

DESCRIPTION

COMPOSITE SHEET FOR FORMING PROTECTIVE FILM

TECHNICAL FIELD

[0001]

The present invention relates to a composite sheet for forming a protective film that is used for forming a protective film on the back surface of a semiconductor chip.

Priority is claimed on Japanese Patent Application No. 2015-114714, filed on June 5, 2015, the content of which is incorporated herein by reference.

BACKGROUND ART

[0002]

In recent years, many semiconductor devices have been produced by 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 chip on the opposite side from the circuit surface sometimes remains exposed.

[0003]

A resin film formed from an organic material is sometimes formed on the exposed back surface of the chip as a protective film, 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 chip following the dicing step and packaging, and/or for bonding the obtained chip to other members such as a die pad or another semiconductor chip.

[0004]

On the other hand, a composite sheet for forming a protective film, which is prepared by providing an adhesive layer on a substrate, and then applying a film for forming a protective film to the adhesive layer, is used for forming the type of protective film described above. In the composite sheet for forming a protective film described above, the film for forming a protective film has a protective film forming ability, whereas the laminated structure of the substrate and the adhesive layer functions as a dicing sheet, meaning the composite sheet can be said to represent an integrated combination of a film for forming a protective film and a dicing sheet.

[0005]

This type of composite sheet for forming a protective film is used, for example, in the following manner. That is, the composite sheet for forming a protective film 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 forming a protective film, and the semiconductor wafer is then converted to semiconductor chips by dicing. Subsequently, the adhesive layer is cured by irradiation with active energy rays, and the semiconductor chips are detached from the adhesive layer and picked up. On the other hand, the film for forming a protective film is picked up together with the semiconductor chip, and finally exists in the form of a cured protective film on the back surface of the semiconductor chip. In one disclosed example of the use of this type of composite sheet for forming a protective film, the film for forming a protective film exists in an uncured state or a partially cured state at the time of pickup of the semiconductor chip, and this uncured or partially cured film for forming a protective film reaches a completely cured or substantially completely cured state at the same time as the bonding of the semiconductor chip and the curing of a sealing material (see Patent Document 1).

PRIOR ART LITERATURE

Patent Documents

[0006]

Patent Document 1: Japanese Unexamined Patent Application, First Publication
No. 2011-228450

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0007]

However, conventional composite sheets for forming a protective film such as the composite sheet disclosed in Patent Document 1 have a problem in that, depending on the usage conditions, the peel strength between the adhesive layer and the film for forming a protective film may sometimes be too large, particularly following curing of the adhesive layer, resulting in chip cracking or chipping during pickup of the semiconductor chips.

[0008]

The present invention has been developed in light of the above circumstances, and has an object of providing a composite sheet for forming a protective film, which is prepared by providing an adhesive layer on a substrate and then providing a film for forming a protective film on the adhesive layer, and is used for forming a protective film on the back surface of a semiconductor chip, wherein the peel strength between the adhesive layer and the film for forming a protective film or the cured protective film is sufficiently large prior to curing of the adhesive layer to enable dicing to be performed in

a stable manner, and is sufficiently small following curing of the adhesive layer to enable pickup of the semiconductor chips to be performed in a stable manner.

Means for Solving the Problems

[0009]

In order to achieve the above object, the present invention provides a composite sheet for forming a protective film that is prepared by providing an adhesive layer on a substrate and then providing a film for forming a protective film on the adhesive layer, the adhesive layer having active energy ray curability, and the film for forming a protective film having heat curability, wherein the composite sheet for forming a protective film is used for producing a semiconductor chip with a protective film by affixing the composite sheet to the back surface of a semiconductor wafer via the film for forming a protective film, and then curing the film for forming a protective film by heating to form a protective film, subsequently dicing the semiconductor wafer to produce semiconductor chips, curing the adhesive layer by irradiation with active energy rays, and then picking up the semiconductor chips together with the protective film affixed to the back surface thereof, and the adhesive layer contains, at least in the layer that contacts the film for forming a protective film, an alkyl (meth)acrylate ester copolymer, the alkyl (meth)acrylate ester copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater.

[0010]

In the composite sheet for forming a protective film of the present invention, the film for forming a protective film preferably contains an epoxy resin, a heat curing agent

that melts upon heating and exhibits curing activity relative to the epoxy resin, and an imidazole.

In the composite sheet for forming a protective film of the present invention, the carbon number of the alkyl group that constitutes the aforementioned alkyl ester is preferably from 11 to 18.

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

[1] A composite sheet for forming a protective film prepared by providing an adhesive layer on a substrate and then providing a film for forming a protective film on the adhesive layer, the adhesive layer having active energy ray curability, and the film for forming a protective film having heat curability, wherein

the composite sheet for forming a protective film is used for producing a semiconductor chip with a protective film by affixing the composite sheet to the back surface of a semiconductor wafer via the film for forming a protective film, and then curing the film for forming a protective film by heating to form a protective film, subsequently dicing the semiconductor wafer to produce semiconductor chips, curing the adhesive layer by irradiation with active energy rays, and then picking up the semiconductor chips together with the protective film affixed to the back surface thereof,

the adhesive layer contains, at least in the layer that contacts the film for forming a protective film, an alkyl (meth)acrylate ester copolymer, and

the alkyl (meth)acrylate ester copolymer has a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater.

[2] The composite sheet for forming a protective film according to [1], wherein the film for forming a protective film contains an epoxy resin, a heat curing agent that melts upon heating and exhibits curing activity relative to the epoxy resin, and an imidazole.

[3] The composite sheet for forming a protective film according to [1] or [2], wherein the carbon number of the alkyl group that constitutes the alkyl ester is from 11 to 18.

Effects of the Invention

[0011]

The present invention is able to provide a composite sheet for forming a protective film, which is prepared by providing an adhesive layer on a substrate and then providing a film for forming a protective film on the adhesive layer, and which is used for forming a protective film on the back surface of a semiconductor chip, wherein the peel strength between the adhesive layer and the film for forming a protective film or the cured protective film obtained upon curing the film for forming a protective film (namely, the protective film composed of the cured product of the film for forming a protective film) is sufficiently large prior to curing of the adhesive layer to enable dicing to be performed in a stable manner, and is sufficiently small following curing of the adhesive layer to enable pickup of the semiconductor chips to be performed in a stable manner.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

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

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

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

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

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0013]

<<Composite Sheet for Forming a Protective Film>>

The composite sheet for forming a protective film according to the present invention is a composite sheet prepared by providing an adhesive layer on a substrate and then providing a film for forming a protective film on the adhesive layer, the adhesive layer having active energy ray curability, and the film for forming a protective film having heat curability, wherein the composite sheet for forming a protective film is used for producing a semiconductor chip with a protective film by affixing the composite sheet to the back surface of a semiconductor wafer via the film for forming a protective film, and then curing the film for forming a protective film by heating to form a protective film, subsequently dicing the semiconductor wafer to produce semiconductor chips, curing the adhesive layer by irradiation with active energy rays, and then picking up the semiconductor chips together with the protective film affixed to the back surface thereof, and the adhesive layer contains, at least in the layer that contacts the film for forming a protective film, an alkyl (meth)acrylate ester copolymer, the alkyl (meth)acrylate ester copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater.

In other words, one aspect of the composite sheet for forming a protective film according to the present invention is:

a composite sheet for forming a protective film containing a substrate, an adhesive layer and a film for forming a protective film, wherein

the adhesive layer is laminated on top of the substrate, and the film for forming a protective film is laminated on top of the adhesive layer;

the adhesive layer has active energy ray curability, and contains an alkyl (meth)acrylate ester copolymer at least in the layer that contacts the film for forming a protective film, and

the alkyl (meth)acrylate ester copolymer is a copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater;

the film for forming a protective film has heat curability; and

the composite sheet for forming a protective film is used for the production of a semiconductor chip with a protective film by:

affixing the composite sheet for forming a protective film to the back surface of a semiconductor wafer via the film for forming a protective film,

curing the film for forming a protective film in the affixed composite sheet for forming a protective film by heating to form a protective film,

dicing the semiconductor wafer having the protective film formed thereon to produce semiconductor chips,

curing the adhesive layer by irradiation with active energy rays, and then picking up the semiconductor chips together with the protective film affixed to the back surface of each semiconductor chip.

In the present description, the laminated structure of the substrate and the adhesive layer is sometimes termed the "support sheet". Further, for the composite sheet for forming a protective film, the composite sheet obtained following curing of the film

for forming a protective film by heating to form a protective film, and the composite sheet obtained following curing of the adhesive layer by irradiation of active energy rays may also be referred to as a composite sheet for forming a protective film, provided the laminated structure of the substrate, the adhesive layer or cured product thereof, and the protective film is maintained.

[0014]

In the composite sheet for forming a protective film according to the present invention, because the layer within the adhesive layer that contacts the film for forming a protective film contains an alkyl (meth)acrylate ester copolymer that satisfies the specific range described above, the peel strength between the adhesive layer and the cured film for forming a protective film (namely, the protective film) is sufficiently large prior to curing of the adhesive layer to enable the semiconductor wafer to be strongly secured in a stable manner, and therefore chip flying and the like is suppressed during dicing of the semiconductor wafer, and dicing can be performed in a stable manner.

[0015]

Further, when using the composite sheet for forming a protective film, in the state where the protective film is affixed to the back surface of the semiconductor wafer but prior to dicing of the semiconductor wafer, printing is sometimes performed on the surface of the protective film by irradiating laser light onto the protective film from the substrate side of the composite sheet for forming a protective film (hereafter also referred to as "laser printing"). In this case, gas generation from the laser-irradiated region occurs due to a decomposition of the protective film that accompanies the laser printing, but as described above, because the peel strength between the adhesive layer and the protective film is sufficiently large, peeling between the adhesive layer and the protective film is suppressed even when exposed to the pressure of the generated gas, and gas

accumulation is suppressed. As a result, not only can dicing be performed in a stable manner as mentioned above, but the printing on the protective film can be clearly recognized visually through the substrate and the adhesive layer.

[0016]

On the other hand, in the composite sheet for forming a protective film according to the present invention, because the layer within the adhesive layer that contacts the film for forming a protective film contains an alkyl (meth)acrylate ester copolymer that satisfies the specific range described above, following curing of the adhesive layer, the peel strength between the cured product of the adhesive layer and the protective film is sufficiently small to enable pickup of the semiconductor chips with a protective film to be performed easily and in a stable manner, and chip cracking or chipping during pickup is suppressed.

Each of the components of the composite sheet for forming a protective film according to the present invention is described below in further detail.

[0017]

<Substrate>

The material for the substrate is preferably any of various resins, and specific examples include polyethylene (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.

In the present description, the term "(meth)acrylic acid" is deemed to include both "acrylic acid" and "methacrylic acid".

[0018]

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 forming a protective film, and the fixability to a semiconductor wafer or semiconductor chip can be improved.

The "thickness" described in the present description can be determined by the method prescribed in JIS K 7130:1999 (ISO 4593:1993).

[0019]

The substrate may be composed of one layer (a single layer), or may be composed of a plurality of two or more 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 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.

[0020]

In order to improve the adhesion with 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.

[0021]

<Adhesive Layer>

The adhesive layer has active energy ray curability, and contains an alkyl (meth)acrylate ester copolymer, at least in the layer that contacts the film for forming a protective film. The alkyl (meth)acrylate ester copolymer has a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater.

The term "derived" means a change in the chemical structure due to polymerization.

In the present description, "active 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 or a xenon lamp or the like as an ultraviolet source. Electron beams can be generated and irradiated from an electron beam accelerator or the like.

[0022]

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 .

[0023]

The adhesive layer is formed from an adhesive composition containing the aforementioned alkyl (meth)acrylate ester copolymer and the like. The ratio between the amounts of those components within the adhesive composition that do not vaporize at normal temperature is typically the same as the ratio between the amounts of those components in the adhesive layer. In this description, "normal temperature" means a temperature at which no particular cooling or heating is performed, namely ordinary room temperature, and for example, is typically a temperature of 15 to 25°C.

Next is a description of the adhesive composition containing the aforementioned alkyl (meth)acrylate ester copolymer, and each of the components within the adhesive composition and the adhesive.

[0024]

[Adhesive Composition]

(Alkyl (meth)acrylate ester copolymer)

The aforementioned alkyl (meth)acrylate ester copolymer has a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater. In the present description, unless specifically stated otherwise, the simplified expression "alkyl (meth)acrylate ester" is assumed to mean an "alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater".

[0025]

The alkyl group having a carbon number of 8 or greater from the alkyl (meth)acrylate ester may be linear, branched or cyclic, and in the case of a cyclic group, may be monocyclic or polycyclic, but is preferably a linear or branched group.

[0026]

The carbon number of the alkyl group that constitutes the alkyl ester may be any number of 8 or greater, and may, for example, be 11 or greater. Further, the carbon number of the alkyl group that constitutes the alkyl ester is preferably not more than 18. In other words, a preferred range for the carbon number of the alkyl group that constitutes the alkyl ester is from 8 to 18, and one example of the range is from 11 to 18. Alkyl (meth)acrylate esters in which the carbon number of the alkyl group that constitutes the alkyl ester is 19 or greater have poor solubility characteristics and the like, and are difficult to handle. In other words, provided the carbon number of the alkyl group that constitutes the alkyl ester is 18 or less, then the solubility is favorable, and the copolymer is easy to handle.

[0027]

By using the aforementioned alkyl (meth)acrylate ester copolymer in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater, the adhesive layer adopts a lower polarity than in those cases where an alkyl (meth)acrylate ester copolymer in which the carbon number is less than 7 is used. Accordingly, in those cases where, for example, the film for forming a protective film contains a high-polarity material such as an epoxy resin, migration of this high-polarity material from the film for forming a protective film to the adhesive layer in the composite sheet for forming a protective film can be suppressed. As a result, any deterioration in the heat curability of the film for forming a protective film is effectively suppressed. Accordingly, because the degree of heat curing upon heating of the film for forming a protective film is increased,

the pickup characteristics can be improved for the semiconductor chips with a protective film described below.

[0028]

Examples of preferred alkyl (meth)acrylate esters in which the carbon number of the alkyl group is 8 or greater include alkyl (meth)acrylate esters having a chain-like alkyl group such as n-octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate (also known as lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (also known as myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (also known as palmityl (meth)acrylate), heptadecyl (meth)acrylate, octadecyl (meth)acrylate (also known as stearyl (meth)acrylate), and isooctadecyl (meth)acrylate (also known as isostearyl (meth)acrylate); and cycloalkyl (meth)acrylate esters such as isobornyl (meth)acrylate and dicyclopentanyl (meth)acrylate.

Among the above compounds, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate and isostearyl (meth)acrylate are preferred.

[0029]

Examples of the aforementioned alkyl (meth)acrylate ester copolymer include active energy ray-polymerizable copolymers that polymerize upon irradiation with active energy rays. Examples of preferred copolymers of this type include copolymers having a hydroxyl group, and having a polymerizable group (such as a (meth)acryloyl group, a vinyl group (ethenyl group) or an allyl group (propenyl group), and preferably a (meth)acryloyl group) as a side chain, and among such copolymers, those having a hydroxyl group and having a polymerizable group bonded as a side chain via a urethane linkage are particularly desirable. These types of alkyl (meth)acrylate ester copolymers

undergo crosslinking, for example, by reaction of the hydroxyl group with an isocyanate group within an isocyanate-based crosslinking agent described below. Further, by having a polymerizable group on a side chain, this type of alkyl (meth)acrylate ester copolymer need not undergo the type of polymerization reaction by irradiation with active energy rays that requires the use of a separate low-molecular weight active energy ray-polymerizable compound, but rather undergoes a polymerization reaction without the use of this type of separate compound, and therefore the peelability from the protective film improves due to a reduction in the adhesiveness of the adhesive layer following the polymerization reaction, yielding improved pickup characteristics that enable easy pickup of the semiconductor chips with a protective film. Further, because there is no necessity to use a separate low-molecular weight active energy ray-polymerizable compound, migration of this type of low-molecular weight active energy ray-polymerizable compound from the adhesive layer into the film for forming a protective film is suppressed, meaning changes in the properties of the film for forming a protective film are also suppressed.

[0030]

The preferred alkyl (meth)acrylate ester copolymer described above can be obtained, for example, by using a composition containing an alkyl (meth)acrylate ester and a hydroxyl group-containing monomer, polymerizing these monomers to obtain a copolymer (hereafter also referred to as a "pre-copolymer"), and then reacting the isocyanate group of a compound having an isocyanate group and a polymerizable group with the hydroxyl group of this copolymer (pre-copolymer).

[0031]

Among the alkyl (meth)acrylate ester copolymers described above, examples of particularly preferred copolymers include those obtained by using the aforementioned

alkyl (meth)acrylate ester and a hydroxyl group-containing (meth)acrylate ester as essential monomers, copolymerizing these monomers to obtain a pre-copolymer, and then reacting the hydroxyl group of the pre-copolymer with the isocyanate group of a compound having an isocyanate group and a polymerizable group.

[0032]

Examples of the hydroxyl group-containing (meth)acrylate ester include hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate.

[0033]

Examples of the compound having an isocyanate group and a polymerizable group include isocyanate compounds such as 2-(meth)acryloyloxyethyl isocyanate, meta-isopropenyl- α,α -dimethylbenzyl isocyanate, methacryloyl isocyanate and allyl isocyanate, and among these, 2-methacryloyloxyethyl isocyanate is preferred.

[0034]

The preferred alkyl (meth)acrylate ester copolymer described above may also be a copolymer obtained by reacting the essential monomers and compounds described above together with one or more optional compounds, wherein these optional compounds may be a monomer or a compound obtained by copolymerizing a monomer. Examples of monomers that can be used as the optional compound include non-hydroxyl group-containing (meth)acrylate esters that do not correspond with the alkyl (meth)acrylate ester described above, (meth)acrylic acid, itaconic acid, and non-(meth)acrylic-based monomers.

[0035]

Examples of the non-hydroxyl group-containing (meth)acrylate esters include alkyl (meth)acrylate esters in which the alkyl group is linear or branched and has a

carbon number of 1 to 7, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, and heptyl (meth)acrylate; aralkyl (meth)acrylate esters such as benzyl (meth)acrylate; cycloalkenyl (meth)acrylate esters such as dicyclopentenyl (meth)acrylate; cycloalkenyloxyalkyl (meth)acrylate esters such as dicyclopentenyoxyethyl (meth)acrylate; (meth)acrylic acid imide; and glycidyl group-containing (meth)acrylate esters such as glycidyl (meth)acrylate.

[0036]

Examples of the non-(meth)acrylic-based monomers include vinyl acetate, acrylonitrile, styrene and N-methylolacrylamide.

[0037]

The components used in the production of the aforementioned alkyl (meth)acrylate ester copolymer, including the alkyl (meth)acrylate ester, the hydroxyl group-containing (meth)acrylate ester, the compound having an isocyanate group and a polymerizable group, and the optional compound (namely, the components of the above copolymer) may each be either a single compound or two or more compounds.

[0038]

The proportion of the aforementioned alkyl (meth)acrylate ester in which the carbon number of the alkyl group is 8 or greater, relative to the total mass of all of the monomers used in the preparation of the alkyl (meth)acrylate ester copolymer, is preferably at least 30% by mass, and more preferably 35% by mass or greater.

In other words, the amount of the structural unit derived from the aforementioned alkyl (meth)acrylate ester in which the carbon number of the alkyl group is 8 or greater, relative to the total mass of all of the structural units that constitute the alkyl

(meth)acrylate ester copolymer, is preferably at least 30% by mass, and more preferably 35% by mass or greater.

[0039]

On the other hand, there are no particular limitations on the upper limit for the amount of the structural unit derived from the alkyl (meth)acrylate ester in which the carbon number of the alkyl group is 8 or greater, and relative to the total mass of all of the structural units that constitute the alkyl (meth)acrylate ester copolymer, the upper limit may be selected, for example, from among 85% by mass, 90% by mass or 95% by mass, and may even be 100% by mass.

In other words, the proportion of the alkyl (meth)acrylate ester in which the carbon number of the alkyl group is 8 or greater, relative to the total mass of all of the monomers used in the preparation of the alkyl (meth)acrylate ester copolymer, is preferably at least 30% by mass but not more than 100% by mass, and may be at least 30% by mass but not more than 95% by mass, at least 30% by mass but not more than 90% by mass, or at least 30% by mass but not more than 85% by mass.

In another aspect, the above amount may be at least 35% by mass but not more than 100% by mass, at least 35% by mass but not more than 95% by mass, at least 35% by mass but not more than 90% by mass, or at least 35% by mass but not more than 85% by mass.

In yet another aspect, the above amount may be at least 40% by mass but not more than 80% by mass.

Moreover, in yet another aspect, the amount of the structural unit derived from the aforementioned alkyl (meth)acrylate ester in which the carbon number of the alkyl group is 8 or greater, relative to the total mass of all of the structural units that constitute the alkyl (meth)acrylate ester copolymer, is preferably at least 30% by mass but not more

than 100% by mass, and may be at least 30% by mass but not more than 95% by mass, at least 30% by mass but not more than 90% by mass, or at least 30% by mass but not more than 85% by mass.

In yet another aspect, the above amount may be at least 35% by mass but not more than 100% by mass, at least 35% by mass but not more than 95% by mass, at least 35% by mass but not more than 90% by mass, or at least 35% by mass but not more than 85% by mass.

Further, in yet another aspect, the above amount may be at least 40% by mass but not more than 80% by mass.

[0040]

The alkyl (meth)acrylate ester copolymer contained in the adhesive layer may be composed of a single copolymer or two or more copolymers.

[0041]

The amount of the alkyl (meth)acrylate ester copolymer, relative to the total mass of the adhesive layer, is preferably at least 75% by mass, and more preferably 80% by mass or greater. In order to form this type of adhesive layer, the amount of the alkyl (meth)acrylate ester copolymer in the aforementioned adhesive composition, relative to the total mass of all of the components in the adhesive composition besides the solvent, is preferably at least 75% by mass, and more preferably 80% by mass or greater.

[0042]

On the other hand, there are no particular limitations on the upper limit for the amount of the alkyl (meth)acrylate ester copolymer in the adhesive layer, and the upper limit may be 100% by mass relative to the total mass of the adhesive layer, but if the inclusion of other components such as those described below is considered, then the upper limit is preferably 97% by mass, and more preferably 95% by mass.

In other words, the amount of the alkyl (meth)acrylate ester copolymer, relative to the total mass of the adhesive layer, may be at least 75% by mass but not more than 100% by mass, and is preferably at least 75% by mass but not more than 97% by mass, and more preferably at least 80% by mass but not more than 95% by mass.

Further, in another aspect, the amount of the alkyl (meth)acrylate ester copolymer in the aforementioned adhesive composition, relative to the total mass of all of the components in the adhesive composition besides the solvent, may be at least 75% by mass but not more than 100% by mass, and is preferably at least 75% by mass but not more than 97% by mass, and more preferably at least 80% by mass but not more than 95% by mass.

[0043]

In those cases where the alkyl (meth)acrylate ester copolymer has a hydroxyl group, and also has a polymerizable group on a side chain, examples of preferred adhesive compositions include those containing an isocyanate-based crosslinking agent and a photopolymerization initiator in addition to the alkyl (meth)acrylate ester copolymer.

[0044]

(Isocyanate-Based Crosslinking Agent)

There are no particular limitations on the isocyanate-based crosslinking agent, provided it is a crosslinking agent having an isocyanate group (-N=C=O), and preferred examples 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 at least one of

tolylene diisocyanate, hexamethylene diisocyanate and xylylene diisocyanate has been added to some or all of the hydroxyl groups of a polyol such as trimethylolpropane, and lysine diisocyanate.

[0045]

The isocyanate-based crosslinking agent contained in the adhesive composition may be either a single compound or two or more compounds.

[0046]

The amount of the isocyanate-based crosslinking agent in the adhesive composition, when the amount of the aforementioned alkyl (meth)acrylate ester copolymer is deemed to be 100 parts by mass, is preferably from 0.01 to 20 parts by mass, and more preferably from 0.1 to 10 parts by mass.

[0047]

(Photopolymerization Initiator)

The photopolymerization initiator may be 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 methoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxyacetophenone, and 2-methyl-1-[4-(methylthio)-phenyl]-2-morpholinopropane-1; benzoin ether-based compounds such as benzoin ethyl ether, benzoin isopropyl ether, and anisoil methyl ether; ketal-based compounds such as benzyl 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; benzophenone-based

compounds such as benzophenone, benzoyl benzoate, and 3,3'-dimethyl-4-methoxybenzophenone; thioxanthone-based compounds such as thioxanthone, 2-chlorothioxanthone, 2-methylthioxanthone, 2,4-dimethylthioxanthone, isopropylthioxanthone, 2,4-dichlorothioxanthone, 2,4-diethylthioxanthone, and 2,4-diisopropylthioxanthone; as well as camphorquinone, halogenated ketones, acyl phosphinoxides, and acyl phosphonates.

[0048]

The amount of the photopolymerization initiator in the adhesive composition, when the amount of the aforementioned alkyl (meth)acrylate ester copolymer is deemed to be 100 parts by mass, is preferably from 0.05 to 20 parts by mass.

[0049]

(Solvent)

The adhesive composition preferably also includes a solvent in addition to the alkyl (meth)acrylate ester copolymer described above.

Although there are no particular limitations on the solvent, examples of preferred solvents include hydrocarbons having a carbon number of 7 to 9, such as toluene and xylene; alcohols having a carbon number of 1 to 6, such as methanol, ethanol, 2-propanol, isobutyl alcohol (also known as 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 (namely, compounds having an amide linkage) such as dimethylformamide and N-methylpyrrolidone.

Among the above solvents, methyl ethyl ketone, toluene and ethyl acetate are preferred.

The solvent contained in the adhesive composition may be either a single solvent or two or more solvents.

[0050]

In those cases where the adhesive composition contains a solvent, the amount of the solvent is preferably sufficient to ensure that the solid fraction concentration of the composition, relative to the total mass of the composition, is from 10 to 50% by mass.

[0051]

(Other Components)

The adhesive composition may also contain, besides the alkyl (meth)acrylate ester copolymer described above, other components that do not correspond with any of the aforementioned isocyanate-based crosslinking agent, photopolymerization initiator or solvent, provided inclusion of these other components does not impair the effects of the present invention.

There are no particular limitations on these other components, and conventional materials may be selected as desired in accordance with the intended purpose. Specific examples of these other components include various additives such as dyes, pigments, degradation inhibitors, antistatic agents, flame retardants, silicone compounds, and chain transfer agents.

[0052]

The adhesive layer may be composed of one layer (a single layer), or may be composed of a plurality of two or more layers. In those cases where the adhesive layer 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 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" has the same meaning as that described above for the substrate.

[0053]

However, when the adhesive layer is composed of one layer (a single layer), this adhesive layer must necessarily be a layer containing the aforementioned alkyl (meth)acrylate ester copolymer, obtained using the adhesive composition described above. If the adhesive layer is composed of a plurality of layers, then among the plurality of layers, at least the layer that contacts the aforementioned film for forming a protective film (namely, the layer that is the most distant from the substrate in the thickness direction of the adhesive layer, hereafter also referred to as the uppermost layer) must be a layer containing the aforementioned alkyl (meth)acrylate ester copolymer, obtained using the adhesive composition described above. When the adhesive layer is composed of a plurality of layers, the one or more layers other than the layer that contacts the film for forming a protective film may all be layers containing the alkyl (meth)acrylate ester copolymer or may all be layers that do not contain the alkyl (meth)acrylate ester copolymer, or only a portion of the layers may be layers containing the alkyl (meth)acrylate ester copolymer.

[0054]

When the adhesive layer is composed of a single layer, the composition of the composite sheet for forming a protective film is simplified, and has the advantage of being able to be produced at lower cost.

On the other hand, when the adhesive layer is composed of a plurality of layers, as described above, the effects of the present invention can be obtained by ensuring that, among the plurality of layers, the layer that contacts the film for forming a protective film (namely, the uppermost layer) is a layer containing the alkyl (meth)acrylate ester copolymer. Moreover, among the plurality of layers, by ensuring that the layer that contacts the substrate (namely, the layer that is adjacent to the substrate in the thickness

direction of the adhesive layer, hereafter also referred to as the lowermost layer) is a layer that provides particularly superior adhesion to the substrate, the stability of the composite sheet for forming a protective film during use can be further improved. In this manner, forming the adhesive layer as a laminate composed of a plurality of layers has the advantage that the overall adhesive layer can be adjusted to form a layer having two or more characteristics.

[0055]

When the adhesive layer is composed of a plurality of layers, an adhesive layer that does not contain the alkyl (meth)acrylate ester copolymer may, for example, be the same as a conventional adhesive layer.

[0056]

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

[0057]

<Film for Forming a Protective Film>

The film for forming a protective film has heat curability, may have pressure-sensitive adhesiveness, and may soften upon heating to enable bonding to all manner of adherends. The film for forming a protective film undergoes heat curing to finally form a protective film having superior impact resistance, and this protective film also exhibits excellent shear strength, and is able to maintain satisfactory adhesion characteristics even under severe conditions of high temperature and high humidity.

[0058]

Although there are no particular limitations on the thickness of the film for forming a protective film, the thickness is preferably from 1 to 100 μm , more preferably

from 5 to 75 μm , and even more preferably from 5 to 50 μm . By ensuring that the thickness of the film for forming a protective film is at least as large as the above lower limit, the adhesive strength to the semiconductor wafer and semiconductor chips that represent the adherend can be improved. Further, by ensuring that the thickness of the film for forming a protective film is not more than the above upper limit, the shear strength can be utilized during pickup of the semiconductor chips to enable the protective film composed of the cured product to be cut more easily.

[0059]

There are no particular limitations on the film for forming a protective film, provided it is a film having heat curability.

Examples of preferred films for forming a protective film include those containing a polymer component (A) and a heat-curable component (B). The polymer component (A) is a component that can be considered to have been formed by a polymerization reaction of a polymerizable compound.

Further, the heat-curable component (B) is a component that can undergo a curing (polymerization) reaction upon heating. In the present invention, polymerization reactions are deemed to also include polycondensation reactions.

[0060]

[Composition for Forming Protective Film]

The film for forming a protective film can be formed from a composition for forming a protective film that contains the components that constitute the film for forming a protective film. The ratio between the amounts of those components within the composition for forming a protective film that do not vaporize at normal temperature is typically the same as the ratio between the amounts of those components in the film for forming a protective film.

Examples of preferred compositions for forming a protective film include those containing a polymer component (A) and a heat-curable component (B), and compositions containing a polymer component (A), a heat-curable component (B), and a curing accelerator (C) are preferred. Next is a description of the components within the aforementioned composition for forming a protective film and film for forming a protective film.

[0061]

(Polymer Component (A))

The polymer component (A) is a polymer compound that imparts the film for forming a protective film with film formability and flexibility and the like. The polymer component (A) may sometimes also correspond with the heat-curable component (B).

For example, phenoxy resins and acrylic-based resins having an epoxy group on a side chain correspond with the polymer component (A), and may also sometimes correspond with the heat-curable component (B). This type of component is treated as a polymer component (A).

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

[0062]

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 resin are preferred.

[0063]

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

The weight average molecular weight (Mw) 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 protective film described below and the cured adhesive layer 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 forming a protective film can more easily conform to any uneven surfaces on the adherend, thus suppressing the occurrence of voids or the like between the adherend and the film for forming a protective film.

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

[0064]

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 peel strength between the protective film described below and the cured adhesive layer is reduced, thus 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, and adhesive strength between the film for forming a protective film and the semiconductor wafer increases, enabling the semiconductor wafer to be secured in a more stable manner.

[0065]

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 having a carbon number of 1 to 18, 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 (lauryl (meth)acrylate), tridecyl (meth)acrylate, tetradecyl (meth)acrylate (myristyl (meth)acrylate), pentadecyl (meth)acrylate, hexadecyl (meth)acrylate (palmityl (meth)acrylate), heptadecyl (meth)acrylate, and octadecyl (meth)acrylate (stearyl (meth)acrylate);

(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.

Further, the acrylic-based resin may also be produced by copolymerization using another monomer such as acrylic acid, methacrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene or N-methylolacrylamide.

Either a single monomer or two or more monomers may constitute the acrylic-based resin.

[0066]

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 (F) described below, or bonded directly to the other compound without requiring a crosslinking agent (F). Bonding the acrylic-based

resin to another compound via the above functional group tends to improve the package reliability of semiconductor devices obtained using the composite sheet for forming a protective film.

[0067]

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

In this manner, when the film for forming a protective film contains an acrylic-based resin as the polymer component (A), the amount of the acrylic-based resin in the film for forming a protective film is preferably from 5 to 50% by mass relative to the total mass of the film for forming a protective film.

[0068]

In the present invention, in terms of improving the pickup characteristics of the semiconductor chips with a protective film by reducing the adhesive strength (also referred to as the peel strength) between the protective film and the cured adhesive layer, and suppressing the occurrence of voids and the like between the adherend and the film for forming a protective film by making the film for forming a protective film 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).

[0069]

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.

[0070]

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.

[0071]

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

[0072]

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

[0073]

(Heat-Curable Component (B))

The heat-curable component (B) is the component used for curing the film for forming a protective film to form a hard protective film. In some cases, the heat-curable component (B) may also correspond with the polymer component (A), but those types of components are dealt with as the polymer component (A).

Either a single compound or a combination of two or more compounds may be used as the heat-curable component (B).

[0074]

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

[0075]

- Epoxy-based heat-curable resins

An epoxy-based heat-curable resin is composed of an epoxy resin (B11) and a heat curing agent (B12).

Either a single resin or a combination of two or more resins may be used as the epoxy-based heat-curable resin.

[0076]

Examples of the epoxy resin (B11) include conventional materials such as polyfunctional epoxy resins, biphenyl compounds, bisphenol A glycidyl ether and hydrogenated products thereof, ortho-cresol novolac epoxy resins, dicyclopentadiene epoxy resins, biphenyl epoxy resins, bisphenol A epoxy resins, bisphenol F epoxy resins, phenylene backbone epoxy resins, and difunctional or higher epoxy compounds. Among the above compounds, bisphenol A epoxy resins and dicyclopentadiene epoxy resins are preferred.

[0077]

An epoxy resin having an unsaturated hydrocarbon group may also be used as the epoxy resin (B11).

Examples of this epoxy resin having an unsaturated hydrocarbon group include compounds in which a portion of the epoxy groups of a polyfunctional epoxy resin have each been substituted with a group containing an unsaturated hydrocarbon group.

[0078]

Although there are no particular limitations on the number average molecular weight of the epoxy resin (B11), from the viewpoints of the curability of the film for forming a protective film, and the strength and heat resistance of the cured protective film, the number average molecular weight is preferably from 100 to 20,000.

Here, the "number average molecular weight" represents the polystyrene-equivalent value measured by a gel permeation chromatography method (GPC) method.

The epoxy equivalent weight of the epoxy resin (B11) is preferably from 100 to 1,100 g/eq, and more preferably from 150 to 1,000 g/eq.

[0079]

Either a single resin or a combination of two or more resins may be used as the epoxy resin (B11).

[0080]

The heat curing agent (B12) functions as a curing agent for the epoxy resin (B11).

Examples of the heat curing agent (B12) include compounds having two or more functional groups that can react with an epoxy group within each molecule. Examples of these functional groups include a phenolic hydroxyl group, alcoholic hydroxyl group, amino group, carboxyl group and acid anhydride group, and of these, a phenolic hydroxyl group, amino group or acid anhydride group is preferred, a phenolic hydroxyl group or amino group is more preferred, and an amino group is particularly desirable.

[0081]

Of the various heat curing agents (B12), examples of phenol-based curing agents having phenolic hydroxyl groups include polyfunctional phenol resins, biphenol, novolac phenol resins, dicyclopentadiene phenol resins and aralkylphenol resins.

Of the various heat curing agents (B12), examples of amine-based curing agents having amino groups include dicyandiamide (hereafter sometimes abbreviated as "DICY") and the like.

[0082]

The heat curing agent (B12) may be a compound having an unsaturated hydrocarbon group.

Examples of this heat curing agent (B12) having an unsaturated hydrocarbon group include compounds in which a portion of the hydroxyl groups of a phenol resin have each been substituted with a group containing an unsaturated hydrocarbon group, and compounds in which a group having an unsaturated hydrocarbon group has been bonded directly to an aromatic ring of a phenol resin.

Examples of the unsaturated hydrocarbon group in the heat curing agent (B12) include the same groups as the unsaturated hydrocarbon group in the aforementioned epoxy resin having an unsaturated hydrocarbon group.

[0083]

Either a single compound or a combination of two or more compounds may be used as the heat curing agent (B12).

[0084]

It is preferable that the heat curing agent (B12) is solid at normal temperature and exhibits no curing activity relative to the epoxy resin (B11), but then melts upon heating, and then exhibits curing activity relative to the epoxy resin (B11) (hereafter also referred to as a "solid dispersion-type latent curing agent"). In other words, the film for forming a protective film preferably contains the epoxy resin (B11), and a solid dispersion-type latent curing agent as the heat curing agent (B12).

This solid dispersion-type latent curing agent is dispersed stably in the epoxy resin (B11) of the film for forming a protective film at normal temperature, but then undergoes mutual dissolution with the epoxy resin (B11) upon heating, causing reaction with the epoxy resin (B11). By using a solid dispersion-type latent curing agent, the storage stability of the composite sheet for forming a protective film improves markedly. For example, migration of the curing agent from the film for forming a protective film into the adjacent adhesive layer is suppressed, and any deterioration in the heat curability of the film for forming a protective film can be effectively suppressed. Consequently, because the degree of heat curing upon heating of the film for forming a protective film can be improved, the pickup characteristics of the semiconductor chips with a protective film described below can be further improved.

[0085]

Examples of the above solid dispersion-type latent curing agent include onium salts, dibasic acid hydrazides, dicyandiamide, and amine adducts of curing agents.

[0086]

The amount of the heat curing agent (B12) in the composition for forming a protective film and the film for forming a protective film, when the amount of the epoxy resin (B11) is deemed to be 100 parts by mass, is preferably from 0.1 to 500 parts by mass, and more preferably from 1 to 200 parts by mass. Ensuring that the amount of the heat curing agent (B12) is at least as large as the above lower limit enables the curing of the film for forming a protective film to proceed more readily.

Further, by ensuring that the amount of the heat curing agent (B12) is not more than the above upper limit, the coefficient of moisture absorption for the film for forming a protective film is reduced, and the package reliability can be further improved.

[0087]

The amount of the heat-curable component (B) in the composition for forming a protective film and the film for forming a protective film, when the amount of the polymer component (A) is deemed to be 100 parts by mass, is preferably from 1 to 100 parts by mass, more preferably from 1.5 to 85 parts by mass, and even more preferably from 2 to 70 parts by mass. By ensuring that the amount of the heat-curable component (B) satisfies this type of range, the adhesive strength (peel strength) between the protective film and the cured adhesive layer can be further reduced, and the pickup characteristics of the semiconductor chips with a protective film are further improved.

[0088]

(Curing Accelerator (C))

The curing accelerator (C) is a component for adjusting the curing rate of the composition for forming a protective film.

Examples of preferred curing accelerators (C) include tertiary amines such as triethylenediamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol and tris(dimethylaminomethyl)phenol; imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole, and 2-phenyl-4-methyl-5-hydroxymethylimidazole (namely, imidazoles in which at least one hydrogen atom has been substituted with a group other than a hydrogen atom); organophosphines such as tributylphosphine, diphenylphosphine, and triphenylphosphine (phosphines in which at least one hydrogen atom has been substituted with an organic group); and tetraphenylborates such as tetraphenylphosphonium tetraphenylborate and triphenylphosphine tetraphenylborate.

Among the above compounds, 2-phenyl-4,5-dihydroxymethylimidazole is preferred.

[0089]

Either a single compound or a combination of two or more compounds may be used as the curing accelerator (C).

[0090]

The composition for forming a protective film preferably contains an aforementioned imidazole as the curing accelerator (C), particularly in those cases where the composition contains an aforementioned solid dispersion-type latent curing agent as the heat curing agent (B12). In other words, the film for forming a protective film preferably contains the epoxy resin (B11), a solid dispersion-type latent curing agent as the heat curing agent (B12), and an imidazole as the curing accelerator (C).

In other words, one aspect of the film for forming a protective film contains the polymer component (A), the epoxy resin (B11), a solid dispersion-type latent curing agent as the heat curing agent (B12), and an imidazole as the curing accelerator (C).

[0091]

In those cases where the curing accelerator (C) is used, the amount of the curing accelerator (C) in the composition for forming a protective film and the film for forming a protective film, when the amount of the heat-curable component (B) is deemed to be 100 parts by mass, is preferably from 0.01 to 10 parts by mass, and more preferably from 0.1 to 4 parts by mass. Provided the amount of the curing accelerator (C) satisfies this type of range, the film for forming a protective film exhibits excellent adhesiveness even under conditions of high temperature and high humidity, and superior package reliability can be achieved even when exposed to severe reflow conditions. By ensuring that the amount of the curing accelerator (C) is at least as large as the above lower limit, the effects obtained by using the curing accelerator (C) manifest more markedly. Further, by ensuring that the amount of the curing accelerator (C) is not more than the above upper limit, although the curing accelerator (C) typically exhibits high polarity, precipitation

within the film for forming a protective film at the bonding interface with the adherend can still be suppressed under conditions of high temperature and high humidity, meaning the package reliability is improved.

[0092]

If necessary, in order to improve any of various physical properties, the film for forming a protective film may also be formed from a composition for forming a protective film that contains other components besides the polymer component (A), the heat-curable component (B) and the curing accelerator (C).

Examples of these other components that may be included in the composition for forming a protective film and the film for forming a protective film include fillers (D), coupling agents (E), crosslinking agents (F), and general-purpose additives (G).

[0093]

(Filler (D))

A filler (D) is usually included in the composition for forming a protective film to facilitate adjustment of the coefficient of thermal expansion. Accordingly, by using this type of composition for forming a protective film, the coefficient of thermal expansion of the cured protective film can be optimized relative to the semiconductor chips, enabling the package reliability to be improved.

Further, by using a composition for forming a protective film that contains the filler (D), the coefficient of moisture absorption of the cured protective film can usually also be reduced.

[0094]

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.

[0095]

Either a single material or a combination of two or more materials may be used as the filler (D).

[0096]

In those cases where the filler (D) is used, the amount of the filler (D) relative to the total mass of the composition for forming a protective film besides the solvent (namely, the amount of the filler (D) within the film for forming a protective film) is preferably from 5 to 80% by mass, and more preferably from 7 to 60% by mass. Ensuring that the amount of the filler (D) falls within this type of range facilitates adjustment of the aforementioned coefficient of thermal expansion.

[0097]

(Coupling Agent (E))

By using a material having a functional group that can react with an inorganic compound or an organic compound as a coupling agent (E), the adhesiveness and adherence of the film for forming a protective film to the adherend can be improved. Further, by including the coupling agent (E), the protective film obtained upon curing of the film for forming a protective film is able to exhibit improved water resistance without losing any heat resistance.

[0098]

The coupling agent (E) is preferably a compound having a functional group that reacts with the functional groups of the polymer component (A) and/or the heat-curable component (B), and is most preferably a silane coupling agent.

Examples of preferred silane coupling agents include γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropylmethyldiethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -(methacryloxypropyl)trimethoxysilane, γ -aminopropyltrimethoxysilane, N-6-(aminoethyl)- γ -aminopropyltrimethoxysilane, N-6-(aminoethyl)- γ -aminopropylmethyldiethoxysilane, N-phenyl- γ -aminopropyltrimethoxysilane, γ -ureidopropyltriethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfan, methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, vinyltriacetoxysilane, and imidazole silane.

[0099]

Either a single compound or a combination of two or more compounds may be used as the coupling agent (E).

[0100]

In those cases where the coupling agent (E) is used, the amount of the coupling agent (E) in the composition for forming a protective film and the film for forming a protective film, when the combined amount of the polymer component (A) and the heat-curable component (B) is deemed to be 100 parts by mass, is preferably from 0.03 to 20 parts by mass, more preferably from 0.05 to 10 parts by mass, and even more preferably from 0.1 to 5 parts by mass. Provided the amount of the coupling agent (E) is at least as large as the above lower limit, the effects obtained by using the coupling agent (E) manifest more markedly, whereas provided the amount of the coupling agent (E) is not more than the above upper limit, the generation of out-gas is better suppressed.

[0101]

(Crosslinking Agent (F))

When 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 (F) may be used to achieve crosslinking by binding this functional group to other compounds. By using the crosslinking agent (F) to achieve crosslinking, the initial adhesive strength and the cohesion of the film for forming a protective film can be adjusted.

[0102]

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

[0103]

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.

[0104]

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.

[0105]

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

[0106]

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

[0107]

In those cases where the crosslinking agent (F) is used, the amount of the crosslinking agent (F) in the composition for forming a protective film, 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 even more preferably from 0.5 to 5 parts by mass.

[0108]

(General-Purpose Additives (G))

Examples of the general-purpose additives (G) include conventional plasticizers, antistatic agents, antioxidants, pigments, dyes and gettering agents.

[0109]

(Solvent)

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

The solvent contained in the composition for forming a protective film may be the same as the solvent used in the adhesive composition described above.

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

The amount of the solvent in the composition for forming a protective film, relative to the total mass of the composition for forming a protective film, is preferably adjusted so that the solid fraction concentration of the composition for forming a protective film is from 35 to 75% by mass.

[0110]

In other words, another aspect of the composition for forming a protective film contains the polymer component (A), the heat-curable component (B), the curing accelerator (C), and one or more components selected from the group consisting of solvents, fillers (D), coupling agents (E), crosslinking agents (F) and general-purpose additives (G) as desired.

Another aspect of the film for forming a protective film contains the polymer component (A), the heat-curable component (B), the curing accelerator (C), and one or more components selected from the group consisting of fillers (D), coupling agents (E), crosslinking agents (F) and general-purpose additives (G) as desired.

Moreover, it is preferable that the heat-curable component (B) contains the epoxy resin (B11) and an aforementioned solid dispersion-type latent curing agent as the heat curing agent (B12), and that the curing accelerator (C) contains an imidazole.

[0111]

The composition for forming a protective film is obtained by blending together the components that constitute the composition, and with the exception that the blend components are different, can be obtained using the same method as that described above for the adhesive composition.

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.

[0112]

The composite sheet for forming a protective film may also have release films provided on the exposed surfaces such as the surface of the film for forming a protective film and the surface of the adhesive layer. These release films may be peeled off (and removed) when the composite sheet for forming a protective film is used.

[0113]

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

The composite sheet 1 for forming a protective film illustrated in the figure is prepared by providing an adhesive layer 12 on a substrate 11 and providing a film 13 for forming a protective film on the adhesive layer 12, and has a structure in which the film 13 for forming a protective film is provided on the adhesive layer 12 of a support sheet 10. Further, the composite sheet 1 for forming a protective film also has a release film

14 provided on the film 13 for forming a protective film. The adhesive layer 12 that contacts the film 13 for forming a protective film is a layer containing an alkyl (meth)acrylate ester copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater.

[0114]

In the composite sheet 1 for forming a protective film, the adhesive layer 12 is laminated on a surface 11a of the substrate 11, and the film 13 for forming a protective film is laminated to a portion of a surface 12a of the adhesive layer 12. The release film 14 is then laminated onto the exposed portion of the surface 12a of the adhesive layer 12 on which the film 13 for forming a protective film has not been laminated and a surface 13a (the upper surface and side surfaces) of the film 13 for forming a protective film.

Voids may exist between the release film 14 and the surface 12a of the adhesive layer 12 or the surface 13a of the film 13 for forming a protective film. For example, voids tend to form readily between the release film 14, and either a region, within the surface 13a of the film 13 for forming a protective film, that is indicated by the symbol 130a (namely, a region on the side near the adhesive layer 12), or a region, within the surface 12a of the adhesive layer 12, that is indicated by a symbol 120a (namely, a region on the side facing the film 13 for forming a protective film). In other words, voids tend to occur more readily in the region where the film 13 for forming a protective film contacts the release film 14 near the interface between the film 13 for forming a protective film and the adhesive layer 12.

[0115]

The composite sheet 1 for forming a protective film illustrated in FIG. 1 is used by removing the release film 14, affixing the back surface of a semiconductor wafer (not

shown in the figure) to the surface 13a of the film 13 for forming a protective film, and affixing the exposed surface of the surface 12a of the adhesive layer 12 to which the film 13 for forming a protective film has not been laminated to a jig such as a ring frame.

[0116]

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

A composite sheet 2 for forming a protective film is the same as the composite sheet 1 for forming a protective film illustrated in FIG. 1, with the exceptions that a film 23 for forming a protective film is formed across the entire surface 12a of the adhesive layer 12, a jig adhesive layer 15 is laminated to a portion of a surface 23a of the film 23 for forming a protective film, and the release film 14 is then laminated onto the exposed portion of the surface 23a of the film 23 for forming a protective film on which the jig adhesive layer 15 has not been laminated and a surface 15a (upper surface and side surface) of the jig adhesive layer 15. The adhesive layer 12 that contacts the film 23 for forming a protective film is a layer containing an alkyl (meth)acrylate ester copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater.

In other words, one aspect of the composite sheet for forming a protective film according to the present invention includes:

a substrate, an adhesive layer, a film for forming a protective film, a jig adhesive layer, and a release film, wherein

the adhesive layer is laminated on top of the substrate,

the film for forming a protective film is laminated across the entire surface of the adhesive layer,

the jig adhesive layer is laminated onto a portion of the surface of the film for forming a protective film,

the release film is laminated onto the exposed portion of the surface of the film for forming a protective film on which the jig adhesive layer has not been laminated, and onto the upper surface and side surface of the jig adhesive layer, and

the adhesive layer that contacts the film for forming a protective film contains an alkyl (meth)acrylate ester copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is at least 8 but not more than 18.

[0117]

The jig adhesive layer 15 may be a single-layer structure containing an adhesive component, or a multilayer structure in which layers containing an adhesive component are laminated to both surfaces of a sheet that functions as a core.

[0118]

Voids may exist between the release film 14 and the surface 23a of the film 23 for forming a protective film or the surface 15a of the jig adhesive layer 15. For example, voids tend to form readily between the release film 14, and a region, within the surface 15a of the jig adhesive layer 15, that is indicated by the symbol 150a (namely, a region on the side near the film 23 for forming a protective film), or a region, within the surface 23a of the film 23 for forming a protective film, that is indicated by a symbol 230a (namely, a region on the side facing the jig adhesive layer 15).

In other words, voids tend to occur more readily in the region where the structure contacts the release film 14 near the interface between the jig adhesive layer 15 and the film 23 for forming a protective film.

[0119]

The composite sheet 2 for forming a protective film illustrated in FIG. 2 is used by removing the release film 14, affixing the back surface of a semiconductor wafer (not shown in the figure) to the surface 23a of the film 23 for forming a protective film, and affixing the upper surface of the surface 15a of the jig adhesive layer 15 to a jig such as a ring frame.

[0120]

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

The composite sheet 3 for forming a protective film illustrated in this figure is the same as the composite sheet 1 for forming a protective film illustrated in FIG. 1, with the exception that the adhesive layer 12 is replaced with an adhesive layer 32 having a two-layer structure obtained by laminating a first adhesive layer 321 and a second adhesive layer 322 in that order from the side of the substrate 11.

When the composite sheet 3 for forming a protective film is viewed in plan view from above, the second adhesive layer 322 has the same surface area as the film 13 for forming a protective film, and is disposed so that the peripheral edges coincide with those of the film 13 for forming a protective film. The film 13 for forming a protective film is provided on the adhesive layer 32 on a surface 32a on the opposite side from the substrate side (namely, a surface 322a of the second adhesive layer 322). The first adhesive layer 321 is provided so as to cover the entire surface of the surface 11a of the

substrate 11, so that when viewed in plan view as described above, the first adhesive layer 321 has a larger surface area than the second adhesive layer 322.

[0121]

In the composite sheet 3 for forming a protective film, the second adhesive layer 322 that contacts the film 13 for forming a protective film contains an alkyl (meth)acrylate ester copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater. The first adhesive layer 321 that does not contact the film 13 for forming a protective film may either contain, or not contain, the above alkyl (meth)acrylate ester copolymer.

In other words, one aspect of the composite sheet for forming a protective film according to the present invention includes:

a substrate, a first adhesive layer, a second adhesive layer, a film for forming a protective film, a jig adhesive layer, and a release film, wherein

the first adhesive layer is provided on top of the substrate so as to cover the upper surface of the substrate,

the second adhesive layer is provided on top of the first adhesive layer,

the film for forming a protective film is provided on top of the second adhesive layer so that the peripheral portions coincide with those of the second adhesive layer,

the release film is laminated onto the upper surface and side surfaces of the film for forming a protective film, the side surfaces of the second adhesive layer, and the surface of the first adhesive layer on which the second adhesive layer has not been laminated, and

when viewed in plan view from above,

the second adhesive layer has the same surface area as the film for forming a protective film, and the first adhesive layer has a larger surface area than the second adhesive layer, and

the second adhesive layer contains an alkyl (meth)acrylate ester copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is at least 8 but not more than 18.

[0122]

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

The composite sheet 4 for forming a protective film illustrated in this figure is the same as the composite sheet 2 for forming a protective film illustrated in FIG. 2, with the exception that the adhesive layer 12 is replaced with an adhesive layer 42 having a two-layer structure obtained by laminating a first adhesive layer 421 and a second adhesive layer 422 in that order from the side of the substrate 11.

When the composite sheet 4 for forming a protective film is viewed in plan view from above, both the first adhesive layer 421 and the second adhesive layer 422 have the same surface area as the film 23 for forming a protective film

The film 23 for forming a protective film is provided on top of a surface 42a of the adhesive layer 42 (namely, a surface 422a of the second adhesive layer 422).

[0123]

In the composite sheet 4 for forming a protective film, the second adhesive layer 422 that contacts the film 23 for forming a protective film contains an alkyl (meth)acrylate ester copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the

alkyl ester is at 8 or greater. The first adhesive layer 421 that does not contact the film 23 for forming a protective film may either contain, or not contain, the above alkyl (meth)acrylate ester copolymer.

In other words, one aspect of the composite sheet for forming a protective film according to the present invention includes:

a substrate, a first adhesive layer, a second adhesive layer, a film for forming a protective film, a jig adhesive layer, and a release film, wherein

the first adhesive layer is laminated on top of the substrate,

the second adhesive layer is laminated on top of the first adhesive layer,

the film for forming a protective film is laminated on top of the second adhesive layer,

the jig adhesive layer is laminated onto a portion of the surface of the film for forming a protective film,

the release film is laminated onto the exposed portion of the surface of the film for forming a protective film onto which the jig adhesive layer has not been laminated, and the upper surface and side surface of the jig adhesive layer, and

when viewed in plan view from above,

the first adhesive layer, the second adhesive layer 422, and the film 23 for forming a protective film have the same surface area, and

the second adhesive layer that contacts the film for forming a protective film contains an alkyl (meth)acrylate ester copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is at least 8 but not more than 18.

[0124]

The composite sheet for forming a protective film according to the present invention is not limited to only the structures illustrated in FIG. 1 to FIG. 4, and composite sheets in which a portion of the structures illustrated in any of FIG. 1 to FIG. 4 have been altered or eliminated, and composite sheets that contain additional structures to those already described may also be used, provided the effects of the present invention are not impaired.

For example, in the composite sheet 3 for forming a protective film illustrated in FIG. 3, when the structure is viewed in plan view from above, the second adhesive layer 322 has the same surface area as the film 13 for forming a protective film but a smaller surface area than the first adhesive layer 321, but the second adhesive layer 322 need not necessarily have the same surface area as the film 13 for forming a protective film, and for example may have a larger surface area than the film 13 for forming a protective film, and in such a case, the second adhesive layer 322 may have the same surface area as the first adhesive layer 321.

[0125]

Furthermore, in both the composite sheet 3 for forming a protective film illustrated in FIG. 3 and the composite sheet 4 for forming a protective film illustrated in FIG. 4, the adhesive layer has a two-layer structure, but the adhesive layer may also have a laminated structure with 3 or more layers. In such cases, the layer among the 3 or more adhesive layers that contacts the film for forming a protective film (namely, the uppermost layer that is most distant from the substrate in the thickness direction of the adhesive layer) contains the alkyl (meth)acrylate ester copolymer, and the other layers may either contain, or not contain, the alkyl (meth)acrylate ester copolymer.

[0126]

As described below in the examples, in a composite sheet for forming a protective film having a size of 25 mm × 150 mm, the peel strength, which is measured as the load required to peel the uncured adhesive layer from the protective film under conditions including a peel angle of 180°, a temperature of 23°C and a pull speed of 300 mm/minute (hereafter sometimes referred to as the "peel strength before adhesive layer curing"), is preferably at least 2,000 mN/25mm, and more preferably at least 2,200 mN/25mm.

[0127]

In a similar manner, and as described in the examples, in a composite sheet for forming a protective film having a size of 25 mm × 150 mm, the peel strength, which is measured as the load required to peel the cured adhesive layer from the protective film under conditions including a peel angle of 180°, a temperature of 23°C and a pull speed of 300 mm/minute (hereafter sometimes referred to as the "peel strength after adhesive layer curing"), is preferably not more than 2,000 mN/25mm, and for example may be not more than 1,700 mN/25mm, not more than 1,200 mN/25mm, or 700 mN/25mm or less.

[0128]

In the present invention, for the aforementioned composite sheet for forming a protective film having a size of 25 mm × 150 mm, the ratio of the aforementioned peel strength before adhesive layer curing relative to the peel strength after adhesive layer curing (namely, [peel strength before adhesive layer curing] / [peel strength after adhesive layer curing]) is preferably at least 1.5, and for example may be at least 3, at least 6, or 12 or greater.

[0129]

<Method for Producing Composite Sheet for Forming a Protective Film>

The composite sheet for forming a protective film according to the present invention can be produced, for example, by forming an adhesive layer from the

aforementioned adhesive composition on a substrate, and then forming a film for forming a protective film from the aforementioned composition for forming a protective film on the adhesive layer.

[0130]

The adhesive layer can be formed by applying the adhesive composition to the surface of the substrate (the surface 11a of the substrate 11 in FIG. 1 and FIG. 2), and then drying the composition. At this time, if required, the applied adhesive composition may be subjected to crosslinking by heating. The heating conditions preferably involve heating at 100 to 130°C for 1 to 5 minutes, but heating is not limited to these conditions. Further, the adhesive layer can also be formed by applying the adhesive composition to the release layer surface of a release material, drying the composition to form an adhesive layer, affixing the adhesive layer to the surface of a substrate, and then removing the release material.

[0131]

Application of the adhesive composition to the surface of a substrate or the release layer surface of a release material 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.

[0132]

The film for forming a protective film can be formed from the composition for forming a protective film using a similar method to that described above for forming the adhesive layer on the substrate, but direct application of the composition for forming a protective film to the adhesive layer is usually problematic. Accordingly, it is preferable to use a method in which the film for forming a protective film is formed separately and

subsequently affixed to the surface of the adhesive layer, for example by applying the composition for forming a protective film to the release layer surface of a release material, drying the composition to form a film for forming a protective film, affixing this film for forming a protective film to the surface of the adhesive layer, and then removing the release material.

[0133]

Furthermore, the composite sheet for forming a protective film according to the present invention can also be produced using other methods besides those described above, for example by forming an adhesive layer from the adhesive composition, forming a film for forming a protective film from the composition for forming a protective film, overlaying the adhesive layer and the film for forming a protective film to form a laminate, and then affixing the adhesive layer surface of this laminate (the surface of the adhesive layer on which the film for forming a protective film is not provided) to a substrate.

In this case, the conditions used for forming the adhesive layer and the film for forming a protective film may be the same as those used in the above method.

[0134]

For example, when a composite sheet for forming a protective film such as that illustrated in FIG. 1 is viewed in plan view from above, in those cases where a composite sheet for forming a protective film is to be produced in which the film for forming a protective film has a smaller surface area than the adhesive layer, by using the above production method, a film for forming a protective film that has been cut in advance to the prescribed size and shape may simply be disposed on the adhesive layer.

[0135]

<Method for Using Composite Sheet for Forming a Protective Film>

A method for using the composite sheet for forming a protective film according to the present invention is as described below.

In other words, the back surface of a semiconductor wafer is first affixed to the film for forming a protective film of the composite sheet for forming a protective film, and the composite sheet for forming a protective film is secured in a dicing apparatus.

Subsequently, the film for forming a protective film is cured by heating (for example, at 130°C for 2 hours) to form a protective film. 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 prior to formation of the protective film.

[0136]

Next, the semiconductor wafer is subjected to dicing to form semiconductor chips. In the period following formation of the protective film until the dicing is performed, the protective film may be irradiated with a laser light from the substrate side of the composite sheet for forming a protective film to form printing on the surface of the protective film. In this case, as described above, because the peel strength between the adhesive layer before curing and the protective film is sufficiently large, even if gas is generated by the laser printing, peeling between the adhesive layer and the protective film is suppressed, and gas accumulation is suppressed. Further, because the semiconductor wafer can be secured in a firm and stable manner on the composite sheet for forming a protective film, chip flying and the like is suppressed during dicing, and dicing can be performed in stable manner. In those cases where laser printing is performed, as mentioned above, because peeling between the adhesive layer and the protective film is suppressed and the occurrence of gas accumulation is also suppressed, the printing formed on the protective film can be clearly recognized visually through the substrate and the adhesive layer.

[0137]

Subsequently, the adhesive layer is cured by irradiation with active energy rays (such as ultraviolet rays or an electron beam), and semiconductor chips with a protective film are then obtained by picking up each of the semiconductor chips, together with the protective film affixed to the back surface of the chip, from the cured adhesive layer. At this time, because the peel strength between the cured adhesive layer and the protective film is sufficiently small, the semiconductor chips with a protective film can be picked up easily in a stable manner, and the occurrence of cracking and chipping of the chips during pickup can be suppressed.

[0138]

For example, when the composite sheet 1 for forming a protective film illustrated in FIG. 1 is used, the back surface of a semiconductor wafer is affixed to the film 13 for forming a protective film of the composite sheet 1 for forming a protective film, and the exposed portion of the adhesive layer 12 is affixed to a dicing jig such as a ring frame (not shown in the figure), thereby securing the composite sheet 1 for forming a protective film to the dicing apparatus. Subsequently, following curing of the film 13 for forming a protective film to form a protective film, dicing is performed, the regions of the adhesive layer 12 other than the location where the adhesive layer is affixed to the jig are cured by irradiation with active energy rays, and the semiconductor chips with the protective film may then be picked up. In this manner, when the composite sheet 1 for forming a protective film is used, it is necessary to ensure that a specific region of the adhesive layer 12 does not undergo curing, to ensure that the composite sheet does not peel off the jig. On the other hand, when the composite sheet 1 for forming a protective film is used, there is no need to provide a separate structure for affixing the composite sheet to the jig.

[0139]

In comparison, when the composite sheet 2 for forming a protective film illustrated in FIG. 2 is used, the back surface of a semiconductor wafer is affixed to the film 23 for forming a protective film of the composite sheet 2 for forming a protective film, and the jig adhesive layer 15 is affixed to a dicing jig such as a ring frame (not shown in the figure), thereby securing the composite sheet 2 for forming a protective film to the dicing apparatus. Subsequently, following curing of the film 23 for forming a protective film to form a protective film, dicing is performed, the adhesive layer 12 is cured by irradiation with active energy rays, and the semiconductor chips with the protective film may then be picked up. In this manner, when the composite sheet 2 for forming a protective film is used, unlike the case where the composite sheet 1 for forming a protective film is used, there is no need to ensure that a specific region of the adhesive layer 23 does not undergo curing. On the other hand, unlike the composite sheet 1 for forming a protective film, the composite sheet 2 for forming a protective film requires the inclusion of the jig adhesive layer 15. By including the jig adhesive layer 15, a much wider range of compositions may be selected for the adhesive layer 12 in accordance with the intended purpose.

[0140]

As described above, the composite sheet for forming a protective film according to the present invention is a sheet that is suitable for the case where the film for forming a protective film is cured to form a protective film, and the adhesive layer is then cured, and when the dicing of the semiconductor wafer and the pickup of the semiconductor chips are performed, the film for forming a protective film is completely cured or substantially completely cured. Moreover, in the composite sheet for forming a protective film according to the present invention, the peel strength between the adhesive layer and the protective film changes markedly from before curing to after curing of the

adhesive layer. This is because the adhesive layer contains the specified alkyl (meth)acrylate ester copolymer as an essential component.

In comparison, in the case of a conventional composite sheet for forming a protective film, such as the composite sheet disclosed in Japanese Unexamined Patent Application, First Publication No. 2011-228450 (Patent Document 1) that was described above, when pickup of the semiconductor chips is performed, the film for forming a protective film remains in either an uncured or partially cured state, and this uncured or partially cured film for forming a protective film undergoes complete curing or substantially complete curing at the same time as the bonding of the semiconductor chip and the curing of a sealing material. In other words, when this conventional composite sheet for forming a protective film is used, at the stages where dicing of the semiconductor wafer and pickup of the semiconductor chips are performed, the film affixed to the back surface of the wafer and chips has completely different characteristics from the film used in the present invention. In this prior document, absolutely no mention is made of compositions of an adhesive layer and a film for forming a protective film that are suitable for the case where curing of the film for forming a protective film is performed prior to dicing.

[0141]

A separate aspect of the composite sheet for forming a protective film according to the present invention contains a substrate, an adhesive layer, and a film for forming a protective film, wherein

the adhesive layer is laminated on top of the substrate, and the film for forming a protective film is laminated on top of the adhesive layer;

the adhesive layer has active energy ray curability and contains an alkyl (meth)acrylate ester copolymer at least in the layer that contacts the film for forming a protective film, and

the alkyl (meth)acrylate ester copolymer is a copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is at least 8 but not more than 18;

the film for forming a protective film has heat curability; and

when the composite sheet for forming a protective film is cut to a size of 25 mm $\times$ 150 mm and then bonded to a silicon wafer at 70°C, and the composite sheet for forming a protective film is subsequently heated at 130°C for 2 hours to cure the film for forming a protective film and form a protective film, the peel strength between the uncured adhesive layer and the protective film (the peel strength before adhesive layer curing), measured under conditions including a peel angle of 180°, a measurement temperature of 23°C and a pull speed of 300 mm/minute, is at least 2,000 mN/25mm, and is preferably at least 2,300 mN/25mm but not more than 6,300 mN/25mm.

Moreover, in this composite sheet for forming a protective film, when the adhesive layer is cured by irradiating ultraviolet rays onto the composite sheet for forming a protective film under conditions including an illuminance of 220 mW/cm² and an irradiation dose of 190 mJ/cm², the peel strength between the cured adhesive layer and the protective film (the peel strength after adhesive layer curing), measured under conditions including a peel angle of 180°, a measurement temperature of 23°C and a pull speed of 300 mm/minute, is not more than 2,000 mN/25mm, and is preferably at least 500 mN/25mm but not more than 1500 mN/25mm.

[0142]

Another aspect of the composite sheet for forming a protective film according to the present invention contains a substrate, an adhesive layer, and a film for forming a protective film, wherein

the adhesive layer is laminated on top of the substrate, and the film for forming a protective film is laminated on top of the adhesive layer;

the adhesive layer has active energy ray curability and contains, at least in a layer that contacts the film for forming a protective film, an alkyl (meth)acrylate ester copolymer containing an alkyl (meth)acrylate ester copolymer, an isocyanate-based crosslinking agent, a photopolymerization initiator, a solvent, and other components as desired, and

the alkyl (meth)acrylate ester copolymer is a copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is at least 8 but not more than 18, and is preferably at least one compound selected from the group consisting of 2-ethylhexyl acrylate, lauryl methacrylate and isostearyl acrylate;

the amount of the structural unit derived from the alkyl (meth)acrylate in which the carbon number of the alkyl group that constitutes the alkyl ester is at least 8, relative to the total mass of all the structural units that constitute the alkyl (meth)acrylate ester copolymer is at least 30% by mass but not more than 100% by mass, and is preferably from 35 to 85% by mass, and more preferably 40 to 80% by mass;

the film for forming a protective film has heat curability, and contains:

a polymer component (A), preferably at least one component selected from the group consisting of acrylic-based resins, polyesters, polyurethanes, acrylic urethane resins, silicone resins, rubber-based polymers and phenoxy resins, and more preferably an acrylic-based polymer,

a heat-curable component (B), preferably an epoxy resin (B11) and a heat curing agent (B12), more preferably at least one resin selected from the group consisting of polyfunctional epoxy resins, biphenyl compounds, bisphenol A glycidyl ether and hydrogenated products thereof, ortho-cresol novolac epoxy resins, dicyclopentadiene epoxy resins, biphenyl epoxy resins, bisphenol A epoxy resins, bisphenol F epoxy resins, phenylene backbone epoxy resins and difunctional or higher epoxy compounds, and at least one curing agent selected from the group consisting of onium salts, dibasic acid hydrazides, dicyandiamide, and amine adducts of curing agents, and even more preferably at least one resin selected from the group consisting of bisphenol A epoxy resins and dicyclopentadiene epoxy resins, and dicyandiamide,

a curing accelerator (C), and preferably 2-phenyl-4,5-dihydroxymethylimidazole, and

at least one material selected from the group consisting of solvents, fillers (D), coupling agents (E), crosslinking agents (F), and general-purpose additives (G) as desired; and

when the composite sheet for forming a protective film is cut to a size of 25 mm $\times$ 150 mm and then bonded to a silicon wafer at 70°C, and the composite sheet for forming a protective film is subsequently heated at 130°C for 2 hours to cure the film for forming a protective film and form a protective film, the peel strength between the uncured adhesive layer and the protective film (the peel strength before adhesive layer curing), measured under conditions including a peel angle of 180°, a measurement temperature of 23°C and a pull speed of 300 mm/minute, is at least 2,000 mN/25mm, and is preferably at least 2,300 mN/25mm but not more than 6,300 mN/25mm.

Moreover, in this composite sheet for forming a protective film, when the adhesive layer is cured by irradiating ultraviolet rays onto the composite sheet for

forming a protective film under conditions including an illuminance of 220 mW/cm^2 and an irradiation dose of 190 mJ/cm^2 , the peel strength between the cured adhesive layer and the protective film (the peel strength after adhesive layer curing), measured under conditions including a peel angle of 180° , a measurement temperature of 23°C and a pull speed of 300 mm/minute , is not more than $2,000 \text{ mN/25mm}$, and is preferably at least 500 mN/25mm but not more than 1500 mN/25mm .

[0143]

Another aspect of the present invention is use of a composite sheet for forming a protective film to produce semiconductor chips with a protective film, wherein

the composite sheet for forming a protective film contains a substrate, an adhesive layer, and a film for forming a protective film, and

the adhesive layer is laminated on top of the substrate, and the film for forming a protective film is laminated on top of the adhesive layer;

the adhesive layer has active energy ray curability and contains, at least in a layer that contacts the film for forming a protective film, an alkyl (meth)acrylate ester copolymer, and

the alkyl (meth)acrylate ester copolymer is a copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is at least 8 but not more than 18;

the film for forming a protective film has heat curability; and

when the composite sheet for forming a protective film is cut to a size of $25 \text{ mm} \times 150 \text{ mm}$ and then bonded to a silicon wafer at 70°C , and the composite sheet for forming a protective film is subsequently heated at 130°C for 2 hours to cure the film for forming a protective film and form a protective film, the peel strength between the uncured adhesive layer and the protective film (the peel strength before adhesive layer

curing), measured under conditions including a peel angle of 180° , a measurement temperature of 23°C and a pull speed of 300 mm/minute, is at least 2,000 mN/25mm, and is preferably at least 2,300 mN/25mm but not more than 6,300 mN/25mm.

Moreover, in this composite sheet for forming a protective film, when the adhesive layer is cured by irradiating ultraviolet rays onto the composite sheet for forming a protective film under conditions including an illuminance of 220 mW/cm^2 and an irradiation dose of 190 mJ/cm^2 , the peel strength between the cured adhesive layer and the protective film (the peel strength after adhesive layer curing), measured under conditions including a peel angle of 180° , a measurement temperature of 23°C and a pull speed of 300 mm/minute, is not more than 2,000 mN/25mm, and is preferably at least 500 mN/25mm but not more than 1500 mN/25mm.

[0144]

A method for producing a semiconductor chip with a protective film, the method including:

affixing a composite sheet for forming a protective film to the back surface of a semiconductor wafer via the film for forming a protective film,

curing the film for forming a protective film in the affixed composite sheet for forming a protective film by heating to form a protective film,

dicing the semiconductor wafer having the protective film formed thereon to produce semiconductor chips,

curing the adhesive layer in the composite sheet for forming a protective film by irradiation with active energy rays, and then picking up the semiconductor chips together with the protective film affixed to the back surface of each semiconductor chip; wherein

the composite sheet for forming a protective film contains a substrate, the adhesive layer and the film for forming a protective film, the adhesive layer is laminated

on top of the substrate, and the film for forming a protective film is laminated on top of the adhesive layer;

the adhesive layer has active energy ray curability and contains, at least in a layer that contacts the film for forming a protective film, an alkyl (meth)acrylate ester copolymer, and

the alkyl (meth)acrylate ester copolymer is a copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is at least 8 but not more than 18; and

the film for forming a protective film has heat curability.

EXAMPLES

[0145]

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.

[0146]

[Example 1]

<Production of Composite Sheet for Forming a Protective Film>

A composite sheet for forming a protective film illustrated in FIG. 1 was produced. Further specifics are as described below.

[0147]

[Production of Support Sheet (Formation of Adhesive Layer)]

An adhesive composition was applied to one surface of a polypropylene film substrate (thickness: 80 μm , manufactured by Mitsubishi Plastics, Inc.) and then dried, thus forming an ultraviolet ray-curable adhesive layer (thickness: 10 μm) and obtaining a

support sheet. The adhesive composition contained 100 parts by mass (solid fraction) of an alkyl (meth)acrylate ester copolymer, 6.6 parts by mass (solid fraction) of a trifunctional xylylene diisocyanate-based crosslinking agent (TAKENATE D110N, manufactured by Mitsui Takeda Chemicals, Inc.) and 3.0 parts by mass (solid fraction) of a photopolymerization initiator (Irgacure 127, manufactured by BASF Corporation), and was prepared as a solution having a solid fraction concentration of 30% by mass using a mixed solvent of methyl ethyl ketone, toluene and ethyl acetate. Further, the alkyl (meth)acrylate ester copolymer was an ultraviolet ray-curable acrylic-based copolymer with a weight average molecular weight of 1,100,000, obtained by preparing a pre-copolymer by copolymerizing 80 parts by mass of 2-ethylhexyl acrylate (hereafter sometimes abbreviated as "2EHA") and 20 parts by mass of 2-hydroxyethyl acrylate (hereafter sometimes abbreviated as "HEA"), and then reacting this pre-copolymer with 21.4 parts by mass of 2-methacryloyloxyethyl isocyanate (2-isocyanatoethyl methacrylate, hereafter sometimes abbreviated as "MOI") (an amount sufficient to provide a total number of moles of isocyanate groups in the 2-methacryloyloxyethyl isocyanate that is 0.8 times the total number of moles of hydroxyl groups in the HEA). The blend amounts of the monomer components used when producing the alkyl (meth)acrylate ester copolymer are shown in Table 1. In Table 1, a value of "-" in a cell for a monomer component means that monomer component was not added.

[0148]

[Production of Composite Sheet for Forming a Protective Film (Formation of Film for Forming a Protective Film)]

A composition for forming a protective film 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 to form a film for forming a protective film (thickness: 25 μm). The composition for forming a protective film was prepared by blending the various components in the amounts (solid fractions) shown in Table 2, and then preparing a composition having a solid fraction concentration of 55% by mass using a mixed solvent of methyl ethyl ketone, toluene and ethyl acetate.

Subsequently, this film for forming a protective film was affixed to the surface of the adhesive layer of the support sheet obtained above, thus obtaining a composite sheet for forming a protective film having a release film on the surface of the film for forming a protective film on the opposite side from the surface on which the adhesive layer is provided.

[0149]

(Polymer Component (A))

(A)-1: an acrylic-based polymer obtained by copolymerizing 85 parts by mass of methyl acrylate and 15 parts by mass of 2-hydroxyethyl acrylate (weight average molecular weight: 370,000, glass transition temperature: 6°C)

(Heat-Curable Component (B))

- Epoxy Resins (B11)

(B11)-1: a bisphenol A epoxy resin (jER828, manufactured by Mitsubishi Chemical Corporation, epoxy equivalent weight: 184 to 194 g/eq)

(B11)-2 a bisphenol A epoxy resin (jER1055, manufactured by Mitsubishi Chemical Corporation, epoxy equivalent weight: 800 to 900 g/eq)

(B11)-3: a dicyclopentadiene epoxy resin (EPICLON HP-7200HH, manufactured by DIC Corporation, epoxy equivalent weight: 255 to 260 g/eq)

- Heat-Curing Agent (B12)

(B12)-1: dicyandiamide (a solid dispersion-type latent curing agent, ADEKA HARDNER EH-3636AS, manufactured by ADEKA Corporation, amount of active hydrogen: 21 g/eq)

(Curing Accelerator (C))

(C)-1: 2-phenyl-4,5-dihydroxymethylimidazole (CUREZOL 2PHZ, manufactured by Shikoku Corporation)

(Filler (D))

(D)-1: a silica filler (SC2050MA, manufactured by Admatechs Co., Ltd., average particle size: 0.5 μm)

(Coupling Agent (E))

(E)-1: a silane coupling agent (A-1110, manufactured by Nippon Uni)

(General-Purpose Additive (G))

(G)-1: carbon black (a colorant, #MA650 manufactured by Mitsubishi Chemical Corporation, average particle size: 28 nm)

[0150]

<Evaluations of Composite Sheets for Forming Protective Films>

[Suppression of Chip Flying during Dicing]

Following removal of the release film from the composite sheet for forming a protective film obtained in the manner described above, the exposed film for forming a protective film was affixed to the dry-polished surface of a silicon wafer (diameter: 6 inches, thickness: 100 μm) at 70°C, the exposed portion of the adhesive layer was affixed to a ring frame, and the resulting structure was left to stand for 30 minutes.

Subsequently, the composite sheet for forming a protective film was heated at 130°C for 2 hours, thereby curing the film for forming a protective film and forming a protective film.

Next, a dicing apparatus was used to dice the silicon wafer into chips having a size of $5\text{ mm} \times 5\text{ mm}$. During this process, the presence or absence of chip flying was ascertained visually, and if chip flying was not observed for a single chip, an evaluation of "A" was recorded, whereas if one or more instances of chip flying was observed, an evaluation of "B" was recorded. The results are shown in Table 3.

[0151]

[Pickup Characteristics]

Following removal of the release film from the composite sheet for forming a protective film obtained in the manner described above, the exposed film for forming a protective film was affixed to the dry-polished surface of a silicon wafer (diameter: 6 inches, thickness: $100\text{ }\mu\text{m}$) at 70°C , the exposed portion of the adhesive layer was affixed to a ring frame, and the resulting structure was left to stand for 30 minutes.

Subsequently, the composite sheet for forming a protective film was heated at 130°C for 2 hours, thereby curing the film for forming a protective film and forming a protective film.

Next, a dicing apparatus was used to dice the silicon wafer into chips having a size of $5\text{ mm} \times 5\text{ mm}$. Using an ultraviolet irradiation apparatus (RAD2000m/8, manufactured by Lintec Corporation), the composite sheet for forming a protective film was then irradiated with ultraviolet rays from the substrate side of the composite sheet, using a high-pressure mercury lamp as the light source, under conditions including an illuminance of 220 mW/cm^2 and an irradiation dose of 190 mJ/cm^2 , thereby curing the adhesive layer.

Subsequently, using a die bonder (BESTEM-D02, manufactured by Canon Machinery Inc.), 20 chips were picked up, and if not a single chip exhibited cracking or chipping, an evaluation of "A" was recorded, whereas if one or more chips suffered

cracking or chipping, an evaluation of "B" was recorded. The results are shown in Table 3.

[0152]

[Peel Strength between Uncured Adhesive layer and Protective Film]

The composite sheet for forming a protective film obtained above was cut to dimensions of 25 mm × 150 mm, the release film was removed, and the exposed film for forming a protective film was then affixed to the dry-polished surface of a silicon wafer (diameter: 6 inches, thickness: 500 μm) at 70°C using a laminator (LAMIPACKER LPD3214, manufactured by Fujipla Inc.).

Subsequently, the composite sheet for forming a protective film was heated at 130°C for 2 hours, thereby curing the film for forming a protective film to form a protective film, and completing preparation of a test piece (1).

Using this test piece (1) and a precision universal tester (Autograph AG-IS, manufactured by Shimadzu Corporation), a peel test was performed to peel the support sheet (the laminate composed of the uncured adhesive layer and the substrate) from the protective film under conditions including a peel angle of 180°, a measurement temperature of 23°C and a pull speed of 300 mm/minute, and the load during the test was measured and recorded as the peel strength between the uncured adhesive layer and the protective film (peel strength before adhesive layer curing). When determining the measured value for the load, of all the measured values obtained during peeling along a 100 mm length of the support sheet, the measured values obtained during the initial 10 mm length of peeling and the final 10 mm length of peeling were excluded from the effective values.

The results are shown in Table 3. The numerical values shown for "before adhesive layer curing" in the row labelled "peel strength (mN/25mm)" in Table 3 represent the obtained results.

[0153]

[Peel Strength between Cured Adhesive layer and Protective Film]

A test piece (1) was prepared in the same manner as described above.

Subsequently, using an ultraviolet irradiation apparatus (RAD2000m/8, manufactured by Lintec Corporation), the composite sheet for forming a protective film was irradiated with ultraviolet rays from the substrate side of the composite sheet, using a high-pressure mercury lamp as the light source, under conditions including an illuminance of 220 mW/cm^2 and an irradiation dose of 190 mJ/cm^2 , thereby curing the adhesive layer and completing preparation of a test piece (2).

Using the same method as that described above for the test piece (1), this test piece (2) was subjected to a peel test to peel the support sheet (the laminate composed of the cured adhesive layer and the substrate) from the protective film, and the load was recorded as the peel strength between the cured adhesive layer and the protective film (peel strength after adhesive layer curing). The results are shown in Table 3. The numerical values shown for "after adhesive layer curing" in the row labelled "peel strength (mN/25mm)" in Table 3 represent the obtained results.

[0154]

<Production and Evaluation of Composite Sheets for Forming a Protective Film>

[Example 2]

With the exception of replacing the aforementioned copolymer with a weight average molecular weight of 1,100,000 that was used as the alkyl (meth)acrylate ester copolymer during formation of the adhesive layer, and instead using an ultraviolet ray-

curable acrylic-based copolymer with a weight average molecular weight of 500,000 which was obtained, as shown in Table 1, by preparing a pre-copolymer by copolymerizing 40 parts by mass of 2EHA, 40 parts by mass of vinyl acetate (hereafter sometimes abbreviated as "VAc") and 20 parts by mass of HEA, and then reacting this pre-copolymer with 21.4 parts by mass of MOI (an amount sufficient to provide a total number of moles of isocyanate groups in the MOI that is 0.8 times the total number of moles of hydroxyl groups in the HEA), a composite sheet for forming a protective film was produced and evaluated using the same methods as those described for Example 1. The results are shown in Table 3.

[0155]

[Example 3]

With the exception of replacing the aforementioned copolymer with a weight average molecular weight of 1,100,000 that was used as the alkyl (meth)acrylate ester copolymer during formation of the adhesive layer, and instead using an ultraviolet ray-curable acrylic-based copolymer with a weight average molecular weight of 600,000 which was obtained, as shown in Table 1, by preparing a pre-copolymer by copolymerizing 80 parts by mass of lauryl methacrylate (hereafter sometimes abbreviated as "LMA") and 20 parts by mass of HEA, and then reacting this pre-copolymer with 21.4 parts by mass of MOI (an amount sufficient to provide a total number of moles of isocyanate groups in the MOI that is 0.8 times the total number of moles of hydroxyl groups in the HEA), a composite sheet for forming a protective film was produced and evaluated using the same methods as those described for Example 1. The results are shown in Table 3.

[0156]

[Example 4]

With the exception of replacing the aforementioned copolymer with a weight average molecular weight of 1,100,000 that was used as the alkyl (meth)acrylate ester copolymer during formation of the adhesive layer, and instead using an ultraviolet ray-curable acrylic-based copolymer with a weight average molecular weight of 600,000 which was obtained, as shown in Table 1, by preparing a pre-copolymer by copolymerizing 80 parts by mass of isostearyl acrylate (hereafter sometimes abbreviated as "ISTA") and 20 parts by mass of HEA, and then reacting this pre-copolymer with 21.4 parts by mass of MOI (an amount sufficient to provide a total number of moles of isocyanate groups in the MOI that is 0.8 times the total number of moles of hydroxyl groups in the HEA), a composite sheet for forming a protective film was produced and evaluated using the same methods as those described for Example 1. The results are shown in Table 3.

[0157]

[Comparative Example 1]

With the exception of replacing the aforementioned copolymer with a weight average molecular weight of 1,100,000 that was used as the alkyl (meth)acrylate ester copolymer during formation of the adhesive layer, and instead using an ultraviolet ray-curable acrylic-based copolymer with a weight average molecular weight of 600,000 which was obtained, as shown in Table 1, by preparing a pre-copolymer by copolymerizing 40 parts by mass of butyl acrylate (hereafter sometimes abbreviated as "BA"), 40 parts by mass of VAc and 20 parts by mass of HEA, and then reacting this pre-copolymer with 21.4 parts by mass of MOI (an amount sufficient to provide a total number of moles of isocyanate groups in the MOI that is 0.8 times the total number of moles of hydroxyl groups in the HEA), a composite sheet for forming a protective film

was produced and evaluated using the same methods as those described for Example 1.

The results are shown in Table 3.

[0158]

[Comparative Example 2]

With the exception of replacing the aforementioned copolymer with a weight average molecular weight of 1,100,000 that was used as the alkyl (meth)acrylate ester copolymer during formation of the adhesive layer, and instead using an ultraviolet ray-curable acrylic-based copolymer with a weight average molecular weight of 600,000 which was obtained, as shown in Table 1, by preparing a pre-copolymer by copolymerizing 40 parts by mass of BA, 40 parts by mass of methyl methacrylate (hereafter sometimes abbreviated as "MMA") and 20 parts by mass of HEA, and then reacting this pre-copolymer with 21.4 parts by mass of MOI (an amount sufficient to provide a total number of moles of isocyanate groups in the MOI that is 0.8 times the total number of moles of hydroxyl groups in the HEA), a composite sheet for forming a protective film was produced and evaluated using the same methods as those described for Example 1. The results are shown in Table 3.

[0159]

[Table 1]

			Example				Comparative Example	
			1	2	3	4	1	2
Monomer components of alkyl (meth)acrylate ester copolymer (parts by mass)	Alkyl (meth)acrylate ester	2EHA	80	40	-	-	-	-
		LMA	-	-	80	-	-	-
		ISTA	-	-	-	80	-	-
		BA	-	-	-	-	40	40
		MMA	-	-	-	-	-	40
	Hydroxyl group-containing monomer	HEA	20	20	20	20	20	20
	Other monomer	VAc	-	40	-	-	40	-
	Isocyanate compound	MOI	21.4	21.4	21.4	21.4	21.4	21.4

[0160]

[Table 2]

		Examples 1 to 4, Comparative Examples 1, 2
Blend components for composition for forming a protective film (parts by mass)	(A)-1	150
	(B11)-1	60
	(B11)-2	10
	(B11)-3	30
	(B12)-1	2
	(C)-1	2
	(D)-1	320
	(E)-1	1.2
	(G)-1	2

[0161]

[Table 3]

			Example				Comparative Example	
			1	2	3	4	1	2
Evaluation results	Suppression of chip flying during dicing		A	A	A	A	A	A
	Pickup characteristics		A	A	A	A	B	B
	Peel strength (mN/25mm)	before adhesive layer curing	2300	6300	4300	3500	8000	20,000
		after adhesive layer curing	500	1500	300	2000	7500	18,000

[0162]

In those cases where the composite sheets for forming a protective film of Examples 1 to 4 were used, because in each case the sheet contained an alkyl (meth)acrylate ester copolymer having a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester was 8 or greater, the peel strength between the uncured adhesive layer and the protective film was sufficiently large to enable dicing to be performed in a stable manner, whereas the peel strength between the cured adhesive layer and the protective film was sufficiently small to enable pickup of the semiconductor chips to be performed in a stable manner.

The ratio between the peel strengths before and after curing of the adhesive layer (namely, [peel strength before adhesive layer curing] / [peel strength after adhesive layer curing]) was 4.6 in Example 1, 4.2 in Example 2, 14.3 in Example 3, and 1.8 in Example 4, with large ratios obtained in Examples 1 to 3, and a particularly large ratio obtained in Example 3, indicating that the effects of the present invention are particularly evident

when the carbon number of the alkyl group that constitutes the alkyl ester is 12 or a value close thereto.

[0163]

In contrast, when the composite sheets for forming a protective film of Comparative Examples 1 and 2 were used, in each case the sheet contained an alkyl (meth)acrylate ester copolymer that did not have a structural unit derived from an alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester was 8 or greater, and therefore although the peel strength between the uncured adhesive layer and the protective film was sufficiently large to enable dicing to be performed in a stable manner, the peel strength between the cured adhesive layer and the protective film was unable to be reduced sufficiently, and pickup of the semiconductor chips was not able to be performed in a stable manner.

INDUSTRIAL APPLICABILITY

[0164]

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

[0165]

1, 2, 3, 4: Composite sheet for forming a protective film

10: Support sheet

11: Substrate

11a: Substrate surface

12, 32, 42: Adhesive layer

12a, 32a, 42a: Surface of adhesive layer

321, 421: First adhesive layer

322, 422: Second adhesive layer

322a, 422a: Surface of second adhesive layer

13, 23: Film for forming a protective film

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

14: Release film

15: Jig adhesive layer

15a: Surface of jig adhesive layer

[CLAIMS]

1. A composite sheet for forming a protective film comprising an adhesive layer on a substrate, and a film for forming a protective film on the adhesive layer, the adhesive layer having active energy ray curability, and the film for forming a protective film having heat curability, wherein

the composite sheet for forming a protective film is used for producing a semiconductor chip with a protective film by affixing the composite sheet to a back surface of a semiconductor wafer via the film for forming a protective film, and then curing the film for forming a protective film by heating to form a protective film, subsequently dicing the semiconductor wafer to produce semiconductor chips, curing the adhesive layer by irradiation with active energy rays, and then picking up the semiconductor chips together with the protective film affixed to a back surface thereof,

the adhesive layer comprises, at least in a layer that contacts the film for forming a protective film, an alkyl (meth)acrylate ester copolymer,

the alkyl (meth)acrylate ester copolymer has a structural unit derived from an alkyl (meth)acrylate ester in which a carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater,

in the composite sheet for forming a protective film, after the film for forming a protective film is cured by heating at 130°C for 2 hours to form the protective film, when the adhesive layer before curing is peeled off from the protective film under conditions of a peel angle of 180°, a temperature of 23°C and a pull speed of 300 mm/minute, the peel strength before adhesive layer curing is at least 2,000 mN/25mm,

in the composite sheet for forming a protective film, after the film for forming a protective film is cured by heating at 130°C for 2 hours to form the protective film and the adhesive layer is cured by irradiating the adhesive layer with ultraviolet rays at an illuminance of 220 mW/cm² and an irradiation dose of 190 mJ/cm², when the adhesive layer after curing is peeled off from the protective film under conditions of a peel angle of 180°, a temperature of 23°C and a pull speed of 300 mm/minute, the peel strength after adhesive layer curing is not more than 2,000 mN/25mm,

the ratio of the peel strength before adhesive layer curing relative to the peel strength after adhesive layer curing is at least 1.5,

the film for forming a protective film comprises an acrylic-based resin, an epoxy resin and a heat curing agent,

the monomer that constitutes the acrylic-based resin comprises an alkyl (meth)acrylate esters in which the alkyl group that constitutes the alkyl ester is a chain-like group having a carbon number of 1 to 18, and a hydroxyl group-containing (meth)acrylate ester,

the heat curing agent is a curing agent for the epoxy resin, and

in the film for forming a protective film, the total amount of the epoxy resin and the heat curing agent is 1 to 100 parts by mass when the amount of the acrylic-based resin is 100 parts by mass.

2. The composite sheet for forming a protective film according to Claim 1, wherein the film for forming a protective film comprises an imidazole,

the heat curing agent is a heat curing agent that melts upon heating and exhibits curing activity relative to the epoxy resin.

3. The composite sheet for forming a protective film according to Claim 1 or 2, wherein the carbon number of the structural unit derived from the alkyl (meth)acrylate ester in which the carbon number of the alkyl group that constitutes the alkyl ester is 8 or greater is within a range from 11 to 18.

4. The composite sheet for forming a protective film according to any one of Claims 1 or 3, wherein the adhesive layer comprises
2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]phenyl}-2-methyl-propan-1-one as a photopolymerization initiator.

5. A method for producing a semiconductor chip with a protective film using the composite sheet for forming a protective film according to any one of Claims 1 to 4 comprising:

affixing the composite sheet to a back surface of a semiconductor wafer via the film for forming a protective film, and then curing the film for forming a protective film by heating to form a protective film, subsequently dicing the semiconductor wafer to produce semiconductor chips, curing the adhesive layer by irradiation with active energy rays, and then picking up the semiconductor chips together with the protective film affixed to a back surface thereof.