

DESCRIPTION

FILM FOR PROTECTIVE FILM FORMATION AND COMPOSITE SHEET FOR PROTECTIVE FILM FORMATION

TECHNICAL FIELD

[0001]

The present invention relates to a film for protective film formation for forming a protective film on the back surface of a semiconductor wafer or a semiconductor chip, and a composite sheet for protective film formation that includes the film for protective film formation.

Priority is claimed on Japanese Patent Application No. 2015-212845, filed on October 29, 2015, the content of which is incorporated herein by reference.

BACKGROUND ART

[0002]

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

[0003]

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

incorporated in a semiconductor device as a semiconductor chip with a protective film. The protective film is used for preventing cracks from developing in the semiconductor chip following the dicing step and packaging.

[0004]

In order to form this type of protective film, a composite sheet for protective film formation is typically used, containing a film for protective film formation provided on a support sheet. In the composite sheet for protective film formation, the film for protective film formation has a protective film formation ability, whereas the support sheet can be used as a dicing sheet, and therefore the composite sheet can function as an integrated combination of a film for protective film formation and a dicing sheet.

[0005]

Up until now, composite sheets having a film for protective film formation that forms a protective film upon curing by heating have mainly been used as the above type of composite sheet for protective film formation. For example, the composite sheet for protective film formation is affixed to the back surface (the surface on the opposite side from the electrode formation surface) of a semiconductor wafer via the film for protective film formation, and the semiconductor wafer is then converted to semiconductor chips by dicing. Subsequently, either the film for protective film formation is cured by heating to form a protective film, and each of the semiconductor chips is then picked up with this protective film affixed thereto, or alternatively, each semiconductor chip is picked up with the film for protective film formation affixed thereto, and the film for protective film formation is then cured by heating to form a protective film.

[0006]

However, because heat curing of the film for protective film formation usually requires a long time of several hours, a shortening of the curing time would be desirable. In this regard, films for protective film formation that can be cured by irradiation with energy rays such as ultraviolet rays are being investigated, and a protective film having a pencil hardness following curing of 5H or higher, and capable of suppressing the occurrence of chipping during dicing of the semiconductor wafer (see Patent Document 1), a film for protective formation film capable of forming a protective film having excellent laser mark legibility, hardness and mounting reliability (see Patent Document 2), and a film for protective formation film capable of forming a protective film having superior hardness and excellent adhesion to semiconductor chips (see Patent Document 3) have all been disclosed.

PRIOR ART LITERATURE

Patent Documents

[0007]

Patent Document 1: Japanese Unexamined Patent Application, First Publication No. 2009-147277

Patent Document 2: Japanese Unexamined Patent Application, First Publication No. 2009-138026

Patent Document 3: Japanese Unexamined Patent Application, First Publication No. 2010-031183

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0008]

However, in order to suppress the occurrence of cracking and chipping, such as the so-called chipping that can occur around the outer periphery of semiconductor chips, it is desirable that a film for protective film formation exhibits a superior protective action for the semiconductor wafer and semiconductor chips, is capable of maintaining that superior protective action even when exposed to large temperature variations, and is capable of forming a protective film having excellent reliability. From these types of viewpoints, conventional films for protective film formation that are capable of being cured by irradiation with energy rays still leave considerable room for improvement.

[0009]

The present invention has been developed in light of the above circumstances, and has an object of providing a film for protective film formation that is capable of forming a protective film having a superior protective action and excellent reliability on the back surface of a semiconductor wafer or semiconductor chip, as well as providing a composite sheet for protective film formation that includes this film for protective film formation.

Means for Solving the Problems

[0010]

In order to achieve the above object, the present invention provides a film for protective film formation which contains an energy ray-curable compound (B) and is used for forming a protective film on the back surface of a semiconductor wafer or a semiconductor chip, wherein a cured product obtained by irradiating the film for protective film formation with energy rays has a Young's modulus of at least 500 MPa and an elongation at break of at least 8%.

In the film for protective film formation of the present invention, the proportion of the total mass of an energy ray-curable compound (B1) having 2 to 4 energy ray-polymerizable groups within a single molecule relative to the total mass of the energy ray-curable compound (B) is preferably at least 90% by mass.

Further, the present invention also provides a composite sheet for protective film formation that contains the above film for protective film formation on one surface of a support sheet.

[0011]

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

[1] A film for protective film formation which contains an energy ray-curable compound (B), has the properties described below, and is used for forming a protective film on the back surface of a semiconductor wafer or a semiconductor chip, wherein when a cured product is formed by curing the film for protective film formation by irradiation with energy rays, the cured product has a Young's modulus of at least 500 MPa and an elongation at break of at least 8%.

[2] The film for protective film formation according to [1], wherein within the film for protective film formation, an amount of an energy ray-curable compound (B1) having 2 to 4 energy ray-polymerizable groups within a single molecule, relative to the total mass of the energy ray-curable compound (B), is at least 90% by mass.

[3] A composite sheet for protective film formation, containing the film for protective film formation according to [1] or [2] provided on one surface of a support sheet.

Effects of the Invention

[0012]

The present invention provides a film for protective film formation that is capable of forming a protective film having a superior protective action and excellent reliability on the back surface of a semiconductor wafer or semiconductor chip, and also provides a composite sheet for protective film formation that includes this film for protective film formation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

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

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

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

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

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

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0014]

<<Film for Protective Film Formation>>

The film for protective film formation according to the present invention contains an energy ray-curable compound (B) and is used for forming a protective film on the back surface of a semiconductor wafer or a semiconductor chip, wherein a cured product obtained by irradiating the film for protective film formation with energy rays (namely, the protective film) has a Young's modulus of at least 500 MPa and an elongation at break of at least 8%. In other words, another aspect of the film for protective film formation according to the present invention contains the energy ray-curable compound (B), and has the properties described below:

when a cured product (protective film) is formed by curing the film for protective film formation by irradiation with energy rays, the cured product has a Young's modulus of at least 500 MPa and an elongation at break of at least 8%.

Ensuring that the cured product, namely the protective film, has a Young's modulus and an elongation at break that are at least as large as the above respective lower limits enables the protective film to exhibit a satisfactorily high protective action relative to the semiconductor wafer or semiconductor chip. For example, when a semiconductor wafer provided with the film for protective film formation or the protective film on the back surface undergoes dicing, the occurrence of cracking and chipping, such as the so-called chipping that can occur around the outer periphery of the semiconductor chips, is suppressed in the semiconductor chips that are finally obtained. Further, by ensuring that the Young's modulus and the elongation at break are at least as large as the above respective lower limits, the protective film is able to maintain the type of superior protective action described above even when exposed to large temperature variations, and has excellent reliability. For example, a semiconductor chip with a protective film is exposed to large temperature variations during mounting of the chip, but the protective

film described above can maintain a superior protective action even under these types of conditions.

In this manner, the film for protective film formation according to the present invention enables the formation of a protective film having a superior protective action and excellent reliability even by irradiation with energy rays.

[0015]

The film for protective film formation contains the energy ray-curable compound (B), and therefore cures upon irradiation with energy rays to form a protective film.

In this description, the term "energy rays" means rays among electromagnetic waves and charged particle beams that have an energy quantum, and specific examples include ultraviolet rays and electron beams.

Ultraviolet rays can be irradiated using a high-pressure mercury lamp, a fusion H lamp, a xenon lamp, or an LED or the like as an ultraviolet source. Electron beams can be generated and irradiated from an electron beam accelerator or the like.

The energy ray irradiation dose varies depending on the type of energy rays, but for example in the case of ultraviolet rays, the illuminance is preferably from 50 to 500 mW/cm², and the irradiation dose is preferably from 200 to 800 mJ/cm².

[0016]

The film for protective film formation can be formed using a composition for protective film formation that contains the components that constitute the film for protective film formation, and for example, can be formed by applying the composition for protective film formation to the surface of a support, and then drying the composition. The ratio between the amounts of those components in the composition for protective film formation that do not volatilize at normal temperature is typically the same as the ratio between the amounts of those components in the film for protective film formation.

In this description, "normal temperature" means a temperature at which no particular cooling or heating is performed, namely ordinary room temperature, and for example, is typically a temperature of 15 to 25°C.

[0017]

There are no particular limitations on the support, provided it is able to maintain the shape of the film for protective film formation, and for example, a support that is used only for formation of the film for protective film formation may be used, or a support may be used which, following use in the formation of the film for protective film formation, remains in a stacked state on the film for protective film formation, and is used for another targeted application. Examples of supports that are used only for formation of the film for protective film formation include release films and the like having a release-treated surface. Examples of supports which, following formation of the film for protective film formation, are used for another application include support sheets and substrates such as the dicing sheet described below.

[0018]

Although there are no particular limitations on the thickness of the film for protective film formation, the thickness is preferably from 1 to 100 μm , more preferably from 5 to 75 μm , and particularly preferably from 5 to 50 μm . By ensuring that the thickness of the film for protective film formation is at least as large as the above lower limit, the adhesive strength relative to the semiconductor wafer or semiconductor chip that acts as the adherend can be increased. Further, by ensuring that the thickness of the film for protective film formation is not more than the above upper limit, a shearing force can be used to more easily cut the protective film that represents the cured product when semiconductor chip pickup is performed.

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

[0019]

<Composition for Protective Film Formation>

The composition for protective film formation contains the energy ray-curable compound (B), preferably contains, for example, a polymer component (A) and the energy ray-curable compound (B), and more preferably contains, for example, the polymer component (A), the energy ray-curable compound (B), and a photopolymerization initiator (C).

Each of the components of the aforementioned composition for protective film formation and film for protective film formation is described below.

[0020]

[Polymer Component (A)]

The polymer component (A) is a component that is considered to have been formed by a polymerization reaction of a polymerizable compound, and is a polymer compound that imparts film formability and flexibility and the like to the film for protective film formation. In this description, the term "polymerization reaction" includes polycondensation reactions.

In those cases where the components within the composition for protective film formation include a component that corresponds with both the polymer component (A) and the energy ray-curable compound (B), that component is treated as the energy ray-curable compound (B). Examples of this type of component include acrylic polymers having a hydroxyl group, and having a polymerizable group bonded via a urethane linkage as a side chain.

A single type of the polymer component (A) may be used alone, or a combination of two or more types may be used.

[0021]

Examples of the polymer component (A) include acrylic-based resins, polyesters, polyurethanes, acrylic urethane resins, silicone resins, rubber-based polymers and phenoxy resins, and acrylic-based resins are preferred.

[0022]

Conventional acrylic polymers may be used as the above acrylic-based resins.

The weight average molecular weight (M_w) of the acrylic-based resin is preferably from 10,000 to 2,000,000, and more preferably from 100,000 to 1,500,000. Provided the weight average molecular weight of the acrylic-based resin is at least as large as the above lower limit, the adhesive strength between the support sheet described below and the protective film is suppressed, thus improving the pickup characteristics of the semiconductor chips with a protective film. Further, provided the weight average molecular weight of the acrylic-based resin is not more than the above upper limit, the film for protective film formation can more easily conform to any uneven surfaces on the adherend (semiconductor wafer, semiconductor chip), thus suppressing the occurrence of voids or the like between the adherend and the film for protective film formation.

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

[0023]

The glass transition temperature (T_g) of the acrylic-based resin is preferably from -60 to 70°C, and more preferably from -30 to 50°C. By ensuring that the T_g of the acrylic-based resin is at least as large as the above lower limit, the adhesive strength

between the support sheet and the protective film is suppressed, thus further improving the pickup characteristics of the semiconductor chips with a protective film. Further, by ensuring that the T_g of the acrylic-based resin is not more than the above upper limit, the adhesive strength between the adherend and the film for protective film formation can be increased.

[0024]

Examples of the monomer that constitutes the acrylic-based resin include alkyl (meth)acrylate esters in which the alkyl group that constitutes the alkyl ester is a chain-like group of 1 to 18 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (also called lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (also called myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (also called palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (also called stearyl (meth)acrylate);

(meth)acrylate esters having a cyclic backbone, such as cycloalkyl (meth)acrylates, benzyl (meth)acrylate, isobornyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, and (meth)acrylic acid imide;

hydroxyl group-containing (meth)acrylate esters such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, and 2-hydroxypropyl (meth)acrylate; and glycidyl group-containing (meth)acrylate esters such as glycidyl (meth)acrylate.

Among the above compounds, examples of preferred monomers for forming the acrylic-based resin include methyl (meth)acrylate, butyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, and glycidyl (meth)acrylate.

[0025]

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

[0026]

Examples of other monomers for forming the acrylic-based resin include monomers other than (meth)acrylate esters, such as (meth)acrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene, and N-methylolacrylamide.

[0027]

The monomer for forming the acrylic-based resin may be composed of a single monomer or two or more monomers.

[0028]

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

[0029]

In those cases where the composition for protective film formation contains an acrylic-based resin as the polymer component (A), the amount of the acrylic-based resin in the composition for protective film formation is preferably from 5 to 50% by mass, and more preferably from 10 to 45% by mass, relative to the total mass of all of the components besides the solvent within the composition for protective film formation. By ensuring that the amount of the acrylic-based resin falls within this type of range, the adhesive strength between the support sheet and the protective film is suppressed, thus further improving the pickup characteristics of the semiconductor chips with a protective film.

When the film for protective film formation contains an acrylic-based resin as the polymer component (A), the amount of the acrylic-based resin in the film for protective film formation is preferably from 5 to 50% by mass, and more preferably from 10 to 45% by mass, relative to the total mass of the film for protective film formation.

[0030]

In the present invention, in terms of improving the pickup characteristics of the semiconductor chips with a protective film by reducing the adhesive strength (peel strength) between the support sheet and the protective film, and suppressing the occurrence of voids and the like between the adherend and the film for protective film formation by making the film for protective film formation conform more easily to uneven surfaces on the adherend, a thermoplastic resin other than an acrylic-based resin (hereafter sometimes abbreviated as simply "the thermoplastic resin") may be either used alone, or used in combination with an acrylic-based resin, as the polymer component (A).

[0031]

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

[0032]

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

[0033]

Examples of the thermoplastic resin include polyester, polyurethane, phenoxy resins, polybutene, polybutadiene and polystyrene.

[0034]

Either a single resin or a combination of two or more resins may be used as the thermoplastic resin.

[0035]

[Energy Ray-Curable Compound (B)]

The energy ray-curable compound (B) is a component that can be cured (polymerized) by irradiation with energy rays. Further, the energy ray-curable compound (B) is a component used for curing the film for protective film formation to form a hard protective film (namely, a cured product obtained by irradiating the film for protective film formation with energy rays), and may be either a monomer or an oligomer.

A single type of the energy ray-curable compound (B) may be used alone, or a combination of two or more types may be used.

The amount of the energy ray-curable compound (B) in the composition for protective film formation is preferably from 3 to 30% by mass, and more preferably from 5 to 25% by mass, relative to the total mass of all the components besides the solvent in the composition for protective film formation.

The amount of the energy ray-curable compound (B) within the film for protective film formation is preferably from 3 to 30% by mass, and more preferably from 5 to 25% by mass, relative to the total mass of the film for protective film formation.

[0036]

Examples of the energy ray-curable compound (B) include compounds having one, or two or more, energy ray-polymerizable groups within a single molecule.

There are no particular limitations on the energy ray-polymerizable group, provided it is a group that undergoes a polymerization reaction upon irradiation with energy rays, and in those cases where the energy ray-curable compound (B) has two or more energy ray-polymerizable groups, these energy ray-polymerizable groups may be the same or different. In other words, the two or more energy ray-polymerizable groups in a single molecule of the energy ray-curable compound (B) may be all the same, all mutually different, or partially the same.

Examples of the energy ray-polymerizable group include a vinyl group and (meth)acryloyl group, and a (meth)acryloyl group is preferred.

[0037]

The energy ray-curable compound (B) preferably includes a polyfunctional compound in which the number of energy ray-polymerizable groups in a single molecule is two or more. The amount of this polyfunctional compound within the composition for protective film formation and the film for protective film formation, relative to the total mass of the energy ray-curable compound (B), is preferably at least 90% by mass but not more than 100% by mass, more preferably at least 95% by mass but not more than 100% by mass, even more preferably at least 98% by mass but not more than 100% by mass, and may be 100% by mass, namely the energy ray-curable compound (B) contained in

the composition for protective film formation and the film for protective film formation may be composed entirely of the polyfunctional compound.

[0038]

The molecular weight of the energy ray-curable compound (B) is preferably not more than 1,000, more preferably from 100 to 1,000, even more preferably from 150 to 800, and particularly preferably from 200 to 550. Ensuring that the molecular weight of the energy ray-curable compound (B) satisfies this type of range further enhances the protective action and the reliability of the formed protective film.

[0039]

The energy ray-curable compound (B) is preferably a (meth)acrylate compound, is more preferably a polyfunctional (meth)acrylate compound having two or more energy ray-polymerizable groups in a single molecule, and is particularly preferably a polyfunctional (meth)acrylate compound having two or more (meth)acryloyl groups in a single molecule. Here, "(meth)acrylate compound" means a (meth)acrylate ester or a derivative thereof. Moreover, in this description, the term "derivative" means a compound in which at least one hydrogen atom of the original compound has been substituted with a group (substituent) other than a hydrogen atom.

[0040]

Examples of the polyfunctional (meth)acrylate compound having two or more (meth)acryloyl groups include difunctional (meth)acrylate compounds such as 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, neopentyl glycol adipate di(meth)acrylate, neopentyl glycol hydroxypivalate di(meth)acrylate, dicyclopentanyl di(meth)acrylate (also known as tricyclodecane dimethylol diacrylate), caprolactone-modified dicyclopentenyl di(meth)acrylate, ethylene oxide-modified phosphoric acid

di(meth)acrylate, di(acryloxyethyl) isocyanurate, and allylated cyclohexyl

di(meth)acrylate;

trifunctional (meth)acrylate compounds such as trimethylolpropane tri(meth)acrylate, dipentaerythritol tri(meth)acrylate, propionic acid-modified dipentaerythritol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, propylene oxide-modified trimethylolpropane tri(meth)acrylate, tris(acryloxyethyl) isocyanurate, bis(acryloxyethyl)hydroxyethyl isocyanurate, isocyanuric acid ethylene oxide-modified diacrylate, isocyanuric acid ethylene oxide-modified triacrylate, and ϵ -caprolactone-modified tris(acryloxyethyl) isocyanurate;

tetrafunctional (meth)acrylate compounds such as diglycerol tetra(meth)acrylate and pentaerythritol tetra(meth)acrylate;

pentafunctional (meth)acrylate compounds such as dipentaerythritol penta(meth)acrylate and propionic acid-modified dipentaerythritol penta(meth)acrylate; and

hexafunctional (meth)acrylate compounds such as dipentaerythritol hexa(meth)acrylate and caprolactone-modified dipentaerythritol hexa(meth)acrylate.

Among the above compounds, tricyclodecane dimethylol diacrylate and ϵ -caprolactone-modified tris(acryloxyethyl) isocyanurate are particularly preferred.

[0041]

In the energy ray-curable compound (B), the number of energy ray-polymerizable groups in a single molecule is preferably from 2 to 4, and is more preferably 2 or 3. Using this type of energy ray-curable compound (B) further enhances the protective action and reliability of the formed protective film. In this description, among the various forms of the energy ray-curable compound (B), compounds having 2 to 4 energy ray-polymerizable groups within a single molecule are sometimes referred to using the

collective term "the energy ray-curable compound (B1)", and compounds having 5 or more energy ray-polymerizable groups within a single molecule are sometimes referred to using the collective term "the energy ray-curable compound (B2)".

The energy ray-curable compound (B1) preferably has 2 or 3 energy ray-polymerizable groups within a single molecule, and specific examples include tricyclodecane dimethylol diacrylate and ϵ -caprolactone-modified tris(acryloxyethyl) isocyanurate.

[0042]

In the composition for protective film formation and the film for protective film formation, the amount of an energy ray-curable compound (B) having 2 to 4 energy ray-polymerizable groups within a single molecule (namely, the energy ray-curable compound (B1)), relative to the total mass of the energy ray-curable compound (B), is preferably at least 90% by mass but not more than 100% by mass, more preferably at least 95% by mass but not more than 100% by mass, particularly preferably at least 98% by mass but not more than 100% by mass, and may be 100% by mass, namely the energy ray-curable compound (B) contained in the composition for protective film formation and the film for protective film formation may be composed entirely of the energy ray-curable compound (B1).

[0043]

In the composition for protective film formation and the film for protective film formation, the amount of an energy ray-curable compound (B) having 2 or 3 energy ray-polymerizable groups within a single molecule, relative to the total mass of the energy ray-curable compound (B), is preferably at least 80% by mass but not more than 100% by mass, more preferably at least 85% by mass but not more than 100% by mass, even more preferably at least 90% by mass but not more than 100% by mass, particularly

preferably at least 95% by mass but not more than 100% by mass, and may be 100% by mass, namely the energy ray-curable compound (B) contained in the composition for protective film formation and the film for protective film formation may be composed entirely of an energy ray-curable compound having 2 or 3 energy ray-polymerizable groups within a single molecule.

[0044]

The amount of the energy ray-curable compound (B) in the composition for protective film formation and the film for protective film formation, when the amount of the polymer component (A) is deemed to be 100 parts by mass, is preferably within a range from 1 to 150 parts by mass, more preferably from 5 to 130 parts by mass, and particularly preferably from 10 to 110 parts by mass. By ensuring that the amount of the energy ray-curable compound (B) is at least as large as the above lower limit, the formed protective film can maintain a superior protective action even if exposed to large temperature variations, and the reliability improves. Further, by ensuring that the amount of the energy ray-curable compound (B) is not more than the above upper limit, the adhesive strength between the support sheet and the protective film is suppressed, thereby further improving the pickup characteristics of the semiconductor chips with a protective film.

[0045]

[Photopolymerization Initiator (C)]

The photopolymerization initiator (C) is a component that generates radicals upon irradiation with energy rays, and is used for initiating the curing reaction of the energy ray-curable compound (B) via a radical polymerization.

The photopolymerization initiator (C) may be a conventional initiator, and specific examples include α -ketol-based compounds such as 4-(2-hydroxyethoxy)phenyl

(2-hydroxy-2-propyl) ketone, α -hydroxy- α,α' -dimethylacetophenone, 2-methyl-2-hydroxypropiophenone, 1-hydroxycyclohexyl phenyl ketone, and 2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]phenyl]-2-methyl-propan-1-one; acetophenone-based compounds such as acetophenone, dimethylaminoacetophenone, methoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxyacetophenone, 2,2-diethoxy-2-phenylacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1; benzoin ether-based compounds such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin n-butyl ether, benzoin isobutyl ether, and anisoin methyl ether; ketal-based compounds such as benzyl dimethyl ketal and acetophenone dimethyl ketal; aromatic sulfonyl chloride-based compounds such as 2-naphthalenesulfonyl chloride; optically active oxime-based compounds such as 1-phenone-1,1-propanedione-2-(O-ethoxycarbonyl)oxime, and ethanone,1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-,1-(O-acetyloxime); benzophenone-based compounds such as benzophenone, p-phenylbenzophenone, benzoyl benzoate, dichlorobenzophenone, 4,4'-diethylaminobenzophenone, and 3,3'-dimethyl-4-methoxybenzophenone; anthraquinone-based compounds such as 2-methylantraquinone, 2-ethylantraquinone, 2-tert-butylantraquinone, and 2-aminoanthraquinone; thioxanthone-based compounds such as thioxanthone, 2-chlorothioxanthone, 2-methylthioxanthone, 2-ethylthioxanthone, isopropylthioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2,4-dichlorothioxanthone, 2,4-diethylthioxanthone, and 2,4-diisopropylthioxanthone; as well as p-dimethylaminobenzoic acid esters, camphorquinone, halogenated ketones, acyl

phosphine oxides such as diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, acyl phosphonates, and oligo[2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone].

Among the above compounds, ethanone,1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-,1-(O-acetyloxime) and the like are preferred.

[0046]

The amount of the photopolymerization initiator (C) in the composition for protective film formation, when the amount of the polymer component (A) is deemed to be 100 parts by mass, is preferably within a range from 0.01 to 10 parts by mass, more preferably from 0.1 to 7 parts by mass, and particularly preferably from 0.2 to 5 parts by mass. Ensuring that the amount of the photopolymerization initiator (C) is at least as large as the above lower limit enables the curing reaction of the energy ray-curable compound (B) to proceed more efficiently. Further, ensuring that the amount of the photopolymerization initiator (C) is not more than the above upper limit further enhances the protective action and the reliability of the formed protective film.

Further, the amount of the photopolymerization initiator (C) in the composition for protective film formation, relative to the total mass of the composition for protective film formation or the film for protective film formation, is preferably from 0.1 to 3% by mass.

[0047]

[Filler (D)]

The composition for protective film formation and the film for protective film formation may also contain a filler (D). By including the filler (D), the coefficient of thermal expansion of the film for protective film formation can be more easily adjusted. Accordingly, by ensuring that the coefficient of thermal expansion of the protective film

formed following curing of the film for protective film formation is optimized for the semiconductor chip, the package reliability can be improved.

Further, by using a composition for protective film formation containing the filler (D), the coefficient of moisture absorption for the cured protective film can be reduced, and the thermal conductivity of the cured protective film can be improved.

[0048]

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

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

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

[0049]

A single type of the filler (D) may be used alone, or a combination of two or more types may be used.

[0050]

In those cases where the filler (D) is used, the amount of the filler (D) relative to the total mass of all the components besides the solvent in the composition for protective film formation (namely, the amount of the filler (D) relative to the total mass of the film for protective film formation) is preferably from 5 to 80% by mass, and more preferably from 7 to 65% by mass. Ensuring that the amount of the filler (D) is at least as large as the above lower limit enables the effects of using the filler (D) to manifest more markedly. Further, ensuring that the amount of the filler (D) is not more than the above

upper limit further enhances the protective action and the reliability of the formed protective film.

[0051]

[Colorant (E)]

The composition for protective film formation and the film for protective film formation may also contain a colorant (E).

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

[0052]

Examples of the organic pigments and organic dyes include aminium-based colorants, cyanine-based colorants, merocyanine-based colorants, croconium-based colorants, squalium-based colorants, azulenium-based colorants, polymethine-based colorants, naphthoquinone-based colorants, pyrylium-based colorants, phthalocyanine-based colorants, naphthalocyanine-based colorants, naphtholactam-based colorants, azo-based colorants, condensed azo-based colorants, indigo-based colorants, perinone-based colorants, perylene-based colorants, dioxazine-based colorants, quinacridone-based colorants, isoindolinone-based colorants, quinophthalone-based colorants, pyrrole-based colorants, thioindigo-based colorants, metal complex-based colorants (metal complex dyes), dithiol metal complex-based colorants, indole phenol-based colorants, triarylmethane-based colorants, anthraquinone-based colorants, dioxazine-based colorants, naphthol-based colorants, azomethine-based colorants, benzimidazolone-based colorants, pyranthrone-based colorants, and threne-based colorants.

[0053]

Examples of the inorganic pigments include carbon blacks, cobalt-based colorants, iron-based colorants, chromium-based colorants, titanium-based colorants,

vanadium-based colorants, zirconium-based colorants, molybdenum-based colorants, ruthenium-based colorants, platinum-based colorants, ITO (indium tin oxide)-based colorants, and ATO (antimony tin oxide)-based colorants.

Among the above colorants, phthalocyanine-based colorants, isoindolinone-based colorants, and anthraquinone-based colorants and the like are preferred.

[0054]

A single type of the colorant (E) may be used alone, or a combination of two or more types may be used.

[0055]

In those cases where the colorant (E) is used, the amount of the colorant (E) in the film for protective film formation is preferably adjusted appropriately in accordance with the intended purpose of the film. For example, the protective film may sometimes be subjected to printing by laser irradiation, and by adjusting the amount of the colorant (E) in the film for protective film formation to adjust the light transmittance of the protective film, the legibility of the printing can be adjusted. In this case, the amount of the colorant (E) relative to the total mass of all the components besides the solvent in the composition for protective film formation (namely, the amount of the colorant (E) relative to the total mass of the film for protective film formation) is preferably within a range from 0.1 to 10% by mass, more preferably from 0.4 to 7.5% by mass, and particularly preferably from 0.8 to 5% by mass. Ensuring that the amount of the colorant (E) is at least as large as the above lower limit enables the effects of using the colorant (E) to manifest more markedly. Further, ensuring that the amount of the colorant (E) is not more than the above upper limit suppresses excessive use of the colorant (E).

[0056]

[Coupling Agent (F)]

The composition for protective film formation and the film for protective film formation may also contain a coupling agent (F). By including a compound having a functional group capable of reacting with inorganic compounds or organic compounds as a coupling agent (F) in the film for protective film formation, the adhesiveness and adhesion to the adherend can be improved. Further, the protective film formed from a film for protective film formation containing the coupling agent (F) exhibits improved water resistance without losing any heat resistance.

[0057]

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

Examples of preferred silane coupling agents include 3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxymethyldiethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-(2-aminoethylamino)propyltrimethoxysilane, 3-(2-aminoethylamino)propylmethyldiethoxysilane, 3-(phenylamino)propyltrimethoxysilane, (3-ureidopropyl)triethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfane, methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, vinyltriacetoxysilane and imidazole silane.

Among the above compounds, 3-methacryloxypropyltrimethoxysilane and the like are preferred.

[0058]

A single type of the coupling agent (F) may be used alone, or a combination of two or more types may be used.

[0059]

In those cases where the coupling agent (F) is used, the amount of the coupling agent (F) in the composition for protective film formation and the film for protective film formation, when the combined amount of the polymer component (A) and the energy ray-curable compound (B) is deemed to be 100 parts by mass, is preferably within a range from 0.03 to 20 parts by mass, more preferably from 0.05 to 10 parts by mass, and particularly preferably from 0.1 to 5 parts by mass. Ensuring that the amount of the coupling agent (F) is at least as large as the above lower limit enables the effects of using the coupling agent (F) to manifest more markedly. Further, ensuring that the amount of the coupling agent (F) is not more than the above upper limit better suppresses the generation of out gas.

[0060]

[Crosslinking Agent (G)]

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

[0061]

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

[0062]

Examples of the organic polyvalent isocyanate compounds include aromatic polyvalent isocyanate compounds, aliphatic polyvalent isocyanate compounds, alicyclic polyvalent isocyanate compounds, as well as trimers, isocyanurates and adducts of these compounds (such as reaction products with low-molecular weight active hydrogen-containing compounds such as ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane or castor oil, for example, a xylylene diisocyanate adduct of trimethylolpropane), and isocyanate-terminated urethane prepolymers obtained by reacting an organic polyvalent isocyanate compound and a polyol compound.

[0063]

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

[0064]

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

Among the above compounds, 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate are preferred as the crosslinking agent (G).

[0065]

In those cases where an isocyanate-based crosslinking agent is used as the crosslinking agent (G), a hydroxyl group-containing polymer is preferably used as the acrylic-based resin of the polymer component (A). When the crosslinking agent (G) has isocyanate groups and the acrylic-based resin has hydroxyl groups, reaction between the crosslinking agent (G) and the acrylic-based resin can easily introduce crosslinked structures into the film for protective film formation.

[0066]

In those cases where the crosslinking agent (G) is used, the amount of the crosslinking agent (G) within the composition for protective film formation or the film for protective film formation, when the amount of the polymer component (A) is deemed to be 100 parts by mass, is preferably from 0.01 to 20 parts by mass, more preferably from 0.1 to 10 parts by mass, and particularly preferably from 0.5 to 5 parts by mass.

[0067]

[General-Purpose Additives (H)]

The composition for protective film formation and the film for protective film formation may also contain general-purpose additives (H) besides the components described above.

Examples of the general-purpose additives (H) include conventional plasticizers, antistatic agents, antioxidants, gettering agents, and sensitizers.

[0068]

[Solvent]

Because the handling of the composition for protective film formation improves upon dilution, the composition preferably also contains a solvent.

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

The solvent contained in the composition for protective film formation may be a single solvent or two or more solvents.

[0069]

In those cases where the composition for protective film formation contains a solvent, the amount of the solvent is preferably adjusted so that the solid fraction concentration of the composition is from 35 to 75% by mass relative to the total mass of the composition.

[0070]

The composition for protective film formation can be obtained by blending together the aforementioned components that constitute the composition.

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

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

[0071]

There are no particular limitations on the method used for mixing the components during blending, and a method may be selected from among conventional methods such

as methods in which mixing is performed by rotation with a stirring bar or stirring blade, methods in which mixing is performed using a mixer, and methods in which mixing is performed by application of ultrasound.

[0072]

As described above, the film for protective film formation according to the present invention can be formed, for example, by applying the composition for protective film formation to the surface of a support, and then drying the composition.

[0073]

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

[0074]

When drying the composition for protective film formation, the drying temperature is preferably within a range from 80 to 130°C, and the drying time is preferably from 10 seconds to 10 minutes.

[0075]

The protective film formed by curing the film for protective film formation according to the present invention by irradiation with energy rays has a Young's modulus of at least 500 MPa and an elongation at break of at least 8%.

The Young's modulus of the protective film can be adjusted by altering the various components contained in the film for protective film formation, such as the energy ray-curable compound (B), and is preferably adjusted to a value of at least 550

MPa, and can also be adjusted to a value of at least 1,000 MPa, at least 1,400 MPa, or at least 1,800 MPa or the like.

On the other hand, although there are no particular limitations on the upper limit for the Young's modulus of the protective film, from the viewpoints of the dicing properties and the package reliability, the Young's modulus is preferably not more than 10,000 MPa, and is more preferably 5,000 MPa or less.

In other words, the Young's modulus of the protective film is typically at least 500 MPa but not more than 10,000 MPa, and is preferably at least 550 MPa but not more than 5,000 MPa, more preferably at least 1,000 MPa but not more than 5,000 MPa, even more preferably at least 1,400 MPa but not more than 5,000 MPa, and particularly preferably at least 1,800 MPa but not more than 5,000 MPa.

[0076]

In this description, the "Young's modulus" means the value determined from the slope of the stress-strain curve at the start of a test (tensile test) in which a test piece is pulled at a tensile speed of 200 mm/minute. The Young's modulus can be measured at the same time as measurement of the "elongation at break" described below.

[0077]

The elongation at break of the protective film can be adjusted by altering the various components contained in the film for protective film formation, such as the energy ray-curable compound (B), and is preferably adjusted to a value of at least 10%, and can also be adjusted to a value that is, for example, at least 15%, at least 20%, at least 30%, at least 40%, or 50% or higher.

On the other hand, although there are no particular limitations on the upper limit for the elongation at break of the protective film, from the viewpoint of achieving

favorable cleavage properties during dicing, the upper limit for the elongation at break is preferably 100%.

In other words, the elongation at break of the protective film is typically at least 8% but not more than 100%, and may be at least 10% but not more than 100%, at least 15% but not more than 100%, at least 20% but not more than 100%, at least 30% but not more than 100%, at least 40% but not more than 100%, or at least 50% but not more than 100%, and a value of 100% is particularly desirable.

[0078]

In this invention, either the tensile strain at break in the case where the test piece has no yield point, or the tensile break induced strain in the case where the test piece has a yield point, determined in accordance with JIS K7161:1999 and JIS K7127:1999, is deemed to represent the "elongation at break".

The elongation at break is determined using a test piece having a width of 15 mm and a length of 140 mm, by measuring the amount of elongation in the test piece when the test piece is pulled at a tensile speed of 200 mm/minute with the distance between the chucks holding the test piece set to 100 mm, and then using the measured value to determine the elongation at break.

Another aspect of the film for protective film formation according to the present invention is a film for protective film formation which, upon irradiation with energy rays, forms a protective film having a Young's modulus of at least 590 MPa but not more than 1,960 MPa, and having an elongation at break of at least 10.7% but not more than 56.0%.

[0079]

<<Composite Sheet for Protective Film Formation>>

The composite sheet for protective film formation according to the present invention has the film for protective film formation according to the present invention described above provided on one surface of a support sheet.

The composite sheet for protective film formation is used for forming a protective film on the back surface of a semiconductor wafer or a semiconductor chip.

[0080]

Examples of the support sheet include supports composed solely of a substrate, and supports having one or more other layers stacked on a substrate.

The composite sheet for protective film formation according to the present invention is described below in further detail.

[0081]

FIG. 1 is a cross-sectional view schematically illustrating one embodiment of the composite sheet for protective film formation according to the present invention. The drawings used in the following description may be drawn with specific portions enlarged as appropriate to facilitate comprehension of the features of the present invention, and the dimensional ratios and the like between the constituent elements may differ from the actual values.

[0082]

The composite sheet for protective film formation 1A illustrated in the figure is prepared by providing an adhesive layer 12 on a substrate 11, and providing a film for protective film formation 13 on the adhesive layer 12. A support sheet 10 is a laminated product of the substrate 11 and the adhesive layer 12, meaning that in other words, the composite sheet for protective film formation 1A has the film for protective film formation 13 formed on one surface 10a of the support sheet 10. Further, the composite sheet for protective film formation 1A also has a release film 15 provided on top of the

film for protective film formation 13. The film for protective film formation 13 is the film for protective film formation according to the present invention described above.

[0083]

In the composite sheet for protective film formation 1A, the adhesive layer 12 is stacked on one surface 11a of the substrate 11, the film for protective film formation 13 is stacked across the entire surface of a surface 12a of the adhesive layer 12 (namely, the surface of the adhesive layer 12 on the opposite side from the surface that contacts the substrate 11), a jig adhesive layer 16 is stacked on a portion of a surface 13a of the film for protective film formation 13 (namely, the surface of the film for protective film formation 13 on the opposite side from the surface that contacts the adhesive layer 12), and the release film 15 is stacked on the portion of the surface 13a of the film for protective film formation 13 on which the jig adhesive layer 16 has not been formed, and on a surface 16a of the jig adhesive layer 16 (namely, an upper surface: the surface of the jig adhesive layer 16 on the opposite side from the surface that contacts the film for protective film formation 13, and a side surface: the side surface of the jig adhesive layer 16 positioned on the central side of the composite sheet for protective film formation 1A).

[0084]

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

[0085]

The composite sheet for protective film formation 1A illustrated in FIG. 1 is used in a state where the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to the surface 13a of the film for

protective film formation 13, and affixing the upper surface of the surface 16a of the jig adhesive layer 16 to a jig such as a ring frame.

[0086]

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

[0087]

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

[0088]

The composite sheet for protective film formation 1B illustrated in FIG. 2 is used in a state where the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to a region in the central portion of the

surface 13a of the film for protective film formation 13, and affixing a region near the periphery of the film for protective film formation 13 to a jig such as a ring frame.

[0089]

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

With the exception of not having the adhesive layer 12, the composite sheet for protective film formation 1C illustrated in FIG. 3 is the same as the composite sheet for protective film formation 1A illustrated in FIG. 1. In other words, in the composite sheet for protective film formation 1C, the support sheet is composed of only the substrate 11. The film for protective film formation 13 is stacked on the surface 11a of the substrate 11, the jig adhesive layer 16 is stacked on a portion of the surface 13a of the film for protective film formation 13 (namely, the surface of the film for protective film formation 13 on the opposite side from the surface that contacts the substrate 11), and the release film 15 is stacked on the portion of the surface 13a of the film for protective film formation 13 on which the jig adhesive layer 16 has not been formed, and on the surface 16a of the jig adhesive layer 16 (namely, the upper surface: the surface of the jig adhesive layer 16 on the opposite side from the surface that contacts the film for protective film formation 13, and the side surface: the side surface of the jig adhesive layer 16 positioned on the central side of the composite sheet for protective film formation 1C). The film for protective film formation 13 is the film for protective film formation according to the present invention described above.

[0090]

The composite sheet for protective film formation 1C is used in a similar manner to the composite sheet for protective film formation 1A, in a state where the release film

15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to the surface 13a of the film for protective film formation 13, and affixing the upper surface of the surface 16a of the jig adhesive layer 16 to a jig such as a ring frame.

[0091]

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

With the exception of not having the jig adhesive layer 16, the composite sheet for protective film formation 1D illustrated in FIG. 4 is the same as the composite sheet for protective film formation 1C illustrated in FIG. 3. In other words, in the composite sheet for protective film formation 1D, the film for protective film formation 13 is stacked on one surface 11a of the substrate 11, and the release film 15 is stacked across the entire surface of the surface 13a of the film for protective film formation 13 (namely, the surface of the film for protective film formation 13 on the opposite side from the surface that contacts the substrate 11). The film for protective film formation 13 is the film for protective film formation according to the present invention described above.

[0092]

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

[0093]

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

With the exception that the shape of the film for protective film formation differs, the composite sheet for protective film formation 1E illustrated in FIG. 5 is the same as the composite sheet for protective film formation 1A illustrated in FIG. 1. In other words, the composite sheet for protective film formation 1E has the adhesive layer 12 provided on the substrate 11, and a film for protective film formation 23 provided on the adhesive layer 12. The support sheet 10 is a laminated product of the substrate 11 and the adhesive layer 12, meaning that in other words, the composite sheet for protective film formation 1E has a stacked structure in which the film for protective film formation 23 is formed on one surface 10a of the support sheet 10 (namely, the surface on the side of the adhesive layer 12). Further, the composite sheet for protective film formation 1E also has a release film 15 provided on top of the film for protective film formation 23. The film for protective film formation 23 is the film for protective film formation according to the present invention described above, and with the exception of having a different shape, is the same as the film for protective film formation 13.

[0094]

In the composite sheet for protective film formation 1E, the adhesive layer 12 is stacked on one surface 11a of the substrate 11, and the film for protective film formation 23 is stacked on a portion of the surface 12a of the adhesive layer 12 (namely, the surface on the opposite side from the surface that contacts the substrate 11a). The release film 15 is stacked on the portion of the surface 12a of the adhesive layer 12 on which the film for protective film formation 23 has not been formed, and on a surface 23a of the film for protective film formation 23 (including an upper surface and a side surface: namely, the

surfaces of the film for protective film formation 23 that do not contact the adhesive layer 12).

[0095]

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

[0096]

The composite sheet for protective film formation 1E illustrated in FIG. 5 is used in a state where the release film 15 has been removed, by affixing the back surface of a semiconductor wafer (not shown in the figure) to the surface 23a of the film for protective film formation 23, and affixing the portion of the surface 12a of the adhesive layer 12 where the film for protective film formation 23 has not been formed to a jig such as a ring frame.

[0097]

The composite sheet for protective film formation according to the present invention is not limited to the configurations illustrated in FIGS. 1 to 5, and configurations in which a portion of one of the configurations illustrated in one of FIGS. 1 to 5 has been altered or eliminated, and configurations having an additional structure to those described above, may also be used, provided they do not impair the effects of the present invention.

For example, in the composite sheets for protective film formation illustrated in FIG. 3 and FIG. 4, an intermediate layer may be provided between the substrate 11 and the film for protective film formation 13 or film for protective film formation 23.

Any arbitrary layer may be selected as this intermediate layer in accordance with the intended purpose.

Further, in the composite sheets for protective film formation illustrated in FIG. 1, FIG. 2 and FIG. 5, an intermediate layer may be provided between the substrate 11 and the adhesive layer 12. In other words, in the composite sheet for protective film formation according to the present invention, the support sheet may be composed of a substrate, an intermediate layer and an adhesive layer stacked in that order. This intermediate layer may be the same as the intermediate layer provided in the composite sheet for protective film formation illustrated in FIG. 3 and FIG. 4.

Furthermore, the composite sheets for protective film formation illustrated in FIGS. 1 to 5 may also include a layer other than the above intermediate layer in any arbitrary location.

Next is a more detailed description of the members other than the film for protective film formation that constitute the composite sheet for protective film formation.

[0098]

<Substrate>

The material for the substrate is preferably any of various resins, and specific examples include polyethylene (including low-density polyethylene (sometimes abbreviated as LDPE), linear low-density polyethylene (sometimes abbreviated as LLDPE) and high-density polyethylene (sometimes abbreviated as HDPE)), polypropylene, ethylene/propylene copolymers, polybutene, polybutadiene, polymethylpentene, polyvinyl chloride films, vinyl chloride copolymers, polyethylene terephthalate, polyethylene naphthalate, polybutylene terephthalate, polyurethane, polyurethane acrylate, polyimide, ethylene/vinyl acetate copolymers, ionomer resins, ethylene/(meth)acrylic acid copolymers, ethylene/(meth)acrylate ester copolymers,

polystyrene, polycarbonate, fluororesins, and hydrogenated products, modified products, crosslinked products and copolymers of any of these resins.

[0099]

The thickness of the substrate may be selected in accordance with the intended purpose, but is preferably from 50 to 300 μm , and more preferably from 60 to 100 μm . By ensuring that the thickness of the substrate falls within this type of range, the flexibility of the composite sheet for protective film formation and the fixability to a semiconductor wafer or semiconductor chip can be improved.

[0100]

The substrate may be composed of one layer (a single layer), or may be composed of a plurality of two or more layers (for example, 2 to 4 layers). In those cases where the substrate is composed of a plurality of layers, these layers may be the same or different. In other words, all of the layers may be the same, all of the layers may be mutually different, or only a portion of the layers may be the same. In those cases where the plurality of layers are mutually different, there are no particular limitations on the combination of the plurality of layers. Here, the expression that the plurality of layers are mutually different means that at least one of the material or the thickness of each layer is different from the other layers.

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

[0101]

In order to improve the adhesion with other layers such as the adhesive layer provided on top of the substrate, the surface of the substrate may be subjected to a roughening treatment such as a sandblasting treatment or solvent treatment, or to an oxidation treatment such as a corona discharge treatment, electron beam irradiation

treatment, plasma discharge treatment, ozone/ultraviolet irradiation treatment, flame treatment, chromic acid treatment or hot air treatment. Further, the surface of the substrate may also be subjected to a primer treatment.

[0102]

<Adhesive Layer>

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

The adhesive layer can be formed using an adhesive composition containing the various components that constitute the adhesive layer. The ratio between the amounts of those components within the adhesive composition that do not volatilize at normal temperature is typically the same as the ratio between the amounts of those components in the adhesive layer.

In those cases where the adhesive layer contains a component that polymerizes upon irradiation with energy rays, irradiation of the adhesive layer with energy rays to reduce the adhesiveness of the adhesive layer enables the semiconductor chips to be picked up more easily. This type of adhesive layer can be formed, for example, by using any of various types of adhesive compositions containing a component that polymerizes upon irradiation with energy rays, such as an energy ray-polymerizable acrylic polymer.

[0103]

Examples of preferred adhesive compositions that contain a component that polymerizes upon irradiation with energy rays (namely, energy ray-curable adhesive compositions) include compositions containing an aforementioned acrylic polymer and an energy ray-polymerizable compound (hereafter also referred to as an "adhesive composition (i)"), compositions containing an acrylic polymer having a hydroxyl group and also having a polymerizable group on a side chain (for example, an acrylic having a hydroxyl group, and having a polymerizable group bonded via a urethane linkage on a

side chain), and also containing an isocyanate crosslinking agent (hereafter also referred to as an "adhesive composition (ii)"), and compositions that also contain a solvent.

[0104]

In addition to the components described above, the adhesive composition may also include any of various additives, including polymerization initiators, dyes, pigments, degradation inhibitors, antistatic agents, flame retardants, silicone compounds, and chain transfer agents.

[0105]

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

[0106]

The thickness of the adhesive layer may be selected in accordance with the intended purpose, but is preferably from 1 to 100 μm , more preferably from 1 to 60 μm , and even more preferably from 1 to 30 μm .

[0107]

The adhesive composition can be obtained, for example, by blending the various components such as the acrylic polymer that constitute the adhesive layer, and with the exception of using different blend components, can be obtained using the same methods as those described above for the composition for protective film formation.

[0108]

The adhesive layer can be formed by applying the adhesive composition to the target location, and then drying the composition.

At this time, if required, crosslinking may be achieved by heating the applied adhesive composition. The heating conditions may, for example, involve heating at 100°C to 130°C for 1 to 5 minutes, but the heating is not limited to these conditions.

[0109]

In those cases where the target location is to be irradiated with energy rays through the support sheet, it is preferable that each of the layers such as the substrate and the adhesive layer that constitute the support sheet exhibit high transmittance of the energy rays.

A method for producing the composite sheet for protective film formation is described below in further detail.

[0110]

<Method for Producing Composite Sheet for Protective Film Formation>

The composite sheet for protective film formation according to the present invention can be produced by forming the film for protective film formation according to the present invention described above on one surface of a support sheet.

For example, a composite sheet for protective film formation having a support sheet composed solely of a substrate can be produced by applying the composition for protective film formation to the surface of the substrate, drying the composition to form a film for protective film formation, and then, if necessary, providing other layers (films) such as a jig adhesive layer or a release film on top of the film for protective film formation. In this case, the conditions for forming the film for protective film formation are the same as those in the method described above.

This type of production method is ideal, for example, as a method for producing the composite sheets for protective film formation illustrated in FIG. 3 and FIG. 4.

[0111]

Further, a composite sheet for protective film formation having a support sheet composed of an adhesive layer stacked on a substrate can be produced by applying the adhesive composition to the surface of the substrate, drying the composition to form the adhesive layer, subsequently providing the film for protective film formation on the adhesive layer using composition for protective film formation, and then, if necessary, providing other layers (films) such as a jig adhesive layer or a release film on top of the film for protective film formation.

[0112]

In this case, the film for protective film formation can be provided, for example, by applying the composition for protective film formation to the adhesive layer. However, normally, the stacked structure of the substrate, the adhesive layer and the film for protective film formation is preferably formed by forming the film for protective film formation separately, and then affixing the film to the surface of the adhesive layer, for example by applying the composition for protective film formation to the release layer surface of a release film, drying the composition to form a film for protective film formation, affixing the film for protective film formation to the surface of the adhesive layer, and then removing the release film as required.

[0113]

Furthermore, besides the method described above, the stacked structure of the substrate, the adhesive layer and the film for protective film formation can also be formed, for example, by forming an adhesive layer on a release film using the adhesive composition, using the composition for protective film formation to form the film for

protective film formation on a separate release film, subsequently bringing together the adhesive layer and the film for protective film formation formed on these release films, removing the release film laminated to the adhesive layer, and affixing the substrate to the exposed surface of the adhesive layer (the surface of the adhesive layer on which the film for protective film formation is not provided).

[0114]

In either of the above methods, a composite sheet for protective film formation having a support sheet formed by stacking an adhesive layer on a substrate can be produced by forming a stacked structure of the substrate, the adhesive layer and the film for protective film formation, and then, if required, providing other layers (films) such as a jig adhesive layer or a release film on the film for protective film formation. In either case, the conditions for forming the adhesive layer and the film for protective film formation are the same as the method described above.

These types of production methods are ideal, for example, as methods for producing the composite sheets for protective film formation illustrated in FIG. 1, FIG. 2, and FIG. 5.

[0115]

For example, when producing a composite sheet for protective film formation such as that illustrated in FIG. 5 which, when viewed from above in plan view, has a film for protective film formation having a smaller surface area than the adhesive layer, a film for protective film formation that has been cut in advance to the required size and shape may be provided on the adhesive layer using the production method described above.

[0116]

<Methods for Using Film for Protective Film Formation or Composite Sheet for Protective Film Formation>

Examples of methods for using the film for protective film formation or the composite sheet for protective film formation according to the present invention include usage methods 1 to 4 described below.

[0117]

[Usage Method 1]

In the usage method 1, first, the film for protective film formation of the composite sheet for protective film formation is affixed to the back surface of a semiconductor wafer, and the composite sheet is secured in a dicing apparatus.

[0118]

Subsequently, the film for protective film formation is cured by irradiation with energy rays to form a protective film. Whereas in the case of a conventional film for protective film formation, this curing is performed by heating and requires a long period of about several hours, the film for protective film formation according to the present invention can be cured by irradiation with energy rays in a very short period of less than one minute, for example about several seconds, meaning semiconductor chips with an attached protective film can be obtained in a much shorter time than has conventionally been possible.

In those cases where a back grind tape is affixed to the surface (the electrode formation surface) of the semiconductor wafer, this back grind tape is usually removed from the semiconductor wafer prior to curing of the film for protective film formation.

[0119]

Next, the semiconductor wafer is subjected to dicing to form semiconductor chips.

Semiconductor chips with a protective film are then obtained by separating and picking up each of the semiconductor chips, together with the protective film affixed to

the back surface of the chip, from the support sheet. In those cases where the support sheet is obtained by stacking an adhesive layer on a substrate, a non-energy ray-curable adhesive layer that does not contain a component that polymerizes upon irradiation with energy rays is used as the adhesive layer.

[0120]

In the usage method 1, printing onto the film for protective film formation or the protective film may also be performed by irradiating a laser light through the support sheet and onto the film for protective film formation or the protective film, at any timing from the time the film for protective film formation is affixed to the semiconductor wafer until dicing is performed. When printing is performed on the film for protective film formation, subsequent curing of the film yields a printed protective film.

When printing is performed, gas tends to be produced, and this gas can sometimes end up causing visible separation between the support sheet and the protective film, but compared with performing printing to the protective film, performing printing onto the film for protective film formation can reduce the frequency and degree of this separation.

It is thought that this is because the adhesion between the film for protective film formation and the support sheet is greater than the adhesion between the protective film and the support sheet.

[0121]

[Usage Method 2]

In the usage method 2, first, the film for protective film formation is affixed to the back surface of a semiconductor wafer.

Subsequently, the film for protective film formation is cured by irradiation with energy rays to form a protective film. In a similar manner to the usage method 1

described above, this enables semiconductor chips with an attached protective film to be obtained in a much shorter time than has conventionally been possible. In those cases where a back grind tape is affixed to the surface (the electrode formation surface) of the semiconductor wafer, this back grind tape is usually removed from the semiconductor wafer prior to curing of the film for protective film formation.

[0122]

Subsequently, a support sheet is affixed to the exposed surface of the protective film. In those cases where the support sheet is a sheet obtained by stacking an adhesive layer on a substrate, either an energy ray-curable layer that contains a component that polymerizes upon irradiation with energy rays, or an aforementioned non-energy ray-curable layer may be used as the adhesive layer.

[0123]

Next, the semiconductor wafer is subjected to dicing to form semiconductor chips.

Semiconductor chips with a protective film are then obtained by separating and picking up each of the semiconductor chips, together with the protective film affixed to the back surface of the chip, from the support sheet. In those cases where the support sheet is obtained by stacking an adhesive layer on a substrate, curing the adhesive layer enables the semiconductor chips with the protective film to be picked up more easily.

[0124]

In the usage method 2, printing onto the film for protective film formation or the protective film may also be performed by irradiating a laser light onto the film for protective film formation, or through the support sheet and onto the protective film, at any timing from the time the film for protective film formation is affixed to the semiconductor wafer until dicing is performed. When printing is performed on the film

for protective film formation, subsequent curing of the film yields a printed protective film.

[0125]

[Usage Method 3]

In the usage method 3, first, the film for protective film formation is affixed to the back surface of a semiconductor wafer.

Subsequently, a support sheet is affixed to the exposed surface of the protective film. In those cases where the support sheet is a sheet obtained by stacking an adhesive layer on a substrate, a non-energy ray-curable layer is used as the adhesive layer.

Next, the film for protective film formation is cured by irradiation with energy rays to form a protective film. In a similar manner to the usage method 1 described above, this enables semiconductor chips with an attached protective film to be obtained in a much shorter time than has conventionally been possible. In those cases where a back grind tape is affixed to the surface (the electrode formation surface) of the semiconductor wafer, this back grind tape is usually removed from the semiconductor wafer prior to curing of the film for protective film formation.

[0126]

Next, the semiconductor wafer is subjected to dicing to form semiconductor chips.

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

[0127]

In the usage method 3, printing onto the film for protective film formation can also be performed by irradiating a laser light onto the film for protective film formation,

either directly or through the support sheet, at any timing from the time the film for protective film formation is affixed to the semiconductor wafer until dicing is performed, or alternatively, printing onto the protective film may be performed by irradiating a laser light through the support sheet and onto the protective film. When printing is performed on the film for protective film formation, subsequent curing of the film yields a printed protective film.

In a similar manner to the usage method 1 described above, when printing is performed after the support sheet has been affixed, compared with performing printing to the protective film, performing printing onto the film for protective film formation can reduce the frequency and degree of separation between the support sheet and the protective film.

[0128]

[Usage Method 4]

In the usage method 4, first, the film for protective film formation is affixed to the back surface of a semiconductor wafer.

Subsequently, a support sheet is affixed to the exposed surface of the protective film. In those cases where the support sheet is a sheet obtained by stacking an adhesive layer on a substrate, a non-energy ray-curable layer is used as the adhesive layer.

Next, the semiconductor wafer is subjected to dicing to form semiconductor chips.

[0129]

Subsequently, the film for protective film formation is cured by irradiation with energy rays to form a protective film. In a similar manner to the usage method 1 described above, this enables semiconductor chips with an attached protective film to be obtained in a much shorter time than has conventionally been possible.

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

[0130]

In the usage method 4, printing onto the film for protective film formation can also be performed by irradiating a laser light onto the film for protective film formation, either directly or through the support sheet, at any timing from the time the film for protective film formation is affixed to the semiconductor wafer until dicing is performed. By curing the printed film for protective film formation, a printed protective film can be obtained.

In the usage method 4, when printing is performed after the support sheet has been affixed, then in a similar manner to the usage method 1 described above, compared with performing printing to the protective film using one of the other methods, performing printing onto the film for protective film formation can reduce the frequency and degree of separation between the support sheet and the protective film.

[0131]

By using the film for protective film formation or the composite sheet for protective film formation according to the present invention, the protective film exhibits a satisfactorily high protective action through until the semiconductor chips with a protective film are obtained. Accordingly, cracking and chipping is suppressed, including chipping of the semiconductor chips. Further, the protective film has excellent reliability, and the above type of superior protective action can be maintained even if the protective film is exposed to large temperature variations.

[0132]

One aspect of the film for protective film formation that represents one embodiment of the present invention is a film for protective film formation used for forming a protective film on the back surface of a semiconductor wafer or a semiconductor chip; wherein

the film for protective film formation contains

an energy ray-curable compound (B), and

if desired, at least one component selected from the group consisting of polymer components (A), photopolymerization initiators (C), fillers (D), colorants (E), coupling agents (F), crosslinking agents (G) and general-purpose additives (H);

the component (B) contains an energy ray-curable compound (B1), which is a (meth)acrylate compound having 2 to 4 energy ray-polymerizable groups within a single molecule,

the component (A) is an acrylic-based resin having a weight average molecular weight (Mw) of 10,000 to 2,000,000 and a glass transition temperature of -60 to 70°C, and

the component (C) is at least one compound selected from the group consisting of ethanone,1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-,1-(O-acetyloxime);

the amount of the component (B), relative to the total mass of the film for protective film formation, is at least 3% by mass but not more than 30% by mass;

in the component (B), the amount of the component (B1), relative to the total mass of the component (B), is at least 90% by mass but not more than 100% by mass, preferably at least 95% by mass but not more than 100% by mass, more preferably at least 98% by mass but not more than 100% by mass, and most preferably 100% by mass;

when the component (A) is included, the amount of the component (A), relative to the total mass of the film for protective film formation, is within a range from 5 to 50% by mass, and preferably from 10 to 45% by mass, and

when the component (C) is included, the amount of the component (C), relative to the total mass of the film for protective film formation, is from 0.1 to 3% by mass;

the total of all the components that constitute the film for protective film formation does not exceed 100% by mass; and

the film for protective film formation has the properties described below.

When a cured product (protective film) is formed by curing the film for protective film formation by irradiation with energy rays, the cured product has a Young's modulus that is at least 500 MPa but not more than 1,000 MPa, and preferably at least 550 MPa but not more than 5,000 MPa, and has an elongation at break that is at least 8% but not more than 100%, and preferably at least 10% but not more than 100%.

The Young's modulus of the cured product may be at least 590 MPa but not more than 1,960 MPa, and the elongation at break may be at least 10.7% but not more than 56%.

[0133]

Another aspect of the film for protective film formation that represents one embodiment of the present invention is a film for protective film formation used for forming a protective film on the back surface of a semiconductor wafer or a semiconductor chip; wherein

the film for protective film formation contains

at least one energy ray-curable compound (B) selected from the group consisting of tricyclodecane dimethylol diacrylate and ϵ -caprolactone-modified tris(acryloxyethyl) isocyanurate;

a polymer component (A) obtained by polymerizing at least one monomer selected from the group consisting of methyl (meth)acrylate, butyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, and glycidyl (meth)acrylate;

ethanone,1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-,1-(O-acetyloxime) (C); and

if desired, at least one component selected from the group consisting of fillers (D), colorants (E), coupling agents (F), crosslinking agents (G) and general-purpose additives (H);

relative to the total mass of the film for protective film formation,
the amount of the component (B) is at least 10% by mass but not more than 20% by mass,

the amount of the component (A) is from 20 to 32% by mass, and

the amount of the component (C) is at least 0.6% by mass; and

when a cured product (protective film) is obtained by curing the film for protective film formation by irradiation with energy rays,

the cured product has a Young's modulus of at least 590 MPa but not more than 1,960 MPa, and an elongation at break of at least 10.7% but not more than 56%.

EXAMPLES

[0134]

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

[0135]

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

- Polymer Component (A)

(A)-1: an acrylic-based resin (weight average molecular weight: 800,000, glass transition temperature: -1°C) obtained by copolymerizing 10 parts by mass of butyl acrylate, 70 parts by mass of methyl acrylate, 15 parts by mass of 2-hydroxyethyl acrylate, and 5 parts by mass of glycidyl methacrylate.

- Energy Ray-Curable Compound (B)

(B1)-1: tricyclodecane dimethylol diacrylate (KAYARAD R-684, manufactured by Nippon Kayaku Co., Ltd., a difunctional ultraviolet-curable compound, molecular weight: 304)

(B1)-2: ϵ -caprolactone-modified tris(2-acryloxyethyl) isocyanurate (A-9300-1CL, manufactured by Shin-Nakamura Chemical Co., Ltd., a trifunctional ultraviolet-curable compound, molecular weight: 537)

(B2)-1: a mixture of dipentaerythritol hexaacrylate (a hexafunctional ultraviolet-curable compound, molecular weight: 578) and dipentaerythritol pentaacrylate (a pentafunctional ultraviolet-curable compound, molecular weight: 525) (KAYARAD DPHA, manufactured by Nippon Kayaku Co., Ltd.)

- Photopolymerization Initiator (C)

(C)-1: ethanone,1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-,1-(O-acetyloxime) (IRGACURE (a registered trademark) OXE02, manufactured by BASF Corporation)

- Filler (D)

(D)-1: a silica filler (fused quartz filler, average particle size: 8 μm)

- Colorant (E)

(E)-1: a pigment obtained by mixing 32 parts by mass of a phthalocyanine-based blue pigment (Pigment Blue 15:3), 18 parts by mass of an isoindolinone-based yellow pigment (Pigment Yellow 139) and 50 parts by mass of an anthraquinone-based red pigment (Pigment Red 177), and then performing pigmentation so that the ratio of (total mass of the above three colorants)/styrene-acrylic resin = 1/3 (mass ratio).

- Coupling Agent (F)

(F)-1: 3-methacryloxypropyltrimethoxysilane (KBM-503, manufactured by Shin-Etsu Chemical Co., Ltd., a silane coupling agent)

[0136]

[Example 1]

<Production of Film for Protective Film Formation>

(Production of Composition for Protective Film Formation)

The polymer component (A)-1 (32 parts by mass), the energy ray-curable compound (B)-1 (10 parts by mass), the photopolymerization initiator (C)-1 (0.3 parts by mass), the photopolymerization initiator (C)-2 (0.3 parts by mass), the filler (D)-1 (56 parts by mass), the colorant (E)-1 (2 parts by mass), and the coupling agent (F)-1 (0.4 parts by mass) were mixed together to obtain a composition for protective film formation. The type and blend amount of each component is shown in Table 1. The blend amounts shown in Table 1 are all solid fraction amounts. Further, in Table 1, each of the components is shown using only the tail-end symbol, such as recording simply "(A)" for the polymer component (A).

[0137]

(Production of Film for Protective Film Formation)

Using a knife coater, the composition for protective film formation obtained above was applied to the release-treated surface of a release film prepared by subjecting

one surface of a polyethylene terephthalate film to a silicone treatment (SP-PET381031, manufactured by Lintec Corporation, thickness: 38 μm), and the composition was then dried at 120°C to form a film for protective film formation (thickness: 25 μm). A release film of the same type as that described above was then affixed to the exposed surface of the obtained film for protective film formation so that the release-treated surface contacted the film for protective film formation, thus obtaining a laminate having the release films provided on both surfaces of the film for protective film formation. The thus obtained laminate was wound up until a roll for storage.

[0138]

<Evaluations of Film for Protective Film Formation>

(Evaluation of Young's Modulus and Elongation at Break for the Protective Film)

The laminate obtained above was unwound, and the film for protective film formation was cured by irradiation with ultraviolet rays with an illuminance of 230 mW/cm^2 and an irradiation dose of 170 mJ/cm^2 , thus forming a protective film.

[0139]

Subsequently, this protective film with attached release films was cut to a size having a width of 15 mm and a length of 140 mm, and the release films were then removed from both surfaces to obtain a test piece. Following the prescription in JIS K7161:1994 and JIS K7127:1999, test cover plates (labels) were affixed to the test piece in portions that extended from both ends to positions 20 mm along the lengthwise direction of the test piece, a universal tester (Autograph AG-IS 500N, manufactured by Shimadzu Corporation) was used to secure these portions with chucks so that the distance between the chucks was 100 mm, and a tensile test was then performed at a tensile speed of 200 mm/minute.

A stress-strain curve was prepared during this tensile test, the Young's modulus was calculated from the slope of the stress-strain curve at the start of the test, and the elongation at break was determined from the amount of elongation of the test piece when the test piece broke. The results are shown in Table 1.

[0140]

(Evaluation of Protective Film Reliability)

The laminate obtained above was unwound, one of the release films was removed from one surface of the film for protective film formation, and a tape mounter (Adwill RAD-3600F/12, manufactured by Lintec Corporation) was used to affix the exposed surface of the film for protective film formation having a release film on one surface to the polished surface of a silicon wafer (diameter: 200 mm, thickness: 280 μm) that had been subjected to #2000 polishing while heating was performed at 70°C. Subsequently, the film for protective film formation was cured by irradiation with ultraviolet rays under conditions including an illuminance of 230 mW/cm^2 and an irradiation dose of 170 mJ/cm^2 , thus forming a protective film on the polished surface of the silicon wafer.

[0141]

Next, the other release film was removed from the protective film, a dicing sheet (Adwill G-562, manufactured by Lintec Corporation) was affixed, and a dicing apparatus (DFD651, manufactured by DISCO Corporation) was used to dice the silicon wafer with the protective film formed thereon into chips having a size 3 mm $\times$ 3 mm, thus obtaining semiconductor chips with a protective film.

[0142]

Subsequently, the semiconductor chips with a protective film obtained in the above manner were subjected to the preconditioning described below to simulate the process when a semiconductor chip is mounted. In other words, the semiconductor chips

with a protective film were baked at 125°C for 20 hours and subsequently subjected to moisture absorption for 168 hours under conditions at 85°C and a relative humidity of 85%, and immediately after removal from this moisture absorption environment, the semiconductor chips with a protective film were passed three times through an IR reflow oven under conditions including a preheat temperature of 160°C and a peak temperature of 260°C. Twenty five of the semiconductor chips with a protective film that had been subjected to operations up until this point were then placed in a thermal shock apparatus (TSE-11-A, manufactured by ESPEC Corporation) and subjected to 1,000 repetitions of a cold-hot cycle consisting of holding at -65°C for 10 minutes followed by holding at 150°C for 10 minutes.

[0143]

All of the semiconductor chips with a protective film were then removed from the thermal shock apparatus, and the existence or absence of lifting or peeling at the joint between the semiconductor chip and the protective film, and the existence or absence of cracking in the semiconductor chip was confirmed by inspecting the cross-section of each of the semiconductor chips with a protective film using a scanning ultrasonic flaw detector (D9600TM CSAM, manufactured by Sonoscan, Inc.). The number of semiconductor chips with a protective film in which at least one of the aforementioned lifting or peeling flaws or cracks had occurred was counted, and if that number (NG number) was 2 or fewer, the reliability was deemed a pass (A), whereas if the number was 3 or greater, the reliability was deemed a fail (B). The results are shown in Table 1.

[0144]

<Production and Evaluation of Films for Protective Film Formation>

[Examples 2 to 4, Comparative Examples 1 to 6]

With the exception of altering the types and blend amounts of the blend components used when producing the composition for protective film formation, a series of films for protective film formation were produced and evaluated using the same methods as Example 1.

The results are shown in Table 1.

[0145]

[Table 1]

	Blend components for composition for protective film formation (parts by mass)						Evaluation results		
	(A)	(B)	(C)	(D)	(E)	(F)	Young's modulus (MPa)	Elongation at break (%)	Reliability
Example 1	(A)-1 (32)	(B1)-1 (10)	(C)-1 (0.6)	(D)-1 (56)	(E)-1 (2)	(F)-1 (0.4)	1080	18.9	A
Example 2	(A)-1 (22)	(B1)-1 (20)	(C)-1 (0.6)	(D)-1 (56)	(E)-1 (2)	(F)-1 (0.4)	1960	11.8	A
Example 3	(A)-1 (30)	(B1)-2 (10)	(C)-1 (0.6)	(D)-1 (57)	(E)-1 (2)	(F)-1 (0.4)	590	56.0	A
Example 4	(A)-1 (20)	(B1)-2 (20)	(C)-1 (0.6)	(D)-1 (57)	(E)-1 (2)	(F)-1 (0.4)	1610	10.7	A
Comparative Example 1	(A)-1 (32)	(B2)-1 (10)	(C)-1 (0.6)	(D)-1 (56)	(E)-1 (2)	(F)-1 (0.4)	1740	6.6	B
Comparative Example 2	(A)-1 (22)	(B2)-1 (20)	(C)-1 (0.6)	(D)-1 (56)	(E)-1 (2)	(F)-1 (0.4)	2800	5.3	B
Comparative Example 3	(A)-1 (41)	(B1)-1 (1)	(C)-1 (0.6)	(D)-1 (56)	(E)-1 (2)	(F)-1 (0.4)	320	>350	- *1
Comparative Example 4	(A)-1 (12)	(B1)-1 (30)	(C)-1 (0.6)	(D)-1 (56)	(E)-1 (2)	(F)-1 (0.4)	6200	0.9	B
Comparative Example 5	(A)-1 (39)	(B2)-1 (1)	(C)-1 (0.6)	(D)-1 (57)	(E)-1 (2)	(F)-1 (0.4)	400	>350	- *1
Comparative Example 6	(A)-1 (10)	(B2)-1 (30)	(C)-1 (0.6)	(D)-1 (57)	(E)-1 (2)	(F)-1 (0.4)	9220	0.8	B

*1: Chipping occurred during dicing, and semiconductor chips with a protective film could not be obtained.

[0146]

As is evident from the above results, the protective films formed from the films for protective film formation of Examples 1 to 4 exhibited high values for the Young's modulus and the elongation at break, had a satisfactory protective action, and also exhibited superior reliability.

In contrast, the protective films formed from the films for protective film formation of Comparative Examples 1, 2, 4 and 6 had low elongation at break values, exhibited an unsatisfactory protective action, and also suffered from poor reliability. It is thought that this is because the energy ray-curable compound (B2)-1 was used in Comparative Examples 1 and 2, and because the amount used of the energy ray-curable compound (B1)-1 was excessive in Comparative Example 4. Both of these reasons apply in the case of Comparative Example 6.

Further, the protective films formed from the films for protective film formation of Comparative Examples 3 and 5 had low Young's modulus values and suffered from chipping during dicing, meaning semiconductor chips with a protective film could not be obtained, thus making evaluation of the reliability of the protective film impossible. It is thought that this is because the amount used of the energy ray-curable compound (B1)-1 was too small in Comparative Example 3, whereas the amount used of the energy ray-curable compound (B2)-1 was too small in Comparative Example 5.

INDUSTRIAL APPLICABILITY

[0147]

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

DESCRIPTION OF THE REFERENCE SIGNS

[0148]

1A, 1B, 1C, 1D, 1E: Composite sheet for protective film formation

10: Support sheet

10a: Support sheet surface

11: Substrate

11a: Substrate surface

12: Adhesive layer

12a: Adhesive layer surface

13, 23: Film for protective film formation

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

15: Release film

16: Jig adhesive layer

16a: Jig adhesive layer surface

CLAIMS

1. A film for protective film formation which comprises an energy ray-curable compound (B), has properties described below, and is used for forming a protective film on a back surface of a semiconductor wafer or a semiconductor chip, wherein
when a cured product is formed by curing the film for protective film formation by irradiation with energy rays, the cured product has a Young's modulus of at least 500 MPa and an elongation at break of at least 8% but not more than 100%.
2. The film for protective film formation according to Claim 1, wherein within the film for protective film formation, an amount of an energy ray-curable compound (B1) having 2 to 4 energy ray-polymerizable groups within a single molecule, relative to a total mass of the energy ray-curable compound (B), is at least 90% by mass.
3. A composite sheet for protective film formation, comprising the film for protective film formation according to Claim 1 or 2 provided on one surface of a support sheet.