductor wafer with a laser light from the side of the laminated pressure-sensitive

adhesive sheet through the laminated pressure-sensitive adhesive sheet, thereby forming a modified region within the interior of the semiconductor wafer, and then subjecting the pressure-sensitive adhesive sheet to an expansion process, the semiconductor wafer can be divided along the dicing lines to produce semiconductor chips.

PRIOR ART LITERATURE

Patent Documents

[0006]

Patent Document 1: Japanese Unexamined Patent Application, First Publication No. 2012-33637

Patent Document 2: Japanese Unexamined Patent Application, First Publication No. 2011-151362

Patent Document 3: Japanese Patent (Granted) Publication No. 3,762,409

DISCLOSURE OF INVENTION

Problems to be Solved by the Invention

[0007]

In stealth dicing, because the pressure-sensitive adhesive sheet is expanded to divide the semiconductor wafer as described above, there are cases where it is desirable that a member positioned between the pressure-sensitive adhesive sheet and the semiconductor wafer is also divided in a similar manner to the semiconductor wafer.

When that member is a protective coating formation film, the protective coating formation film is sometimes cooled in order to achieve satisfactory division of the film.

[0008]

An object of the present invention is to provide a protective coating-forming sheet having a protective coating formation film for use in stealth dicing, wherein when the member positioned between the pressure-sensitive adhesive sheet and the workpiece such as a semiconductor wafer is a protective coating formed from the protective coating formation film, the protective coating can be appropriately divided when the pressure-sensitive adhesive sheet is expanded. Further, in another aspect, the present invention has an object of providing a method for manufacturing processed products, such as semiconductor chips with an attached protective coating, using the above protective coating-forming sheet.

Means for Solving the Problems

[0009]

In order to achieve the above objects, the provided present invention includes the aspects described below.

(1) A protective coating-forming sheet having a first support sheet and a protective coating formation film laminated to a first surface side of the first support sheet, wherein the protective coating formation film is formed from a curable material, and a protective coating obtained upon curing the protective coating formation film has a breaking strain at 50°C of not more than 20%, and a breaking stress at 50°C of not more than 2.0×10^7 Pa.

[0010]

(2) The protective coating-forming sheet according to (1) above, wherein the protective coating has a storage modulus at 25°C of 3.0×10^9 Pa or greater.

[0011]

(3) The protective coating-forming sheet according to (1) or (2) above, wherein the protective coating has a loss tangent at 25°C of 0.4 or less.

[0012]

(4) The protective coating-forming sheet according to any one of (1) to (3) above, wherein the protective coating has a light transmittance at a wavelength of 1,064 nm of 40% or greater.

[0013]

(5) The protective coating-forming sheet according to any one of (1) to (4) above, wherein the protective coating-forming sheet also has a second support sheet laminated to the surface of the protective coating formation film opposite the surface facing the first support sheet.

[0014]

(6) A method for manufacturing a chip with an attached protective coating, the method including a bonding step of exposing a surface of the protective coating formation film provided in the protective coating-forming sheet according to any one of (1) to (5) above, the exposed surface being opposite the surface facing the first support sheet, and affixing the exposed surface to one surface of a workpiece to obtain a first laminate containing the protective coating-forming sheet and the workpiece; a first curing step of curing the protective coating formation film provided in the protective coating-forming sheet of the first laminate to obtain the protective coating; a first dividing step of expanding the first support sheet of the protective coating-forming sheet with the temperature of the protective coating provided on the protective coating-forming sheet of the first laminate that has undergone the first curing step held within a range from 40°C to 70°C, thereby dividing the protective coating together with the workpiece and obtaining a second laminate in which a plurality of chips with an attached protective

coating, formed as a result of dividing the laminate of the workpiece and the protective coating, are arranged on one surface of the first support sheet; and a first pickup step of separating, from the first support sheet, each of the plurality of chips with an attached protective coating provided in the second laminate, thereby obtaining each of the chips with an attached protective coating as a processed product, wherein prior to starting the first dividing step, a modified layer formation step is performed in which an infrared laser light is irradiated in a manner that focuses the laser light on a focus point set within the interior of the workpiece, thereby forming a modified layer inside the workpiece.

[0015]

(7) A method for manufacturing a chip with an attached protective coating, the method including a lamination step of exposing a surface of the protective coating formation film provided in the protective coating-forming sheet according to any one of (1) to (5) above, the exposed surface being opposite the surface facing the first support sheet, affixing the exposed surface to one surface of a workpiece, and peeling the first support sheet of the protective coating-forming sheet from the protective coating formation film to obtain a third laminate containing the workpiece and the protective coating formation film; a second curing step of curing the protective coating formation film of the third laminate to obtain the protective coating; a second bonding step of affixing a surface of a third pressure-sensitive adhesive layer of a process sheet provided with a third substrate and the third pressure-sensitive adhesive layer laminated to one surface of the third substrate, to the surface of the protective coating of the third laminate that has undergone the second curing step, thus obtaining a fourth laminate containing the process sheet and the third laminate; a second dividing step of expanding the process sheet of the fourth laminate with the temperature of the protective coating provided on the fourth laminate held within a range from 40°C to 70°C, thereby dividing the

protective coating together with the workpiece and obtaining a fifth laminate in which a plurality of chips with an attached protective coating, formed as a result of dividing the laminate of the workpiece and the protective coating, are arranged on one surface of the process sheet; and a second pickup step of separating, from the process sheet, each of the plurality of chips with an attached protective coating provided on the fifth laminate, thereby obtaining each of the chips with an attached protective coating as a processed product, wherein prior to starting the second dividing step, a modified layer formation step is performed in which an infrared laser light is irradiated in a manner that focuses the laser light on a focus point set within the interior of the workpiece, thereby forming a modified layer inside the workpiece.

[0016]

In other words, the invention of the present application includes the aspects described below.

[1] A protective coating-forming sheet having a first support sheet and a protective coating formation film laminated to a first surface side of the first support sheet, wherein the protective coating formation film is formed from a curable material, and the protective coating formation film has the following characteristics:

when the protective coating formation film is cured to form a protective coating, the protective coating has a breaking strain at 50°C of not more than 20%, and a breaking stress at 50°C of not more than 2.0×10^7 Pa.

[2] The protective coating-forming sheet according to [1], wherein the protective coating formation film also has the following characteristic:

the protective coating has a storage modulus at 25°C of 3.0×10^9 Pa or greater.

[3] The protective coating-forming sheet according to [1] or [2], wherein the protective coating formation film also has the following characteristic:

the protective coating has a loss tangent at 25°C of 0.4 or less.

[4] The protective coating-forming sheet according to any one of [1] to [3], wherein the protective coating formation film also has the following characteristic:

the protective coating has a light transmittance at a wavelength of 1,064 nm of 40% or greater.

[5] The protective coating-forming sheet according to any one of [1] to [4], further including a second support sheet laminated to the surface of the protective coating formation film opposite the surface facing the first support sheet.

[6] A method for manufacturing a chip with an attached protective coating, the method including:

a bonding step of exposing a surface of the protective coating formation film provided in the protective coating-forming sheet according to any one of [1] to [5], the exposed surface being opposite the surface facing the first support sheet, and affixing the exposed surface to one surface of a workpiece to obtain a first laminate containing the protective coating-forming sheet and the workpiece;

a first curing step of curing the protective coating formation film in the first laminate to obtain the protective coating;

a first dividing step of expanding the first support sheet with the temperature of the protective coating in the first laminate that has undergone the first curing step held within a range from 40°C to 70°C, and dividing the protective coating together with the workpiece, thus obtaining a second laminate in which a plurality of chips with an attached protective coating, formed as a result of dividing the laminate of the workpiece and the protective coating such that cut sections occur in the thickness direction, are arranged on one surface of the first support sheet; and

a first pickup step of separating, from the first support sheet, each of the plurality of chips with an attached protective coating provided in the second laminate, thereby obtaining each of the chips with an attached protective coating as a processed product,

the method also including, prior to starting the first dividing step, a modified layer formation step of irradiating an infrared laser light in a manner that focuses the laser light on a focus point set within the interior of the workpiece, thereby forming a modified layer inside the workpiece.

[7] A method for manufacturing a chip with an attached protective coating, the method including:

a lamination step of

exposing a surface of the protective coating formation film provided in the protective coating-forming sheet according to any one of [1] to [5], the exposed surface being opposite the surface facing the first support sheet,

affixing the exposed surface to one surface of a workpiece, and

peeling the first support sheet from the protective coating formation film to obtain a third laminate containing the workpiece and the protective coating formation film;

a second curing step of curing the protective coating formation film of the third laminate to obtain the protective coating;

a second bonding step of affixing a surface of a third pressure-sensitive adhesive layer of a process sheet provided with a third substrate and the third pressure-sensitive adhesive layer laminated to one surface of the third substrate, to the surface of the protective coating of the third laminate that has undergone the second curing step, thus obtaining a fourth laminate containing the process sheet and the third laminate;

a second dividing step of expanding the process sheet of the fourth laminate with the temperature of the protective coating provided on the fourth laminate held within a range from 40°C to 70°C, and dividing the protective coating together with the workpiece, thus obtaining a fifth laminate in which a plurality of chips with an attached protective coating, formed as a result of dividing the laminate of the workpiece and the protective coating such that cut sections occur in the thickness direction, are arranged on one surface of the process sheet; and

a second pickup step of separating, from the process sheet, each of the plurality of chips with an attached protective coating provided on the fifth laminate, thereby obtaining each of the chips with an attached protective coating as a processed product,

the method also including, prior to starting the second dividing step, a modified layer formation step of irradiating an infrared laser light in a manner that focuses the laser light on a focus point set within the interior of the workpiece, thereby forming a modified layer inside the workpiece.

Effects of the Invention

[0017]

By using the protective coating-forming sheet according to the present invention, even if the protective coating formed from the aforementioned protective coating formation film is a member positioned between a pressure-sensitive adhesive sheet and a workpiece such as a semiconductor wafer, the protective coating can be suitably divided when the pressure-sensitive adhesive sheet is expanded during stealth dicing.

Accordingly, semiconductor chips with an attached protective coating can be produced with good stability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

FIG. 1 is a cross-sectional view conceptually illustrating a protective coating-forming sheet according to one embodiment of the present invention.

FIG. 2 is a cross-sectional view conceptually illustrating a state in which a release sheet has been removed from a protective coating-forming sheet according to one embodiment of the present invention.

FIG. 3 is a cross-sectional view conceptually illustrating a first laminate obtained following a first bonding step of a method for manufacturing a chip with an attached protective coating according to one embodiment of the present invention.

FIG. 4 is a cross-sectional view conceptually illustrating a second laminate obtained following a first dividing step of a method for manufacturing a chip with an attached protective coating according to one embodiment of the present invention.

FIG. 5 is a cross-sectional view conceptually illustrating a state during execution of a first pickup step of a method for manufacturing a chip with an attached protective coating according to one embodiment of the present invention.

FIG. 6 is a cross-sectional view conceptually illustrating a protective coating-forming sheet according to another embodiment of the present invention.

FIG. 7 is a cross-sectional view conceptually illustrating a third laminate obtained following a lamination step of a method for manufacturing a chip with an attached protective coating according to another embodiment of the present invention.

FIG. 8 is a cross-sectional view conceptually illustrating a fourth laminate obtained following a second bonding step of a method for manufacturing a chip with an attached protective coating according to another embodiment of the present invention.

FIG. 9 is a cross-sectional view conceptually illustrating a fifth laminate obtained following a second dividing step of a method for manufacturing a chip with an attached protective coating according to another embodiment of the present invention.

FIG. 10 is a cross-sectional view conceptually illustrating a state during execution of a second pickup step of a method for manufacturing a chip with an attached protective coating according to another embodiment of the present invention.

FIG. 11 is a cross-sectional view conceptually illustrating a protective coating-forming sheet according to yet another embodiment of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0019]

Embodiments of the present invention are described below.

FIG. 1 is a cross-sectional view of a protective coating-forming sheet according to one embodiment of the present invention. As illustrated in FIG. 1, the protective coating-forming sheet 3 according to this embodiment has a structure including a first support sheet 4, a protective coating formation film 1 laminated to one surface (hereafter referred to as "the first surface", the upper surface in FIG. 1) of the first support sheet 4, and a jig pressure-sensitive adhesive layer 5 laminated to the peripheral portions of the surface of the protective coating formation film 1 opposite the surface facing the first support sheet 4. The jig pressure-sensitive adhesive layer 5 is a layer used for attaching the protective coating-forming sheet 3 to a jig such as a ring frame. Further, the protective coating-forming sheet 3 according to the present embodiment also includes a release sheet 6 formed on the protective coating formation film 1 and the jig pressure-sensitive adhesive layer 5 (on the opposite side from the first support sheet 4). This release sheet 6 is a sheet that is peeled off and removed when the protective coating-

forming sheet 3 is used, and is not an essential structural element of the protective coating-forming sheet 3.

In other words, one aspect of the protective coating-forming sheet according to an embodiment of the present invention contains the first support sheet 4, the protective coating formation film 1 laminated to one surface of the first support sheet 4, the jig pressure-sensitive adhesive layer 5 laminated to the peripheral portions of the surface of the protective coating formation film 1 opposite the surface facing the first support sheet 4, and if desired, the release sheet 6 formed on the protective coating formation film 1 and the jig pressure-sensitive adhesive layer 5.

[0020]

When processing a workpiece, the protective coating-forming sheet 3 according to the present embodiment is affixed to the workpiece, and is used for holding the workpiece, and for forming a protective coating on the workpiece or the processed product obtained by processing the workpiece. This protective coating is composed of the cured protective coating formation film 1.

[0021]

In one example, the protective coating-forming sheet 3 according to the present embodiment is used for holding a semiconductor wafer workpiece during dicing processing of the semiconductor wafer, and for forming a protective coating on the semiconductor chips obtained as a result of the dicing, but the sheet is not limited to this particular use.

[0022]

The protective coating-forming sheet 3 according to the present embodiment is usually formed in an elongated shape, wound onto a roll, and used in roll-to-roll processing.

[0023]

1. Support Sheet

The first support sheet 4 in the protective coating-forming sheet 3 according to an embodiment of the present invention has a structure including a substrate 41, and a pressure-sensitive adhesive layer 42 laminated to one surface of the substrate 41 (namely, the surface to which the protective coating formation film 1 is laminated, the upper surface in FIG. 1). In this description, the surface of the first support sheet 4 to which the protective coating formation film 1 is laminated is termed "the first surface", and the opposite surface (the lower surface in FIG. 1) is termed "the second surface". In the first support sheet 4, the pressure-sensitive adhesive layer 42 is laminated on the first surface side of the first support sheet 4, and the substrate 41 is laminated on the second surface side of the first support sheet 4.

[0024]

1-1. Substrate

There are no particular limitations on the substrate 41 in the protective coating-forming sheet 3 according to an embodiment of the present invention, provided it is a substrate typically used as a substrate for pressure-sensitive adhesive sheets used in stealth dicing. The substrate 41 may have a single-layer structure or a laminated structure. In those cases where the protective coating formation film 1 is a film that forms the protective coating upon heating, and the substrate 41 is also subjected to heating when the protective coating formation film 1 is heated to form the protective coating, it is desirable that the substrate 41 can still be used appropriately (for example, can still be expanded appropriately) even after the heating.

[0025]

For this reason, the melting point of the substrate 41 is preferably from 90 to 180°C, more preferably from 100 to 160°C, and even more preferably from 110 to 150°C.

[0026]

There are no particular limitations on the method used for adjusting the melting point of the substrate 41, and the melting point can generally be adjusted by selection of the resin material used. Further, a desired melting point may also be achieved by mixing a plurality of resin materials having different melting points, or copolymerizing a plurality of monomers.

[0027]

The storage modulus of the substrate 41 at 130°C is preferably from 1 to 100 MPa. By ensuring that the storage modulus at 130°C satisfies the above range, the likelihood of problems occurring when the first support sheet 4 is expanded can be reduced, while maintaining good heat resistance for the substrate 41. From the viewpoint of achieving a combination of enhanced heat resistance for the substrate 41 and simple expansion of the first support sheet 4, the storage modulus of the substrate 41 at 130°C is preferably from 2 to 80 MPa, and particularly preferably from 5 to 50 MPa. The method used for measuring the storage modulus is as described below in the test examples.

[0028]

There are no particular limitations on the method used for adjusting the storage modulus of the substrate 41 at 130°C, and generally, the storage modulus can mainly be adjusted via the storage modulus of the resin material used. Further, even if the chemical structure is the same, the storage modulus generally tends to increase with increasing molecular weight, and tends to also increase with crosslinking and a narrower molecular weight distribution. The storage modulus can be adjusted to a desired value by taking these tendencies into consideration.

[0029]

In those cases where a laser light with a wavelength of 1,064 nm is used in stealth dicing or the like, the light transmittance of the substrate 41 at a wavelength of 1,064 nm following heating is preferably at least 40% but not more than 100%, more preferably at least 50% but not more than 99.9%, and even more preferably at least 60% but not more than 99.5%. By ensuring that the light transmittance of the substrate 41 at a wavelength of 1,064 nm following heating satisfies the above range, excellent divisibility of workpieces can be achieved by stealth dicing.

[0030]

Further, in those cases where a laser light with a wavelength of 532 nm is used for laser marking or the like of the protective coating, the light transmittance of the substrate 41 at a wavelength of 532 nm following heating is preferably at least 0% but not more than 40%, more preferably at least 0.01% but not more than 35%, and even more preferably at least 0.05% but not more than 30%. By ensuring that the light transmittance of the substrate 41 at a wavelength of 532 nm following heating satisfies the above range, excellent laser printability can be achieved.

[0031]

Specific examples of the resin film that constitutes the substrate 41 include polyolefin-based films, including polyethylene films such as low-density polyethylene (LDPE) films, linear low-density polyethylene (LLDPE) films and high-density polyethylene (HDPE) films, as well 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)acrylate ester copolymer films; polyvinyl

chloride-based films such as polyvinyl chloride films and vinyl chloride copolymer films; polyester-based films such as polyethylene terephthalate films and polybutylene terephthalate films; as well as polyurethane films, polyimide films, polystyrene films, polycarbonate films and fluororesin films. Further, modified films of the above films such as crosslinked films and ionomer films can also be used. Laminated films formed by laminating a plurality of the above films may also be used.

In the present description, the term "(meth)acrylic acid" means both acrylic acid and methacrylic acid. Other similar terms are similarly defined.

[0032]

Among the above, polyolefin-based films are preferred, polyethylene films, polypropylene films and ethylene-propylene copolymer films are more preferred, and ethylene-propylene copolymer films are particularly desirable. These resin films make it easier to satisfy the physical properties described above, and particularly in the case of an ethylene-propylene copolymer film, the above properties can easily be achieved by adjusting the copolymerization ratio between the ethylene monomer and the propylene monomer. Further, these resin films are also preferred from the viewpoints of workpiece affixability and chip releasability.

[0033]

If desired, either one surface or both surfaces of the above resin film may be subjected to either a surface treatment using an oxidation method or a roughening method, or a primer treatment, for the purpose of improving the adhesion to the pressure-sensitive adhesive layer 42 laminated to the surface of the resin film. Examples of the oxidation method include a corona discharge treatment, plasma discharge treatment, chromium oxidation treatment (wet), flame treatment, hot air treatment, ozone treatment

and ultraviolet irradiation treatment, whereas examples of the roughening method include a sandblasting method and a thermal spraying method.

[0034]

The substrate 41 may also include any of various additives such as colorants, flame retardants, plasticizers, antistatic agents, lubricants and fillers within the resin film described above.

[0035]

There are no particular limitations on the thickness of the substrate 41, provided the substrate functions satisfactorily in each of the steps in which the protective coating-forming sheet 3 is used, but the thickness is preferably within a range from 20 μm to 450 μm , more preferably from 25 μm to 400 μm , and even more preferably from 50 μm to 350 μm .

The "thickness" is the value representing the average of five thickness values measured using a contact thickness meter at five random locations.

[0036]

1-2. Pressure-Sensitive Adhesive Layer

The pressure-sensitive adhesive layer 42 of the first support sheet 4 of the protective coating-forming sheet 3 according to one embodiment of the present invention may be composed of a non-energy ray-curable pressure-sensitive adhesive or an energy ray-curable pressure-sensitive adhesive. The non-energy ray-curable pressure-sensitive adhesive preferably has the desired levels of adhesive force and removability, and examples include acrylic-based pressure-sensitive adhesives, rubber-based pressure-sensitive adhesives, silicone-based pressure-sensitive adhesives, urethane-based pressure-sensitive adhesives, polyester-based pressure-sensitive adhesives, and polyvinyl ether-based pressure-sensitive adhesives. Among these, acrylic-based pressure-sensitive

adhesives are preferred, as they exhibit superior adhesion to the protective coating formation film 1.

[0037]

On the other hand, energy ray-curable pressure-sensitive adhesives exhibit a reduction in adhesive force when irradiated with energy rays, and therefore by using an energy ray-curable pressure-sensitive adhesive, when the first support sheet 4 requires separation from a workpiece or processed product, separation can be performed easily by irradiation with energy rays.

Ultraviolet rays or an electron beam or the like are typically used as the energy rays. The irradiation dose of the energy rays differs depending on the type of energy rays used, but in the case of ultraviolet rays, a dose of 50 to 1,000 mJ/cm² is preferred, and a dose of 100 to 500 mJ/cm² is more desirable. In the case of an electron beam, a dose of about 10 to 1,000 krad is preferred.

[0038]

When the pressure-sensitive adhesive layer 42 is composed of an energy ray-curable pressure-sensitive adhesive, the pressure-sensitive adhesive layer 42 in the protective coating-forming sheet 3 is preferably cured. A material composed of a cured energy ray-curable pressure-sensitive adhesive usually has a high elastic modulus and a high degree of surface smoothness, and therefore when the protective coating formation film 1 that is in contact with the cured portion of this material is cured to form the protective coating, the surface of the protective coating where it contacts the cured portion of the pressure-sensitive adhesive layer 42 exhibits superior smoothness (gloss), resulting in a chip protective coating having excellent aesthetics. Further, when laser printing is performed on such a protective coating having superior surface smoothness, the legibility of the printing improves.

[0039]

The energy ray-curable pressure-sensitive adhesive that constitutes the pressure-sensitive adhesive layer 42 may contain a polymer having energy ray curability as the main component, or may contain a mixture of a polymer having no energy ray curability and at least one component selected from the group consisting of energy ray-curable polyfunctional monomers and oligomers as the main component.

[0040]

The case in which the energy ray-curable pressure-sensitive adhesive contains a polymer having energy ray curability as the main component is described below.

Here, the expression "main component" means that the component represents at least 60% by mass of the total mass of the energy ray-curable pressure-sensitive adhesive.

[0041]

The polymer having energy ray curability is preferably a (meth)acrylate ester (co)polymer (A) (hereafter also referred to as the "energy ray-curable polymer (A)") in which functional groups having energy ray curability (namely, energy ray-curable groups) have been introduced as side chains. This energy ray-curable polymer (A) is preferably obtained by reacting a (meth)acrylic-based copolymer (a1) having functional group-containing monomer units, and an unsaturated group-containing compound (a2) having a substituent that bonds to that functional group.

[0042]

The acrylic-based copolymer (a1) is formed from at least a structural unit derived from a functional group-containing monomer, and a structural unit derived from a (meth)acrylate ester monomer or a derivative thereof.

[0043]

The functional group-containing monomer for the aforementioned structural unit derived from a functional group-containing monomer is preferably a monomer having a polymerizable double bond, and a functional group such as a hydroxyl group, amino group, substituted amino group or epoxy group within each molecule.

[0044]

More 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, and these compounds may be used individually or in combinations containing two or more compounds.

[0045]

Examples of compounds that may be used as the aforementioned (meth)acrylate ester monomer include alkyl (meth)acrylates in which the alkyl group has a carbon number of 1 to 20, cycloalkyl (meth)acrylates in which the alkyl group has a carbon number of 3 to 11, and benzyl (meth)acrylate. Among these, alkyl (meth)acrylates in which the alkyl group has a carbon number of 1 to 18 are preferred, and specific examples include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, and 2-ethylhexyl (meth)acrylate.

[0046]

The acrylic-based copolymer (a1) typically contains 3 to 100% by mass, and preferably 5 to 40% by mass, of structural units derived from the above functional group-containing monomer, and typically contains 0 to 97% by mass, and preferably 60 to 95% by mass, of structural units derived from the (meth)acrylate ester monomer or derivative thereof, relative to the total mass of the acrylic-based copolymer (a1).

In other words, the acrylic-based copolymer (a1) preferably contains from 3 to 100% by mass of structural units derived from the above functional group-containing

monomer, and from 0 to 97% by mass of structural units derived from the (meth)acrylate ester monomer or derivative thereof, relative to the total mass of the acrylic-based copolymer (a1); and more preferably contains from 5 to 40% by mass of structural units derived from the above functional group-containing monomer, and from 60 to 95% by mass of structural units derived from the (meth)acrylate ester monomer or derivative thereof.

The combined mass of the structural units derived from the functional group-containing monomer and the structural units derived from the (meth)acrylate ester monomer or derivative thereof does not exceed 100% by mass.

[0047]

The acrylic-based copolymer (a1) can be obtained by copolymerizing the functional group-containing monomer and the (meth)acrylate ester monomer or derivative thereof using typical methods, and other compounds besides these monomers, such as dimethylacrylamide, vinyl formate, vinyl acetate or styrene, may also be copolymerized.

[0048]

The energy ray-curable polymer (A) can be obtained by reacting the acrylic-based copolymer (a1) having the aforementioned functional group-containing monomer units (namely, structural units derived from the functional group-containing monomer) with the unsaturated group-containing compound (a2) having a substituent that bonds to that functional group.

[0049]

The substituent of the unsaturated group-containing compound (a2) may be selected appropriately in accordance with the type of functional group within the functional group-containing monomer units of the acrylic-based copolymer (a1). For

example, if the functional group is a hydroxyl group, amino group or substituted amino group, then an isocyanate group or epoxy group is preferred as the substituent, whereas if the functional group is an epoxy group, then an amino group, carboxyl group or aziridinyl group is preferred as the substituent.

[0050]

Further, the unsaturated group-containing compound (a2) typically contains 1 to 5, and preferably 1 to 2, energy ray-curable carbon-carbon double bonds within each molecule. Specific examples of this type of unsaturated group-containing compound (a2) include 2-methacryloyloxyethyl isocyanate, meta-isopropenyl- α,α -dimethylbenzyl isocyanate, methacryloyl isocyanate, allyl isocyanate, 1,1-(bisacryloyloxymethyl)ethyl isocyanate, acryloyl monoisocyanate compounds obtained by reacting a diisocyanate compound or a polyisocyanate compound with hydroxyethyl (meth)acrylate, acryloyl monoisocyanate compounds obtained by reacting a diisocyanate compound or a polyisocyanate compound with a polyol compound and hydroxyethyl (meth)acrylate, as well as glycidyl (meth)acrylate, (meth)acrylic acid, 2-(1-aziridinyl)ethyl (meth)acrylate, and alkenyloxazoline compounds such as 2-vinyl-2-oxazoline and 2-isopropenyl-2-oxazoline.

Among the above compounds, 2-methacryloyloxyethyl isocyanate is preferred.

[0051]

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

[0052]

In the reaction between the acrylic-based copolymer (a1) and the unsaturated group-containing compound (a2), the reaction temperature, pressure, solvent and time, the presence or absence of a catalyst, and the type of catalyst used may all be selected appropriately in accordance with the combination of the functional group and the substituent. As a result, the functional groups that exist within the acrylic-based copolymer (a1) and the substituent within the unsaturated group-containing compound (a2) react, unsaturated groups are introduced as side chains within the acrylic-based copolymer (a1), and the energy ray-curable polymer (A) is obtained.

[0053]

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

[0054]

Even in those cases where the energy ray-curable pressure-sensitive adhesive contains a polymer having energy ray curability as the main component, the energy ray-curable pressure-sensitive adhesive may also contain at least one component (B) selected from the group consisting of energy ray-curable monomers and oligomers.

[0055]

Examples of the one or more components (B) selected from the group consisting of energy ray-curable monomers and oligomers include esters of a polyhydric alcohol and (meth)acrylic acid.

[0056]

Specific examples of the one or more components (B) selected from the group consisting of energy ray-curable monomers and oligomers include monofunctional acrylate esters such as cyclohexyl (meth)acrylate and isobornyl (meth)acrylate, polyfunctional acrylate 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 dimethyloltricyclodecane di(meth)acrylate, as well as polyester oligo(meth)acrylates and polyurethane oligo(meth)acrylates.

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

[0057]

In those cases where at least one component (B) selected from the group consisting of energy ray-curable monomers and oligomers is added, the amount of the component (B) within the energy ray-curable pressure-sensitive adhesive is preferably from 5 to 80% by mass, and more preferably from 20 to 60% by mass, relative to the total mass of the energy ray-curable pressure-sensitive adhesive.

[0058]

In those cases where ultraviolet rays are used as the energy rays used for curing the energy ray-curable resin composition, a photopolymerization initiator (C) is preferably also added, and using this photopolymerization initiator (C) enables the polymer curing time and the light irradiation dose to be reduced.

[0059]

Specific examples of the photopolymerization initiator (C) include benzophenone, acetophenone, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin benzoic acid, methyl benzoin benzoate, benzoin

dimethyl ketal, 2,4-diethylthioxanthone, 1-hydroxycyclohexyl phenyl ketone, benzyl diphenyl sulfide, tetramethylthiuram monosulfide, azobisisobutyronitrile, benzil, dibenzil, 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 compounds may be used individually, or combinations of two or more compounds may be used.

[0060]

The photopolymerization initiator (C) is typically used in an amount of 0.1 to 10 parts by mass, and preferably 0.5 to 6 parts by mass, per 100 parts by mass of the energy ray-curable copolymer (A) (or in the case where at least one component (B) selected from the group consisting of energy ray-curable monomers and oligomers is added, 100 parts by mass of the combination of the energy ray-curable copolymer (A) and the one or more components (B) selected from the group consisting of energy ray-curable monomers and oligomers).

[0061]

The energy ray-curable pressure-sensitive adhesive may also include other suitable components in addition to the components described above. Examples of these other components include a polymer component or oligomer component (D) that does not have energy ray curability, and a crosslinking agent (E).

In other words, one aspect of the energy ray-curable pressure-sensitive adhesive includes the energy ray-curable copolymer (A), and also includes, according to need, at least one component selected from the group consisting of one or more components (B) selected from the group consisting of energy ray-curable monomers and oligomers,

photopolymerization initiators (C), polymer components or oligomer components (D) that do not have energy ray curability, and crosslinking agents (E).

[0062]

Examples of the polymer component or oligomer component (D) that does not have energy ray curability include polyacrylate esters, polyesters, polyurethanes, polycarbonates and polyolefins, and polymers or oligomers having a weight-average molecular weight (Mw) of 3,000 to 2,500,000 are preferred.

[0063]

Polyfunctional compounds that exhibit reactivity with the functional groups of the energy ray-curable copolymer (A) and the like can be used as the crosslinking agent (E). Specific examples of such polyfunctional compounds 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 phenol resins.

[0064]

By including these types of other components (D) and (E) within the energy ray-curable pressure-sensitive adhesive, properties such as the pressure-sensitive adhesiveness and releasability prior to curing, and the strength, adhesiveness to other layers and storage stability and the like following curing can be improved. There are no particular limitations on the amounts added of these other components, and the amounts may be set appropriately within a range from 0 to 40 parts by mass per 100 parts by mass of the energy ray-curable copolymer (A).

[0065]

Next is a description of the case in which the energy ray-curable pressure-sensitive adhesive contains a mixture of a polymer component having no energy ray curability and at least one component selected from the group consisting of energy ray-curable polyfunctional monomers and oligomers as the main component.

[0066]

For the polymer component having no energy ray curability, the same components as those described above for the acrylic-based copolymer (a1) can be used. The amount of the polymer component having no energy ray curability within the energy ray-curable resin composition is preferably from 20 to 99.9% by mass, and more preferably from 30 to 80% by mass, relative to the total mass of the energy ray-curable resin composition.

[0067]

For the one or more components selected from the group consisting of energy ray-curable polyfunctional monomers and oligomers, the same compounds as those described above for the component (B) may be selected. The blend ratio between the polymer component having no energy ray curability and the one or more components selected from the group consisting of energy ray-curable polyfunctional monomers and oligomers is preferably set so that the amount of the one or more components selected from the group consisting of polyfunctional monomers and oligomers is from 10 to 150 parts by mass, and more preferably from 25 to 100 parts by mass, per 100 parts by mass of the polymer component having no energy ray curability.

[0068]

The aforementioned photopolymerization initiator (C) and crosslinking agent (E) may also be added in this case, in a similar manner to that described above.

In other words, one aspect of the energy ray-curable pressure-sensitive adhesive includes the polymer component having no energy ray curability and the one or more components selected from the group consisting of energy ray-curable polyfunctional monomers and oligomers, and also includes, according to need, at least one component selected from the group consisting of photopolymerization initiators (C) and crosslinking agents (E).

[0069]

There are no particular limitations on the thickness of the pressure-sensitive adhesive layer 42, provided it is capable of functioning appropriately in each of the steps in which the protective coating-forming sheet 3 is used. Specifically, the thickness is preferably from 1 μm to 50 μm , more preferably from 2 μm to 30 μm , and even more preferably from 3 μm to 20 μm .

[0070]

2. Protective Coating Formation Film

The protective coating formation film 1 is a film for forming a protective coating on a workpiece or a processed product obtained by processing the workpiece. This protective coating is formed from the cured protective coating formation film 1. Examples of the workpiece include semiconductor wafers and the like, and examples of the processed product obtained by processing the workpiece include semiconductor chips and the like, although the present invention is not limited to these examples. When the workpiece is a semiconductor wafer, the protective coating is formed on the back surface of the semiconductor wafer (the surface on which electrodes such as bumps have not been formed).

[0071]

The protective coating formation film 1 may be a film composed of a single layer or a film composed of a plurality of layers, but in terms of the ease of controlling the light transmittance and the production costs, a film composed of a single layer is preferred.

[0072]

The protective coating formation film 1 is preferably formed from a curable material, and specific examples of such materials include uncured curable adhesives. In this case, by curing the protective coating formation film 1 once the workpiece such as a semiconductor wafer has been overlaid on the protective coating formation film 1, the protective coating formed from the cured protective coating formation film 1 can be bonded strongly to the workpiece, and a protective coating having good durability can be formed on the chip or the like.

In other words, one aspect of the protective coating-forming sheet according to an embodiment of the present invention contains a protective coating formation film formed from an uncured curable material.

[0073]

The protective coating formation film 1 preferably either has pressure-sensitive adhesiveness at normal temperatures, or develops pressure-sensitive adhesiveness upon heating. As a result, when the workpiece such as a semiconductor wafer is overlaid on the protective coating formation film 1 in the manner mentioned above, the two can be stuck together. Accordingly, positioning can be performed reliably prior to curing of the protective coating formation film 1.

[0074]

The curable adhesive that constitutes the protective coating formation film 1 having the types of properties described above preferably contains a curable component and a binder polymer component.

A thermosetting component, an energy ray-curable component, or a mixture of the two can be used as the curable component, but the use of a thermosetting component is particularly preferred. In other words, the protective coating formation film 1 is preferably composed of a thermosetting adhesive.

[0075]

Examples of the thermosetting component include epoxy resins, phenol resins, melamine resins, urea resins, polyester resins, urethane resins, acrylic resins, polyimide resins, benzoxazine resins, and mixtures thereof. Among these, an epoxy resin, a phenol resin, or a mixture thereof can be used particularly favorably.

[0076]

Upon exposure to heat, epoxy resins develop a three dimensional network structure, forming a strong coating film. All manner of conventional epoxy resins can be used as the epoxy resin, but typically, epoxy resins having a molecular weight (formula weight) of about 300 to 2,000 are preferred, and epoxy resins having a molecular weight of 300 to 500 are more preferred. Moreover, the use of a blend of an epoxy resin having a molecular weight of 330 to 400 that is liquid at normal temperature, and an epoxy resin having a molecular weight of 400 to 2,500, and particularly a molecular weight of 500 to 2,000, that is solid at normal temperature is also preferred. Further, the epoxy equivalent weight of the epoxy resin is preferably from 50 to 5,000 g/eq.

[0077]

Specific examples of the above types of epoxy resins 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 or alkylglycidyl epoxy resins obtained by substituting an active hydrogen bonded to a nitrogen atom of aniline isocyanurate or the like with a glycidyl group; and so-called alicyclic epoxides in which an epoxy group has been introduced, for example, by oxidizing an intramolecular carbon-carbon double bond, 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, epoxy resins having a biphenyl backbone, a dicyclohexadiene backbone, or a naphthalene backbone or the like may also be used.

[0078]

Among these, bisphenol-based glycidyl epoxy resins, o-cresol novolac epoxy resins and phenol novolac epoxy resins can be used particularly favorably. These epoxy resins may be used individually, or a combination of two or more resins may be used.

[0079]

When an epoxy resin is used, a heat-activated latent epoxy resin curing agent is preferably also used as an auxiliary. A "heat-activated latent epoxy resin curing agent" is a curing agent which does not react with the epoxy resin at room temperature, but is activated by heating to a certain temperature, wherein reaction with the epoxy resin proceeds. Examples of the method used for activating the heat-activated latent epoxy resin curing agent include methods in which heating causes a chemical reaction that produces an active moiety (anion or cation); methods in which the curing agent remains stably dispersed within the epoxy resin at temperatures close to room temperature, but then becomes compatible with or dissolves in the epoxy resin at higher temperature, thereby initiating the curing reaction; methods which use a molecular sieve-encapsulated

curing agent, which is eluted at high temperatures and initiates the curing reaction; and methods which use microcapsules.

[0080]

Specific examples of the heat-activated latent epoxy resin curing agent include high-melting point active hydrogen compounds such as various onium salts, dibasic acid dihydrazide compounds, dicyandiamide, amine adduct curing agents, and imidazole compounds. These heat-activated latent epoxy resin curing agents may be used individually, or combinations of two or more compounds may be used. The amount used of this type of heat-activated latent epoxy resin curing agent is preferably from 0.1 to 20 parts by weight, more preferably from 0.2 to 10 parts by weight, and even more preferably from 0.3 to 5 parts by weight, per 100 parts by weight of the epoxy resin.

[0081]

For the phenol-based resin, condensation products of a phenol such as an alkylphenol, polyhydric phenol or naphthol with an aldehyde can be used without any particular limitations. Specific examples of resins that may be used include phenol novolac resins, o-cresol novolac resins, p-cresol novolac resins, t-butylphenol novolac resins, dicyclopentadiene cresol resins, poly-para-vinylphenol resins, bisphenol A novolac resins, and modified products of these resins.

[0082]

The phenolic hydroxyl groups contained within these phenol-based resins readily undergo an addition reaction with the epoxy groups of the aforementioned epoxy resin under heating, enabling formation of a cured product having excellent impact resilience. Accordingly, a combination of an epoxy resin and a phenol-based resin may be used.

[0083]

Examples of the energy ray-curable component include the components described above for the polymer having energy ray curability or the one or more components (B) selected from the group consisting of energy ray-curable monomers and oligomers used in the pressure-sensitive adhesive layer 42.

[0084]

The binder polymer component imparts an appropriate level of tack to the protective coating formation film 1, thus enhancing the usability of the protective coating-forming sheet 3. The weight-average molecular weight of the binder polymer is typically within a range from 50,000 to 2,000,000, preferably from 100,000 to 1,500,000, and more preferably from 200,000 to 1,000,000. If the weight-average molecular weight of the binder polymer is too low, then the film formability of the protective coating formation film 1 tends to be unsatisfactory, whereas if the weight-average molecular weight is too high, then the compatibility with other components deteriorates, hindering the formation of a uniform film. In other words, provided the weight-average molecular weight is at least as large as the lower limit mentioned above, film formation of the protective coating formation film 1 is satisfactory, and provided the weight-average molecular weight is not more than the above upper limit, the compatibility with other components is favorable, resulting in formation of a uniform film. Examples of polymers that may be used as this type of binder polymer include acrylic-based polymers, polyester resins, phenoxy resins, urethane resins, silicone resins and rubber-based polymers, and acrylic-based polymers can be used particularly favorably.

[0085]

Examples of the acrylic-based polymers include (meth)acrylate ester copolymers containing structural units derived from a (meth)acrylate ester monomer and a (meth)acrylic acid derivative. The (meth)acrylate ester monomer is preferably an alkyl

(meth)acrylate ester in which the alkyl group has a carbon number of 1 to 18, and specific examples include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate and butyl (meth)acrylate. Further, examples of the (meth)acrylic acid derivative include (meth)acrylic acid, glycidyl (meth)acrylate, and hydroxyethyl (meth)acrylate.

[0086]

Among the above, introducing glycidyl groups into the acrylic-based polymer by using glycidyl methacrylate or the like as a structural unit improves the compatibility with the epoxy resin used as the aforementioned thermosetting component, and increases the glass transition temperature (T_g) of the protective coating formation film 1 following curing, resulting in improved heat resistance. Further, among the above, introducing hydroxyl groups into the acrylic-based polymer by using hydroxyethyl acrylate or the like as a structural unit enables the adhesiveness or pressure-sensitive adhesiveness to the workpiece to be better controlled.

[0087]

The weight-average molecular weight of the polymer in those cases where an acrylic-based polymer is used as the binder polymer is preferably at least 100,000, and more preferably from 150,000 to 1,000,000. The glass transition temperature of the acrylic-based polymer is typically not higher than 20°C , and preferably about -70 to 0°C , and the polymer preferably has pressure-sensitive adhesiveness at normal temperature (23°C).

[0088]

The blend ratio between the thermosetting component and the binder polymer component is adjusted so that relative to 100 parts by weight of the binder polymer, the amount of the thermosetting component is preferably within a range from 50 to 1,500

parts by weight, more preferably from 70 to 1,000 parts by weight, and even more preferably from 80 to 800 parts by weight. By blending the thermosetting component and the binder polymer component in this type of ratio, the film exhibits an appropriate level of tack prior to curing, meaning the affixing operation can be performed with good stability, but then yields a protective coating with excellent coating film strength following curing.

[0089]

The protective coating formation film 1 may also include at least one component selected from the group consisting of colorants and fillers.

[0090]

Conventional colorants may be used as the colorant, including inorganic pigments, organic pigments and organic dyes, and from the viewpoint of enhancing the controllability of the light transmittance, the colorant preferably includes an organic colorant. From the viewpoint of improving the chemical stability of the colorant (and specifically, improving the resistance to elution and resistance to color migration, and minimizing the color changes over time), the colorant is preferably composed of a pigment.

[0091]

Examples of the filler include silica such as crystalline silica, fused silica and synthetic silica, and other inorganic fillers such as alumina and glass balloons. Among these, silica is preferred, synthetic silica is more preferred, and a synthetic silica in which α -radiation sources, which are a primary cause of semiconductor device malfunctions, have been removed as much as possible is the most desirable. Examples of the form of the filler include spherical, needle-like and amorphous forms, but a spherical form is preferred, and a perfectly spherical form is particularly preferred. When the filler is

spherical or perfectly spherical, diffuse reflection of light is unlikely, and the spectral profile of the light transmittance for the protective coating formation film 1 can be more easily controlled.

The amount of the one or more components selected from the group consisting of colorants and fillers is preferably from 5 to 75% by mass relative to the total mass of the protective coating formation film.

The average particle size of the filler is preferably from 0.005 to 20 μm .

[0092]

The protective coating formation film 1 may also include a coupling agent. By including a coupling agent, the adhesiveness or pressure-sensitive adhesiveness between the protective coating and the workpiece following curing of the protective coating formation film 1 can be improved without impairing the heat resistance of the protective coating, and the water resistance (moist heat resistance) can also be improved. In terms of versatility and cost, a silane coupling agent is preferred as the coupling agent.

[0093]

Specific examples of the silane coupling agent include γ -glycidoxypentyltrimethoxysilane, γ -glycidoxypentylmethyldiethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -(methacryloxypropyl)trimethoxysilane, γ -aminopentyltrimethoxysilane, N-6-(aminoethyl)- γ -aminopentyltrimethoxysilane, N-6-(aminoethyl)- γ -aminopentylmethyldiethoxysilane, N-phenyl- γ -aminopentyltrimethoxysilane, γ -ureidopentyltriethoxysilane, γ -mercaptopentyltrimethoxysilane, γ -mercaptopentylmethyldimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfan, methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, vinyltriacetoxysilane, and imidazole silane. Among these, γ -

glycidoxypyltrimethoxysilane is preferred. These silane coupling agents may be used individually, or mixtures of two or more coupling agents may be used.

In those cases where the protective coating formation film 1 includes a binder polymer component and a curable component, the amount of the coupling agent is preferably from 0.1 to 5 parts by mass per 100 parts by mass of the combination of the binder polymer component and the curable component.

[0094]

In order to regulate the cohesion of the protective coating formation film 1 prior to curing, the protective coating formation film 1 may also include a crosslinking agent such as an organic polyvalent isocyanate compound, an organic polyvalent imine compound or an organic metal chelate compound. Further, in order to suppress static electricity and improve the reliability of the resulting chips, the protective coating formation film 1 may also include an antistatic agent. Moreover, in order to improve the flame retardancy performance of the protective coating and improve the reliability as a package, the protective coating formation film 1 may also include a flame retardant such as a phosphoric acid compound, bromine compound or phosphorus-based compound.

In other words, one aspect of the protective coating formation film 1 includes the curable component and the binder polymer component, and also includes, according to need, at least one component selected from the group consisting of colorants and fillers, and at least one component selected from the group consisting of coupling agents, crosslinking agents, antistatic agents and flame retardants.

[0095]

In order to ensure effective functionality as a protective coating, the thickness of the protective coating formation film 1 is preferably from 3 μm to 300 μm , more preferably from 5 μm to 200 μm , and still more preferably from 7 μm to 100 μm .

[0096]

3. Protective Coating

The protective coating formed from the protective coating formation film 1 according to an embodiment of the present invention has the characteristics described below.

The protective coating has a breaking strain at 50°C of at least 0.1% but not more than 20%. By ensuring that this breaking strain is not more than 20%, the protective coating on the first support sheet 4 can be divided appropriately when the first support sheet 4 is expanded under the conditions described below. If the breaking strain at 50°C exceeds 20%, then division of the protective coating is more likely to be unsatisfactory, and a phenomenon in which the material that forms the protective coating adopts a string-like form within some of the division locations (also referred to as the "stringing phenomenon" in the present description) is more likely to occur. From the viewpoint of achieving suitable division of the protective coating in a more stable manner, the breaking strain at 50°C for the protective coating is preferably at least 0.2% but not more than 15%, more preferably at least 0.3% but not more than 13%, and even more preferably at least 0.5% but not more than 10%.

[0097]

The protective coating has a breaking stress at 50°C of at least 1.0×10^3 Pa but not more than 2.0×10^7 Pa. By ensuring that this breaking stress is not more than 2.0×10^7 Pa, the protective coating on the first support sheet 4 can be divided appropriately when the first support sheet 4 is expanded under the conditions described below. From the viewpoint of achieving suitable division of the protective coating in a more stable manner, the breaking stress at 50°C for the protective coating is preferably at least 5.0×10^3 Pa but not more than 1.9×10^7 Pa, more preferably at least 8.0×10^3 Pa but not

more than 1.8×10^7 Pa, and even more preferably at least 1.0×10^4 Pa but not more than 1.7×10^7 Pa.

The "breaking strain at 50°C" and the "breaking stress at 50°C" for the protective coating can be measured using the methods disclosed within the test examples described below.

[0098]

The protective coating has a storage modulus at 25°C that is preferably at least 3.0×10^9 Pa but not more than 5.0×10^{11} Pa, and more preferably at least 5.0×10^9 Pa but not more than 1.0×10^{11} Pa. Ensuring that the storage modulus at 25°C for the protective coating is at least 3.0×10^9 Pa minimizes damage to the protective coating during separation of the semiconductor chips with an attached protective coating from the first support sheet 4.

[0099]

The protective coating has a loss tangent at 25°C that is preferably at least 0.01 but not more than 0.4. Ensuring that the loss tangent at 25°C for the protective coating is not more than 0.4 minimizes damage to the protective coating during separation of the semiconductor chips with an attached protective coating from the first support sheet 4. The loss tangent at 25°C for the protective coating is more preferably at least 0.03 but not more than 0.3, and even more preferably at least 0.05 but not more than 0.2.

The "storage modulus at 25°C" and the "loss tangent at 25°C" for the protective coating can be measured using the methods disclosed within the test examples described below.

[0100]

The protective coating has a light transmittance at a wavelength of 1,064 nm that is preferably at least 40% but not more than 100%. By ensuring that the light

transmittance of the protective coating at a wavelength of 1,064 nm is 40% or greater, the laser light used for stealth dicing is able to efficiently reach into the interior of the workpiece such as the semiconductor wafer. From the viewpoint of ensuring that the laser light efficiently reaches the interior of the semiconductor wafer in a more stable manner, the light transmittance of the protective coating at a wavelength of 1,064 nm is more preferably at least 50% but not more than 99.9%, and even more preferably at least 60% but not more than 99.5%.

[0101]

The protective coating has a loss tangent peak temperature T1 within a range from 25°C to 60°C. By ensuring that the loss tangent peak temperature T1 is within this range, the protective coating on the first support sheet 4 can be divided appropriately when the first support sheet 4 is expanded under the conditions described below (specifically, with the temperature of the protective coating held within a range from 40°C to 70°C during expansion of the first support sheet 4 in the first dividing step). If the temperature T1 is too low, then the protective coating softens, and the breaking strain of the protective coating at 50°C is more likely to exceed 20%. If the temperature T1 is too high, then the protective coating hardens, and achieving appropriate division of the protective coating during expansion of the first support sheet 4 becomes more difficult. From the viewpoint of achieving satisfactory division of the protective coating in a more stable manner, the temperature of the protective coating during expansion of the first support sheet 4 in the first dividing step is preferably equal to or higher than the loss tangent peak temperature T1.

The "loss tangent peak temperature" of the protective coating can be measured using the method disclosed within the test examples described below.

[0102]

In other words, one aspect of the protective coating-forming sheet of the present invention has the protective coating formation film described above, wherein the protective coating formation film has the characteristics described below:

a breaking strain at 50°C of at least 0.2% but not more than 20%, and a breaking stress at 50°C of at least 5.0×10^3 Pa but not more than 2.0×10^7 Pa.

The protective coating formation film may also have at least one of the characteristics described below:

a storage modulus at 25°C of at least 3.0×10^9 Pa but not more than 5.0×10^{11} Pa,
 a loss tangent at 25°C of at least 0.01 but not more than 0.4,
 a light transmittance at a wavelength of 1,064 nm of at least 40% but not more than 100%, and

a loss tangent peak temperature T1 within a range from 25°C to 60°C.

Here, the term "characteristics" means the chemical or physical characteristics of the protective coating formation film.

[0103]

4. Jig Pressure-Sensitive Adhesive Layer

The pressure-sensitive adhesive that constitutes the jig pressure-sensitive adhesive layer 5 is preferably a pressure-sensitive adhesive having the desired levels of adhesive force and removability, and examples of pressure-sensitive adhesives that may be used include acrylic-based pressure-sensitive adhesives, rubber-based pressure-sensitive adhesives, silicone-based pressure-sensitive adhesives, urethane-based pressure-sensitive adhesives, polyester-based pressure-sensitive adhesives, and polyvinyl ether-based pressure-sensitive adhesives. Among these, acrylic-based pressure-sensitive adhesives are preferred, as they exhibit good adhesion to the jig such as the ring frame, and effectively inhibit detachment of the protective coating-forming sheet 3 from the ring

frame or the like during the dicing step or the like. A substrate that functions as a core may be interposed partway through the thickness direction of the jig pressure-sensitive adhesive layer 5.

[0104]

On the other hand, from the viewpoint of the adhesiveness to the jig such as the ring frame, the thickness of the jig pressure-sensitive adhesive layer 5 is preferably from 5 μm to 200 μm , and more preferably from 10 μm to 100 μm .

The "thickness of the jig pressure-sensitive adhesive layer" is the value representing the average of five thickness values obtained by cutting the layer through the thickness direction and measuring the thickness of the resulting cross-section at five random locations.

[0105]

5. Release Sheet

The release sheet 6 of the protective coating-forming sheet 3 according to an embodiment of the present invention protects the protective coating formation film 1 and the jig pressure-sensitive adhesive layer 5 in the period prior to use of the protective coating-forming sheet 3.

[0106]

The composition of the release sheet 6 is arbitrary, and examples include sheets prepared by subjecting a plastic film to a release treatment with a release agent or the like. 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. For the release agent, silicone-based release agents, fluorine-based release agents, and long chain alkyl-based release agents and the like may be used, but among these, silicone-based release agents are preferred, as

they are inexpensive and provide stable performance. Although there are no particular limitations on the thickness of the release sheet 6, the thickness is typically about 20 μm to 250 μm .

[0107]

6. Method for Manufacturing Protective Coating-Forming Sheet

The protective coating-forming sheet 3 is preferably manufactured by separately preparing a laminate containing the protective coating formation film 1 (also referred to as "laminate I" in this description) and a laminate containing the first support sheet 4 (also referred to as "laminate II" in this description), and then laminating the protective coating formation film 1 and the first support sheet 4 together using the laminate I and the laminate II, although manufacturing is not limited to this particular method.

[0108]

In order to manufacture the laminate I, the protective coating formation film 1 is formed on the release surface of a first release sheet. Specifically, a coating agent for forming the protective coating formation film is first prepared, containing the curable adhesive that constitutes the protective coating formation film 1 and also containing a solvent if required, and this coating agent is then applied to the release surface of the first release sheet using a coating device such as a roll coater, knife coater, roll knife coater, air knife coater, die coater, bar coater, gravure coater or curtain coater, and subsequently dried to form the protective coating formation film 1 on the release surface of the first release sheet. Subsequently, the release surface of a second release sheet is overlaid on the exposed surface of the protective coating formation film 1, and the resulting laminated structure is crimped, thus forming a laminate (the laminate I) in which the protective coating formation film 1 is sandwiched between the two release sheets.

[0109]

If desired, this laminate I may be subjected to half cutting to form the protective coating formation film 1 (and the second release sheet) into a desired shape such as a circular shape. In such a case, the excess portions of the protective coating formation film 1 and the second release sheet produced as a result of the half cutting may be removed appropriately.

[0110]

On the other hand, in order to manufacture the laminate II, a coating agent for forming the pressure-sensitive adhesive layer, containing the pressure-sensitive adhesive that constitutes the pressure-sensitive adhesive layer 42 and also containing a solvent if required, is applied to the release surface of a third release sheet, and the coating agent is then dried to form the pressure-sensitive adhesive layer 42 on the third release sheet. Subsequently, the substrate 41 is crimped to the exposed surface of the pressure-sensitive adhesive layer 42, thus obtaining a laminate (the laminate II) containing the first support sheet 4 composed of the substrate 41 and the pressure-sensitive adhesive layer 42, and the third release sheet.

[0111]

In those cases where the pressure-sensitive adhesive layer 42 is formed from an energy ray-curable pressure-sensitive adhesive, energy rays may be irradiated onto the pressure-sensitive adhesive layer 42 at this stage to cure the pressure-sensitive adhesive layer 42, or the irradiation of energy rays to cure the pressure-sensitive adhesive layer 42 may be performed after lamination of the protective coating formation film 1. Further, in those cases where the pressure-sensitive adhesive layer 42 is cured after lamination of the protective coating formation film 1, the pressure-sensitive adhesive layer 42 may be cured either before the dicing step or after the dicing step.

[0112]

Ultraviolet rays or an electron beam or the like are typically used as the energy rays. The irradiation dose of the energy rays differs depending on the type of energy rays used, but in the case of ultraviolet rays, a dose of 50 to 1,000 mJ/cm² is preferred, and a dose of 100 to 500 mJ/cm² is more desirable. In the case of an electron beam, a dose of about 10 to 1,000 krad is preferred.

[0113]

Once the laminate I and the laminate II have been obtained in the manner described above, the second release sheet in the laminate I and the third release sheet in the laminate II are peeled off, and the protective coating formation film 1 exposed within the laminate I and the pressure-sensitive adhesive layer 42 of the first support sheet 4 exposed in the laminate II are superimposed and crimped together. If desired, the first support sheet 4 may be subjected to half cutting to form a desired shape, for example a circular shape having a diameter that is larger than the protective coating formation film 1. In such a case, the excess portions of the first support sheet 4 produced as a result of the half cutting may be removed appropriately.

[0114]

In this manner, the protective coating-forming sheet 3 can be obtained, composed of the first support sheet 4 containing the pressure-sensitive adhesive layer 42 laminated to the substrate 41, the protective coating formation film 1 laminated to the pressure-sensitive adhesive layer 42 side of the first support sheet 4, and the first release sheet that is laminated to the opposite side of the protective coating formation film 1 from the surface facing the first support sheet 4. Finally, the first release sheet is peeled off, and the jig pressure-sensitive adhesive layer 5 is formed around the peripheral portions of the protective coating formation film 1 on the surface opposite the surface facing the first support sheet 4. The jig pressure-sensitive adhesive layer 5 can be formed by a coating

process using the same method as that described above for the pressure-sensitive adhesive layer 42.

[0115]

7. Method for Using Protective Coating-Forming Sheet

A method for manufacturing chips with an attached protective coating from a semiconductor wafer workpiece is described below as one example of a method for using the protective coating-forming sheet 3 according to an embodiment of the present embodiment.

[0116]

(1) First Bonding Step

First, the surface of the aforementioned protective coating formation film 1 of the protective coating-forming sheet 3 according to one embodiment of the present invention that is opposite the surface facing the first support sheet 4 is exposed. In the case of the protective coating-forming sheet 3 illustrated in FIG. 1, the release sheet 6 is peeled away as illustrated in FIG. 2.

[0117]

Next, the exposed surface is affixed to one surface of a semiconductor wafer 7 as a workpiece, specifically the surface (back surface) of the wafer opposite the circuit formation surface, thus obtaining a first laminate 10 including the protective coating-forming sheet 3 and the workpiece 1 (FIG. 3). The first laminate 10 illustrated in FIG. 3 also includes the jig pressure-sensitive adhesive layer 5 and a ring frame 8. As described above, the jig pressure-sensitive adhesive layer 5 is one element of the protective coating-forming sheet 3, and the jig pressure-sensitive adhesive layer 5 of the protective coating-forming sheet 3 is bonded to the ring frame 8 when the protective coating

formation film 1 of the protective coating-forming sheet 3 is bonded to the semiconductor wafer 7 in the first bonding step.

In other words, one aspect of the first bonding step includes exposing a surface of the protective coating formation film provided in the protective coating-forming sheet according to an embodiment of the present invention, the exposed surface being opposite the surface facing the first support sheet, and affixing the exposed surface to one surface of a workpiece to obtain a first laminate containing the protective coating-forming sheet and the workpiece.

[0118]

(2) First Curing Step

The protective coating formation film 1 provided in the protective coating-forming sheet 3 of the first laminate 10 obtained in the first bonding step is cured to obtain a protective coating. The curing conditions used for obtaining the protective coating are set appropriately in accordance with the material that constitutes the protective coating formation film 1. In those cases where the protective coating formation film 1 is a thermosetting adhesive, the protective coating formation film 1 is heated at a prescribed temperature for a suitable period of time. Further, in those cases where the protective coating formation film 1 is not a thermosetting adhesive, a separate heating treatment is performed.

In other words, one aspect of the first curing step includes obtaining a protective coating by curing the protective coating formation film in the first laminate.

The heating time and the heating temperature differ depending on the material that constitutes the film, but typically, heating at 90 to 170°C for 0.5 to 5 hours is preferred.

[0119]

(3) First Dividing Step

The first support sheet 4 of the protective coating-forming sheet 3 is expanded with the temperature of the protective coating provided on the protective coating-forming sheet 3 of the first laminate 10 that has undergone the first curing step held within a range from 40°C to 70°C, thereby dividing the protective coating together with the semiconductor wafer 7. As a result, as illustrated in FIG. 4, a second laminate 20 is obtained in which a plurality of (for example, 2 to 20,000) chips 9 with an attached protective coating, formed as a result of dividing the laminate of the semiconductor wafer 7 and the protective coating such that cut sections occur in the thickness direction, are arranged on one surface of the first support sheet 4.

In other words, one aspect of the first dividing step includes expanding the first support sheet with the temperature of the protective coating in the first laminate that has undergone the first curing step held within a range from 40°C to 70°C, and dividing the laminate of the workpiece and the protective coating, thus obtaining a second laminate in which a plurality of chips with an attached protective coating are arranged on one surface of the first support sheet.

[0120]

There are no particular limitations on the method used for expanding the first support sheet 4. As illustrated in FIG. 4, a ring-shaped member R may be pressed against the surface of the first support sheet 4 opposite the surface facing the ring frame 8, thereby altering the relative positioning between the ring frame 8 and the ring-shaped member R in the vertical direction and expanding the first support sheet 4. In other words, the stress generated within the first support sheet 4 as a result of this expansion includes a vector quantity in the horizontal direction or the direction parallel with the back surface of the semiconductor wafer 7.

[0121]

When the first support sheet 4 is expanded, the member positioned between the first support sheet 4 and the semiconductor wafer 7 is usually the protective coating formation film 1. The protective coating formation film 1 is generally composed of a curable material that can form a protective coating upon curing, and a typical example of this material is an uncured curable adhesive. Upon application of a tensile force, this type of material is able to undergo a large amount of deformation before breaking (namely, has a large breaking strain), and may sometimes not be divisible even when the first support sheet 4 is expanded. Accordingly, when expanding the first support sheet 4, the protective coating formation film 1 is often cooled to about 0°C to -20°C (generally by cooling the first laminate 10 to achieve this temperature) to reduce the breaking strain of the protective coating formation film 1. However in general, compared with heating, cooling tends to require comparatively expensive cooling equipment, and the amount of energy required for cooling is greater than the amount of energy required for heating. As a result, cooling of the protective coating formation film 1, generally by cooling the first laminate 10, tends to cause increases in the initial capital costs and the running costs associated with the method for manufacturing chips with an attached protective coating.

[0122]

In contrast, in the method for manufacturing chips with an attached protective coating according to an embodiment of the present invention, the member positioned between the first support sheet 4 and the semiconductor wafer 7 when the first support sheet 4 is expanded is the protective coating. Because the protective coating is obtained by curing the protective coating formation film 1, the breaking strain of the protective coating is less than that of the protective coating formation film 1. Accordingly, division defects caused as a result of the breaking strain are less likely to occur. However,

because the protective coating is a cured material, the breaking stress is sometimes increased, meaning there is a possibility of division defects occurring due to the large breaking stress. Accordingly, in the method for manufacturing chips with an attached protective coating according to an embodiment of the present invention, the temperature of the protective coating is preferably held within a range from 40°C to 70°C during expansion of the first support sheet 4.

[0123]

In other words, by performing heated expansion rather than the conventional cooled expansion, the possibility of division defects occurring in the protective coating can be reduced. Provided the protective coating is heated to about 40°C, the reduction in the breaking stress compared with that at room temperature (23°C) is significant, and the effects derived from performing the heated expansion (a reduction in division defects) can be achieved with good stability. On the other hand, if the temperature of the protective coating during expansion of the first support sheet 4 exceeds 70°C, then there is an increased possibility of other problems arising, including operational problems (specific examples of which include a reduction in the amount of expansion, and fusing of the first support sheet 4 to the table) caused by an increase in the breaking strain of the protective coating, and a change in the mechanical properties of the first support sheet 4 (such as a reduction in the Young's modulus, and softening of the support sheet).

Accordingly, by ensuring that the temperature of the protective coating during expansion of the first support sheet 4 is not more than 70°C, the likelihood of problems occurring during the manufacture of the chips with an attached protective coating can be reduced in a stable manner. From the viewpoint of reducing the likelihood of these types of problems occurring in a more stable manner, the temperature of the protective coating during expansion of the first support sheet 4 may sometimes preferably be at least 42°C

but not more than 65°C, may sometimes be more preferably at least 43°C but not more than 60°C, and is sometimes most preferably at least 45°C but not more than 55°C.

[0124]

(4) First Pickup Step

In the first pickup step, each of the plurality of chips 9 with an attached protective coating provided in the second laminate 20 obtained by performing the first dividing step is separated from the first support sheet 4 to obtain an individual chip 9 with an attached protective coating as a processed product. There are no limitations on this separation method. For example, as illustrated in FIG. 5, a thrust pin P and a vacuum suction collet C may be used. This enables chips 9 having an attached protective coating to be obtained.

In other words, one aspect of the first pickup step includes separating each of the plurality of chips with an attached protective coating provided in the second laminate from the first support sheet, thereby obtaining each of the chips with an attached protective coating as a processed product.

[0125]

(5) Modified Layer Formation Step

Prior to starting the first dividing step, a modified layer formation step is performed in which a laser light in the infrared region (for example, 1,064 nm) is irradiated in a manner that focuses the laser light on a focus point set within the interior of the semiconductor wafer 7 (the workpiece), thereby forming a modified layer inside the semiconductor wafer 7. In the first dividing step, by expanding the first support sheet bonded to the semiconductor wafer 7 that has been subjected to the modified layer formation step, division of the semiconductor wafer 7 along planned division lines can be achieved.

In other words, one aspect of the modified layer formation step includes, prior to starting the first dividing step, irradiating an infrared laser light in a manner that focuses the laser light on a focus point set within the interior of the workpiece, thereby forming a modified layer inside the workpiece.

[0126]

8. Other Embodiments of the Protective Coating-Forming Sheet

(1) Cases in which the first support sheet lacks a jig pressure-sensitive adhesive layer

FIG. 6 is a cross-sectional view of a protective coating-forming sheet according to another embodiment of the present invention. As illustrated in FIG. 6, the protective coating-forming sheet 3A according to this embodiment has a structure including a first support sheet 4 prepared by laminating a pressure-sensitive adhesive layer 42 to one surface of a substrate 41, a protective coating formation film 1 laminated to the surface of the first support sheet 4 to which the pressure-sensitive adhesive layer 42 has been laminated, and a release sheet 6 formed on a surface of the protective coating formation film 1 opposite the surface facing the first support sheet 4. The protective coating formation film 1 in this embodiment is formed of a size that is either substantially the same as, or slightly larger than, the workpiece in the in-plane direction, but smaller than the first support sheet 4 in the in-plane direction. The portions of the pressure-sensitive adhesive layer 42 to which the protection membrane-forming film 1 is not laminated can be used for affixing a jig such as a ring frame.

[0127]

The material and thickness of each of the members of the protective coating-forming sheet 3A according to the present embodiment may be the same as the material and thickness of each of the members of the protective coating-forming sheet 3 described above. However, in those cases where the pressure-sensitive adhesive layer 42 is formed

from an energy ray-curable pressure-sensitive adhesive, it is preferable that the energy ray-curable pressure-sensitive adhesive is cured in those portions of the pressure-sensitive adhesive layer 42 that contact the protective coating formation film 1, but the energy ray-curable pressure-sensitive adhesive is not cured in the remaining portions. This enables the smoothness (gloss) of the protective coating formed by curing the protective coating formation film 1 to be enhanced, while maintaining superior adhesive force to the jig such as the ring frame.

[0128]

A jig pressure-sensitive adhesive layer similar to the jig pressure-sensitive adhesive layer 5 of the protective coating-forming sheet 3 described above may also be separately provided on the peripheral portions of the pressure-sensitive adhesive layer 42 of the first support sheet 4 of the protective coating-forming sheet 3A, on the opposite side from the substrate 41.

[0129]

(2) Cases in which the first support sheet lacks a pressure-sensitive adhesive layer

As illustrated in FIG. 11, a first support sheet of a protective coating-forming sheet 3B according to yet another embodiment of the present invention may lack a pressure-sensitive adhesive layer, and be composed (solely) of a substrate. In this case, the surface of the substrate on the side of the protective coating formation film corresponds with the first surface of the first support sheet.

[0130]

In those cases where the first support sheet is formed from a substrate, a jig pressure-sensitive adhesive layer similar to the jig pressure-sensitive adhesive layer 5 illustrated in FIG. 1 is preferably provided around the peripheral portions of the surface

of the protective coating formation film on the opposite side from the surface facing the substrate (the first support sheet).

[0131]

(3) Cases in which the first support sheet is a release sheet

A first support sheet of a protective coating-forming sheet according to yet another embodiment of the present invention may be a release sheet having a release surface. In this case, the release surface corresponds with the first surface of the first support sheet. There are no limitations on the specific structure of the release sheet.

[0132]

(4) Cases including a second support sheet

The protective coating-forming sheet according to yet another embodiment of the present invention may include a second support sheet laminated to the surface of the protective coating formation film opposite the surface facing the first support sheet. The second support sheet may be a release sheet, positioned so that the release surface faces the protective coating formation film.

[0133]

(5) Cases in which the first support sheet is peeled from the protective coating formation film

As illustrated in FIG. 2 to FIG. 5, in the aforementioned method for manufacturing the chips 7 having an attached protective coating according to an embodiment of the present invention, the protective coating is formed from the protective coating formation film 1 in the first curing step, and then in the subsequent first pickup step, the protective coating, or more specifically the divided portion of the protective coating that represents a portion of the chip 7 with an attached protective coating, is separated from the first support sheet 4.

[0134]

In a method for manufacturing chips with an attached protective coating according to yet another embodiment of the present invention, the protective coating formation film is peeled away from the first support sheet, and is subsequently cured to form the protective coating. One example of this type of manufacturing method is described below.

[0135]

In other words, as illustrated in FIG. 7 to FIG. 10, one aspect of the manufacturing method according to this embodiment includes:

a lamination step of exposing a surface of the protective coating formation film 1 provided in the protective coating-forming sheet according to an embodiment of the present invention, the exposed surface being opposite the surface facing the first support sheet, affixing the exposed surface to one surface of a workpiece 7 such as a semiconductor wafer, and peeling the first support sheet of the protective coating-forming sheet from the protective coating formation film to obtain a third laminate 11 containing the workpiece 7 and the protective coating formation film 1;

a second curing step of curing the protective coating formation film of the third laminate 11 to obtain a protective coating;

a second bonding step of affixing a surface of a third pressure-sensitive adhesive layer 131 of a process sheet 13 provided with a third substrate 132 and the third pressure-sensitive adhesive layer 131 laminated to one surface of the third substrate, to the surface of the protective coating of the third laminate 11 that has undergone the second curing step, thus obtaining a fourth laminate 12 containing the process sheet 13 and the third laminate 11;

a second dividing step of expanding the process sheet 13 of the fourth laminate 12 with the temperature of the protective coating provided on the fourth laminate 12 held within a range from 40°C to 70°C, and dividing the protective coating together with the workpiece 7, thus obtaining a fifth laminate 14 in which a plurality of (for example, 2 to 20,000) chips 9 with an attached protective coating, formed as a result of dividing the laminate of the workpiece 7 and the protective coating such that cut sections occur in the thickness direction, are arranged on one surface of the process sheet 13; and

a second pickup step of separating, from the process sheet 13, each of the plurality of chips 9 with an attached protective coating provided on the fifth laminate 14, thereby obtaining each of the chips 9 with an attached protective coating as a processed product,

the method also including, prior to starting the second dividing step, a modified layer formation step of irradiating an infrared laser light in a manner that focuses the laser light on a focus point set within the interior of the workpiece 7, thereby forming a modified layer inside the workpiece 7.

[0136]

Here, the third substrate 132 of the process sheet 13 may have the same characteristics as the substrate 41 of the first support sheet 4. Further, the third pressure-sensitive adhesive layer 131 of the process sheet 13 may have the same characteristics as the pressure-sensitive adhesive layer 42 of the first support sheet 4.

Furthermore, the temperature of the protective coating of the fourth laminate 12 during the second dividing step is preferably equal to or higher than the aforementioned temperature T1.

[0137]

The embodiments described above have been presented in order to facilitate comprehension of the present invention, but do not limit the present invention in any way. Accordingly, the various elements described in the above embodiments are deemed to include all the various design modifications and equivalent items included within the technical scope of the present invention.

[0138]

For example, one or more other layers may be interposed between the substrate 41 and the pressure-sensitive adhesive layer 42 in the first support sheet 4. Further, other layers may be laminated to the first surface of the first support sheet 4 formed from the substrate 41. Examples of these other layers include layers for adjusting the adhesiveness between the substrate 41 and the pressure-sensitive adhesive layer 42 such as a primer layer, and layers for adjusting the adhesiveness between the first support sheet 4 and the protective coating formation film 1.

[0139]

The method described above for manufacturing chips with an attached protective coating may also use a protective coating formation film different from the protective coating formation film according to an embodiment of the present invention.

In other words, another aspect of the method for manufacturing a chip with an attached protective coating according to an embodiment of the present invention includes:

a bonding step of exposing a surface of a protective coating formation film provided in a protective coating-forming sheet containing a first support sheet and a protective coating formation film (different from the protective coating formation film according to an embodiment of the present invention) laminated to the first surface side of the first support, the exposed surface being opposite the surface facing the first support

sheet, and affixing the exposed surface to one surface of a workpiece to obtain a first laminate containing the protective coating-forming sheet and the workpiece;

a first curing step of curing the protective coating formation film in the first laminate to obtain a protective coating;

a first dividing step of expanding the first support sheet with the temperature of the protective coating in the first laminate that has undergone the first curing step held within a range from 40°C to 70°C, and dividing the protective coating together with the workpiece, thus obtaining a second laminate in which a plurality of chips with an attached protective coating, formed as a result of dividing the laminate of the workpiece and the protective coating such that cut sections occur in the thickness direction, are arranged on one surface of the first support sheet; and

a first pickup step of separating, from the first support sheet, each of the plurality of chips with an attached protective coating provided in the second laminate, thereby obtaining each of the chips with an attached protective coating as a processed product,

the method also including, prior to starting the first dividing step, a modified layer formation step of irradiating an infrared laser light in a manner that focuses the laser light on a focus point set within the interior of the workpiece, thereby forming a modified layer inside the workpiece.

Further, the temperature of the protective coating of the first laminate during the first dividing step is preferably equal to or higher than the aforementioned temperature T1.

[0140]

Furthermore, yet another aspect of the method for manufacturing a chip with an attached protective coating according to an embodiment of the present invention includes:

a lamination step of exposing a surface of a protective coating formation film provided in a protective coating-forming sheet containing a first support sheet and a protective coating formation film (different from the protective coating formation film according to an embodiment of the present invention) laminated to the first surface side of the first support, the exposed surface being opposite the surface facing the first support sheet, affixing the exposed surface to one surface of a workpiece, and peeling the first support sheet from the protective coating formation film to obtain a third laminate containing the workpiece and the protective coating formation film;

a second curing step of curing the protective coating formation film of the third laminate to obtain a protective coating;

a second bonding step of affixing a surface of a third pressure-sensitive adhesive layer of a process sheet provided with a third substrate and the third pressure-sensitive adhesive layer laminated to one surface of the third substrate, to the surface of the protective coating of the third laminate that has undergone the second curing step, thus obtaining a fourth laminate containing the process sheet and the third laminate;

a second dividing step of expanding the process sheet of the fourth laminate with the temperature of the protective coating provided on the fourth laminate held within a range from 40°C to 70°C, and dividing the protective coating together with the workpiece, thus obtaining a fifth laminate in which a plurality of chips with an attached protective coating, formed as a result of dividing the laminate of the workpiece and the protective coating such that cut sections occur in the thickness direction, are arranged on one surface of the process sheet; and

a second pickup step of separating, from the process sheet, each of the plurality of chips with an attached protective coating provided on the fifth laminate, thereby obtaining each of the chips with an attached protective coating as a processed product,

the method also including, prior to starting the second dividing step, a modified layer formation step of irradiating an infrared laser light in a manner that focuses the laser light on a focus point set within the interior of the workpiece, thereby forming a modified layer inside the workpiece.

Further, the temperature of the protective coating of the fourth laminate during the second dividing step is preferably equal to or higher than the aforementioned temperature T1.

EXAMPLES

[0141]

The present invention is described below in further detail using a series of examples and the like, but the scope of the present invention is in no way limited by these examples and the like.

[0142]

[Example 1]

The components listed below were mixed together in the blend ratio (solid fraction amounts) shown in Table 1, and then the mixture was diluted with methyl ethyl ketone to achieve a solid fraction concentration of 50% by mass relative to the total mass of the coating agent for protective coating formation film, thus completing preparation of a coating agent for a protective coating formation film.

(A-1) Binder polymer: a (meth)acrylate ester copolymer (weight-average molecular weight: 400,000, glass transition temperature: -1°C) obtained by copolymerizing 10 parts by mass of n-butyl acrylate, 70 parts by mass of methyl acrylate, 5 parts by mass of glycidyl methacrylate and 15 parts by mass of 2-hydroxyethyl acrylate

(A-2) Binder polymer: a (meth)acrylate ester copolymer (weight-average molecular weight: 400,000, glass transition temperature: -6°C) obtained by copolymerizing 85 parts by mass of methyl acrylate and 15 parts by mass of 2-hydroxyethyl acrylate

(A-3) Binder polymer: a (meth)acrylate ester copolymer (weight-average molecular weight: 800,000, glass transition temperature: -28°C) obtained by copolymerizing 55 parts by mass of n-butyl acrylate, 10 parts by mass of methyl acrylate, 20 parts by mass of glycidyl methacrylate and 15 parts by mass of 2-hydroxyethyl acrylate

(B-1) Bisphenol A epoxy resin (jER828, manufactured by Mitsubishi Chemical Corporation, epoxy equivalent weight: 184 to 194 g/eq)

(B-2) Bisphenol A epoxy resin (jER1055, manufactured by Mitsubishi Chemical Corporation, epoxy equivalent weight: 800 to 900 g/eq)

(B-3) Dicyclopentadiene epoxy resin (EPICLON HP-7200HH, manufactured by DIC Corporation, epoxy equivalent weight: 255 to 260 g/eq)

(B-4) Cresol novolac epoxy resin (EOCN-104, manufactured by Nippon Kayaku Co., Ltd., epoxy equivalent weight: 220 g/eq)

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

(D) Curing accelerator: 2-phenyl-4,5-dihydroxymethylimidazole (CUREZOL 2PHZ, manufactured by Shikoku Corporation)

(E-1) Epoxy group-modified spherical silica filler (SC2050MA, manufactured by Admatechs Co., Ltd., average particle size: 0.5 μm)

(E-2) Vinyl group-modified spherical silica filler (YA050C-MJA, manufactured by Admatechs Co., Ltd., average particle size: 0.05 μm)

(E-3) Amorphous silica filler (SV-10, manufactured by Tatsumori Ltd., average particle size: 8 μm)

(F) Silane coupling agent: γ -glycidoxypyriltrimethoxysilane (KBM403, manufactured by Shin-Etsu Chemical Co., Ltd., methoxy equivalent weight: 12.7 mmol/g, molecular weight: 236.3)

[0143]

[Table 1]

Blended components		Example 1	Example 2	Comparative Example 1	Comparative Example 2
Binder polymer	A-1	26.0	26.1		
	A-2			70.5	
	A-3				19.0
Epoxy resin	B-1	10.4			11.4
	B-2	1.7	12.2		1.9
	B-3	5.2	5.2		5.7
	B-4			7.9	
Curing agent	C	0.4	0.3	0.2	0.5
Curing accelerator	D	0.4	0.3	0.2	0.5
Silica filler	E-1	55.5	55.6		6.1
	E-2			20.4	
	E-3				54.5
Silane coupling agent	F	0.4	0.3	0.8	0.4

[0144]

The coating agent for a protective coating formation film described above was applied with a knife coater to a release sheet (SP-PET381031, manufactured by Lintec Corporation) composed of a silicone-based release agent layer formed on one surface of a polyethylene terephthalate (PET) film, in an amount sufficient to obtain a final

protective coating formation film with a thickness of 25 μm , and the coating agent was then dried for 2 minutes in an oven at 120°C, thus forming a protective coating formation film. Subsequently, the release surface of a release sheet (SP-PET251130, manufactured by Lintec Corporation) composed of a silicone-based release agent layer formed on one surface of a PET film was overlaid on the protective coating formation film, and the two were bonded together to obtain a protective coating-forming sheet.

[0145]

[Example 2]

With the exception of altering the components used in forming the protective coating formation film and the blend amount of each component as shown in the column labeled Example 2 in Table 1, and then preparing a coating agent for a protective coating formation film by diluting the components with methyl ethyl ketone to achieve a solid fraction concentration of 50%, a protective coating-forming sheet was produced in the same manner as that described for Example 1.

[0146]

[Comparative Example 1]

With the exception of altering the components used in forming the protective coating formation film and the blend amount of each component as shown in the column labeled Comparative Example 1 in Table 1, and then preparing a coating agent for a protective coating formation film by diluting the components with methyl ethyl ketone to achieve a solid fraction concentration of 50%, a protective coating-forming sheet was produced in the same manner as that described for Example 1.

[0147]

[Comparative Example 2]

With the exception of altering the components used in forming the protective coating formation film and the blend amount of each component as shown in the column labeled Comparative Example 2 in Table 1, and then preparing a coating agent for a protective coating formation film by diluting the components with methyl ethyl ketone to achieve a solid fraction concentration of 50%, a protective coating-forming sheet was produced in the same manner as that described for Example 1. The (E-3) amorphous silica filler (SV-10) was dispersed in advance in methyl ethyl ketone for 24 hours using a beads mill prior to use.

[0148]

[Test Example 1] <Measurement of Viscoelasticity>

(1) Preparation of Cured Sample

The two release sheets were peeled from the protective coating-forming sheet obtained in each of the examples and comparative examples, and layers of the thus obtained protective coating formation film were laminated to achieve a thickness of 200 μm . The thus obtained protective coating formation layer was heated at 130°C for 2 hours in an oven (under normal atmospheric conditions) to obtain a cured sample of the protective coating with a thickness of 200 μm .

(2) Measurement of Breaking Strain and Breaking Stress at 50°C Following Curing

The obtained cured sample was cut to prepare test pieces having dimensions of width 5 mm $\times$ length 20 mm $\times$ thickness 200 μm . Using a Dynamic Mechanical Analyzer (DMA Q800, manufactured by TA Instruments, Inc.), a tensile test was performed on a test piece (chuck distance: 5 mm). The test piece was held for one minute in an environment at a temperature of 50°C, and the tensile test was then performed while the load was increased at a constant rate of 1 N/minute. The breaking

stress and the breaking strain were extracted from the results of the tensile test. The results are shown in Table 2.

(3) Measurement of Storage Modulus and Loss Tangent at 25°C for Cured Sample

The obtained cured sample was cut to prepare test pieces having dimensions of width 4.5 mm × length 20 mm × thickness 200 μm. Using a Dynamic Mechanical Analyzer (DMA Q800, manufactured by TA Instruments, Inc.), measurement of the storage modulus and the loss modulus was performed under the following conditions.

Measurement mode: tensile mode

Measurement start temperature: 0°C

Measurement end temperature: 300°C

Rate of temperature increase: 3°C/minute

Frequency: 11 Hz

Measurement atmosphere: open atmosphere

The loss tangent ($\tan \delta$) was calculated from the obtained storage modulus and loss modulus values, and the storage modulus at 25°C and the loss tangent at 25°C were calculated. The results are shown in Table 2.

(4) Measurement of Loss Tangent Peak Temperature for Cured Sample

The loss tangent ($\tan \delta$) was calculated from the storage modulus and loss modulus values obtained under the above conditions, and the temperature where the loss tangent reached a maximum was deemed the loss tangent peak temperature. The results revealed a loss tangent peak temperature of 52°C in Example 1, 27°C in Example 2, 39°C in Comparative Example 1, and 88°C in Comparative Example 2.

[0149]

[Test Example 2] <Evaluation of Divisibility>

Using a laminator (RAD-3600F/12, manufactured by Lintec Corporation), a workpiece composed of a silicon wafer having a thickness of 100 μm and an external diameter of 8 inches was bonded to a protective coating formation film that had been cut to the same shape as the silicon wafer, and the resulting laminate was heated in an oven (under normal atmospheric conditions) at 130°C for 2 hours to cure the film and prepare a wafer with an attached protective coating.

Using a mounter (RAD-2700F/12, manufactured by Lintec Corporation), a dicing tape for stealth dicing (Adwill D-821HS, manufactured by Lintec Corporation) was affixed to the protective coating surface of the wafer with an attached protective coating. At this time, the dicing tape was also affixed to the ring frame.

Using a laser irradiation device, a laser (1,064 nm) was irradiated through the dicing tape and the protective coating so as to be focused on a point inside the interior of the wafer. During this process, irradiation was performed while the laser was scanned along planned division lines that had been set so as to form chips having dimensions of 5 mm $\times$ 5 mm.

Subsequently, an expansion apparatus (DDS2300, manufactured by DISCO Corporation) was used under an atmosphere at a temperature of 50°C to expand the dicing tape affixed to the wafer with the attached protective coating at a rate of 100 mm/second and by an expansion amount of 10 mm.

As a result, in those cases where the protective coating divided together with the wafer along all of the planned division lines, the protective coating divisibility was evaluated as good ("A" in Table 2), whereas in those cases where the stringing phenomenon was observed in the protective coating following the division process ("B" in Table 2), or those cases where the protective coating did not divide in some locations

("C" in Table 2), the protective coating divisibility was evaluated as poor. The results are shown in Table 2.

[0150]

[Test Example 3] <Evaluation of Protective Coating Strength>

Following the divisibility evaluation performed in Test Example 2, the expansion apparatus described above and an IR oven in which the heat source had been set to a temperature of 550°C were used to heat the sections of laminate (the fourth laminate) containing the divided wafer and protective coating (namely, the plurality of chips with an attached protective coating) as well as the dicing tape for a period of 5 minutes, thereby correcting any sagging of the dicing tape that had occurred during expansion of the dicing tape. Subsequently, using a die bonder (Bestem-D02, manufactured by Canon Machinery Inc.), and with a 3 mm expansion applied, a thrust pin was pressed up against the surface of the dicing tape opposite the surface facing the divided wafer and the protective coating, and the thrust up chip with an attached protective coating was lifted up by a vacuum suction collet, thereby picking up the chip with an attached protective coating.

The picked up chip with an attached protective coating was inspected, if no impression from the thrust pin could be discerned in the protective coating, the protective coating strength was evaluated as good ("A" in Table 2), if an impression of the pin was observed but was of a level unlikely to cause problems, the strength was evaluated as acceptable ("B" in Table 2), whereas if a significant impression of the pin could be seen, then the protective coating strength was evaluated as poor ("C" in Table 2). The results are shown in Table 2. Because the protective coating according to Comparative Example 2 did not divide satisfactorily in Test Example 2, only the fourth laminates containing the protective coatings according to Example 1, Example 2 and Comparative Example 1 (a

portion that divided satisfactorily was used for the evaluation) were subjected to this evaluation.

[0151]

[Table 2]

	Tensile characteristics at 50°C		Storage modulus at 25°C (Pa)	Loss tangent at 25°C	Divisibility	Protective coating strength
	Breaking strain (%)	Breaking stress (Pa)				
Example 1	8.2	1.71×10^7	6.5×10^9	0.11	A	A
Example 2	14	1.02×10^7	3.1×10^9	0.41	A	B
Comparative Example 1	38	8.90×10^6	1.4×10^9	1.71	B	C
Comparative Example 2	6.7	2.27×10^7	7.6×10^9	0.10	C	not evaluated

[0152]

As is evident from Table 2, the protective coating-forming sheets of the Examples, provided with a protective coating having a breaking strain at 50°C of not more than 20% and a breaking stress at 50°C of not more than 2.0×10^7 Pa, exhibited excellent divisibility and also displayed excellent protective coating strength.

INDUSTRIAL APPLICABILITY

[0153]

The protective coating-forming sheet according to the present invention can be used favorably in methods including a step in which division is performed while heating the protective coating, and is therefore extremely useful industrially.

DESCRIPTION OF THE REFERENCE SIGNS

[0154]

- 1: Protective coating formation film
- 3, 3A, 3B: Protective coating-forming sheet
- 4: Support sheet
- 41: Substrate
- 42: Pressure-sensitive adhesive layer
- 5: Jig pressure-sensitive adhesive layer
- 6: Release sheet
- 7: Semiconductor wafer
- 8: Ring frame
- 9: Chip with attached protective coating
- 10: First laminate
- 11: Second laminate
- 12: Third laminate
- 13: Process sheet
- 131: Third pressure-sensitive adhesive layer
- 132: Third substrate
- 14: Fourth laminate
- R: Ring-shaped member
- P: Thrust pin
- C: Vacuum suction collet

CLAIMS

1. A protective coating-forming sheet comprising a first support sheet and a protective coating formation film laminated to a first surface side of the first support sheet, wherein

the protective coating formation film is formed from a curable material, and

the protective coating formation film has characteristics described below:

when the protective coating formation film is cured to form a protective coating, the protective coating has a breaking strain at 50°C of not more than 20%, and a breaking stress at 50°C of not more than 2.0×10^7 Pa.
2. The protective coating-forming sheet according to Claim 1, wherein the protective coating formation film also has a characteristic described below:

the protective coating has a storage modulus at 25°C of 3.0×10^9 Pa or greater.
3. The protective coating-forming sheet according to Claim 1 or 2, wherein the protective coating formation film also has a characteristic described below:

the protective coating has a loss tangent at 25°C of 0.4 or less.
4. The protective coating-forming sheet according to any one of Claims 1 to 3, wherein the protective coating formation film also has a characteristic described below:

the protective coating has a light transmittance at a wavelength of 1,064 nm of 40% or greater.

5. A method for manufacturing a chip with an attached protective coating, the method comprising:

a bonding step of exposing a surface of the protective coating formation film provided in the protective coating-forming sheet according to any one of Claims 1 to 4, the exposed surface being opposite a surface facing the first support sheet, and affixing the exposed surface to one surface of a workpiece to obtain a first laminate comprising the protective coating-forming sheet and the workpiece;

a first curing step of curing the protective coating formation film in the first laminate to obtain the protective coating;

a first dividing step of expanding the first support sheet with a temperature of the protective coating in the first laminate that has undergone the first curing step held within a range from 40°C to 70°C, and dividing the protective coating together with the workpiece, thus obtaining a second laminate in which a plurality of chips with an attached protective coating, formed as a result of dividing the laminate of the workpiece and the protective coating such that cut sections occur in a thickness direction, are arranged on one surface of the first support sheet; and

a first pickup step of separating, from the first support sheet, each of the plurality of chips with an attached protective coating provided in the second laminate, thereby obtaining each of the chips with an attached protective coating as a processed product,

the method also comprising, prior to starting the first dividing step, a modified layer formation step of irradiating an infrared laser light in a manner that focuses the laser light on a focus point set within an interior of the workpiece, thereby forming a modified layer inside the workpiece.

6. A method for manufacturing a chip with an attached protective coating, the method comprising:

a lamination step of

exposing a surface of the protective coating formation film provided in the protective coating-forming sheet according to any one of Claims 1 to 4, the exposed surface being opposite a surface facing the first support sheet,

affixing the exposed surface to one surface of a workpiece, and

peeling the first support sheet from the protective coating formation film to obtain a third laminate comprising the workpiece and the protective coating formation film;

a second curing step of curing the protective coating formation film of the third laminate to obtain the protective coating;

a second bonding step of affixing a surface of a third pressure-sensitive adhesive layer of a process sheet, comprising a third substrate and the third pressure-sensitive adhesive layer laminated to one surface of the third substrate, to a surface of the protective coating of the third laminate that has undergone the second curing step, thus obtaining a fourth laminate comprising the process sheet and the third laminate;

a second dividing step of expanding the process sheet of the fourth laminate with a temperature of the protective coating provided on the fourth laminate held within a range from 40°C to 70°C, and dividing the protective coating together with the workpiece, thus obtaining a fifth laminate in which a plurality of chips with an attached protective coating, formed as a result of dividing the laminate of the workpiece and the protective coating such that cut sections occur in a thickness direction, are arranged on one surface of the process sheet; and

a second pickup step of separating, from the process sheet, each of the plurality of chips with an attached protective coating provided on the fifth laminate, thereby obtaining each of the chips with an attached protective coating as a processed product,

the method also comprising, prior to starting the second dividing step, a modified layer formation step of irradiating an infrared laser light in a manner that focuses the laser light on a focus point set within an interior of the workpiece, thereby forming a modified layer inside the workpiece.