

DESCRIPTION

Title of Invention

ADHESIVE SHEET FOR SEMICONDUCTOR PROCESSING

Technical Field

[0001]

The present invention relates to a semiconductor processing pressure sensitive adhesive sheet. In particular, the present invention relates to a pressure sensitive adhesive sheet for semiconductor wafer surface protection, which is used for protecting the surface of a semiconductor wafer with bumps.

Background Art

[0002]

Along with a rapid progress of thinning, downsizing, and multi-functionalizing of an information terminal instrument, thinning and densification of a semiconductor device to be mounted thereon are also required, and thinning of a semiconductor wafer is also demanded. In order to cope with such demands, thinning has hitherto been performed by grinding the back surface of the semiconductor wafer. In addition, in recent years, in a semiconductor wafer, there is a case where bumps made of solder or the like having a height of approximately several tens to several hundred μm are formed on the semiconductor wafer surface. In the case of grinding the back surface of such a semiconductor wafer with bumps, in order to protect a bump portion, a surface protective sheet is attached on the wafer surface on which the bumps are formed.

[0003]

As disclosed in PTL 1, it has hitherto been known to use, as the surface protective sheet, a pressure sensitive adhesive sheet in which an intermediate layer and a pressure sensitive adhesive layer are provided in this order on a substrate. In PTL 1, customary pressure sensitive adhesives, such as acrylic pressure sensitive adhesives, silicone-based pressure sensitive adhesives, and rubber-based pressure sensitive adhesives, are used. In addition, it is also disclosed that a crosslinking agent may be blended in the pressure sensitive adhesive, thereby introducing a crosslinking structure.

Furthermore, PTL 1 discloses that when the pressure sensitive adhesive is

blended with an energy ray-curable oligomer, or a carbon-carbon double bond is introduced into a polymer constituting the pressure sensitive adhesive, the pressure sensitive adhesive is made energy ray-curable. In the surface protective sheet, in view of the matter that the energy ray-curable pressure sensitive adhesive is used, an adhesive strength of the pressure sensitive adhesive layer is lowered upon irradiation with an energy ray, and therefore, after being used, the surface protective sheet becomes easy to be released from the semiconductor wafer.

[0004]

In addition, an extremely high-strength gel having a double network structure has hitherto been known. For example, as described in NPL. 1, the extremely high-strength gel is obtained by polymerizing poly(2-acrylamide-2-methylpropanesulfonic acid) to obtain a gel (PAMPS gel), dipping the PAMPS gel in an acrylamide monomer solution, and then polymerizing the acrylamide in the interior of the PAMPS gel.

Citation List

Patent Literature

[0005]

PTL 1: Japanese Patent No. 4367769

NPL 1: "Creation of Double Network Hydrogels with Extremely High Strength and Its Anomalous Fracture Mechanism", *Kobunshi Ronbunshu* (Japanese Journal of Polymer Science and Technology), Vol. 65, No. 12 (2008), pp.707-715

Summary of Invention

Technical Problem

[0006]

In recent years, following more densification and downsizing of semiconductor devices, the bump height tends to become large. But, as for semiconductor wafers having a large bump height, a pressure sensitive adhesive residue (adhesive residue) is liable to be generated in the bumps at the time of releasing the surface protective sheet. The adhesive residue tends to be reduced by making the pressure sensitive adhesive energy ray-curable. However, in recent years, contamination of the semiconductor wafer is being demanded to be more

reduced, and there is a case where when the pressure sensitive adhesive is merely made energy ray-curable, the adhesive residue cannot be reduced to a desired level.

In addition, in NPL 1, it is not attempted to apply the extremely high-strength gel having a double network structure for a pressure sensitive adhesive, or to modify it to be energy ray-curable.

[0007]

In view of the foregoing actual circumstances, the present invention has been made, and a problem of the present invention is to provide a semiconductor processing pressure sensitive adhesive sheet in which when released, an adhesive residue is hardly generated on the work surface of a semiconductor wafer or the like.

Solution to Problem

[0008]

The present inventors made extensive and intensive investigations. As a result, it has been found that the aforementioned problem can be solved by blending two polymers in a pressure sensitive adhesive composition constituting a pressure sensitive adhesive layer and crosslinking the respective polymers in a different crosslinking system from each other and also making one of the polymers energy ray-curable, thereby leading to accomplishment of the present invention. Specifically, the present invention provides the following semiconductor processing pressure sensitive adhesive sheets (1) to (10).

(1) A semiconductor processing pressure sensitive adhesive sheet including a substrate and a pressure sensitive adhesive layer provided on one surface of the substrate, the pressure sensitive adhesive layer being formed of a pressure sensitive adhesive composition, wherein

the pressure sensitive adhesive composition contains a polymer (A) having a reactive functional group (A1); a polymer (B) having a reactive functional group (B1) different from the reactive functional group (A1) and an energy ray-polymerizable group (B2); a crosslinking agent (C) that reacts with the reactive functional group (A1); and a crosslinking agent (D) that reacts with the reactive functional group (B1).

(2) The semiconductor processing pressure sensitive adhesive sheet as set forth in the above (1), wherein a weight average molecular weight of the polymer (A) is

higher than a weight average molecular weight of the polymer (B).

(3) The semiconductor processing pressure sensitive adhesive sheet as set forth in the above (1) or (2), wherein the polymer (A) and the polymer (B) each are an acrylic polymer.

(4) The semiconductor processing pressure sensitive adhesive sheet as set forth in the above (3), wherein a weight average molecular weight of the acrylic polymer constituting the polymer (A) is higher than a weight average molecular weight of the acrylic polymer constituting the polymer (B), and a difference therebetween is 200,000 or more.

(5) The semiconductor processing pressure sensitive adhesive sheet as set forth in the above (4), wherein the weight average molecular weight of the acrylic polymer constituting the polymer (A) is from 300,000 to 1,000,000, and the weight average molecular weight of the acrylic polymer constituting the polymer (B) is from 5,000 to 100,000.

(6) The semiconductor processing pressure sensitive adhesive sheet as set forth in any one of the above (3) to (5), wherein the acrylic polymer constituting the polymer (A) is an acrylic copolymer (A') containing a structural unit derived from a functional group monomer (a1) having the reactive functional group (A1) and a structural unit derived from an alkyl (meth)acrylate (a2).

(7) The semiconductor processing pressure sensitive adhesive sheet as set forth in any one of the above (3) to (6), wherein the acrylic polymer constituting the polymer (B) is a reaction product obtained by allowing a part of the reactive functional group (B1) of an acrylic copolymer (B') containing a structural unit derived from a functional group monomer (b1) having the reactive functional group (B1) and a structural unit derived from an alkyl (meth)acrylate (b2) to react with an energy ray-polymerizable group-containing compound (S) having the energy ray-polymerizable group (B2).

(8) The semiconductor processing pressure sensitive adhesive sheet as set forth in any one of the above (1) to (7), wherein the reactive functional group (A1) is a carboxy group, and the reactive functional group (B1) is a hydroxy group.

(9) The semiconductor processing pressure sensitive adhesive sheet as set forth in the above (8), wherein the crosslinking agent (C) is an epoxy-based crosslinking agent, and the crosslinking agent (D) is an isocyanate-based crosslinking agent.

(10) The semiconductor processing pressure sensitive adhesive sheet as set forth in any one of the above (1) to (9), wherein the content of the crosslinking agent (D)

is larger than the content of the crosslinking agent (C) on a mass basis in the pressure sensitive adhesive composition, and the content of the crosslinking agent (D) in the pressure sensitive adhesive composition is from 2 to 20 parts by mass based on 100 parts by mass of the polymer (B).

Advantageous Effects of Invention

[0009]

In accordance with the present invention, it is possible to provide a semiconductor processing pressure sensitive adhesive sheet in which when released, an adhesive residue is hardly generated on the work surface.

Brief Description of Drawings

[0010]

Fig. 1 is a stress-strain curve prepared by subjecting a pressure sensitive adhesive layer of Example 1 after energy ray curing to a cyclic tensile test.

Fig. 2 is a stress-strain curve prepared by subjecting a pressure sensitive adhesive layer of Example 1 before energy ray curing to a cyclic tensile test.

Fig. 3 is a stress-strain curve prepared by subjecting a pressure sensitive adhesive layer of Comparative Example 1 after energy ray curing to a cyclic tensile test.

Description of Embodiments

[0011]

In the following description, the term "weight average molecular weight (Mw)" is a value expressed in terms of polystyrene as measured by the gel permeation chromatography (GPC), and specifically, it is a value measured on a basis of the method as described in the section of Examples.

In addition, in the description of this specification, for example, the term "(meth)acrylate" is used as a term expressing both "acrylate" and "methacrylate", and the same is also applicable to other analogous terms.

[0012]

The present invention is hereunder described in more detail by reference to embodiments.

The semiconductor processing pressure sensitive adhesive sheet of the present invention (hereinafter also referred to simply as "pressure sensitive

adhesive sheet") includes a substrate and a pressure sensitive adhesive layer provided on one surface of the substrate. In addition, the pressure sensitive adhesive sheet may include an intermediate layer between the substrate and the pressure sensitive adhesive layer. In the light of the above, the pressure sensitive adhesive sheet may be constituted of two layers or three layers and may be further provided with other layer. For example, a release material may be further provided on the pressure sensitive adhesive layer.

The respective members constituting the pressure sensitive adhesive sheet are hereunder described in detail.

[0013]

<Substrate>

Though the substrate which is used for the pressure sensitive adhesive sheet is not particularly limited, it is preferably a resin film. The resin film is preferred in view of the facts that it is suitable for a processing member of an electronic part because it produces a less amount of dust as compared with papers, nonwoven fabrics, and so on and that it is easily available. The substrate may be a single-layer film composed of a single resin film, or may be a multilayer film obtained by laminating plural resin films.

Examples of the resin film which is used as the substrate include a polyolefin-based film, a vinyl halide polymer-based film, an acrylic resin-based film, a rubber-based film, a cellulose-based film, a polyester-based film, a polycarbonate-based film, a polystyrene-based film, a polyphenylene sulfide-based film, and a cycloolefin polymer-based film.

Among them, from the viewpoint that on grinding a wafer ultrathin, the wafer can be stably kept and also from the viewpoint of a film with high thickness precision, a polyester-based film is preferred. Among the polyester-based films, a polyethylene terephthalate film is more preferred from the viewpoint of easiness of availability and high thickness precision.

Though a thickness of the substrate is not particularly limited, it is preferably 10 to 200 μm , more preferably 25 to 150 μm , and still more preferably 25 to 100 μm .

[0014]

From the viewpoint of improving adhesive properties of the substrate to the pressure sensitive adhesive layer or the intermediate layer, a substrate in which a primer layer is further provided on the surface of the resin film may also

be used. Furthermore, the substrate which is used in the present invention may contain a filler, a colorant, an antistatic agent, an antioxidant, an organic lubricant, a catalyst, or the like within a range where the effects of the present invention are not impaired. In addition, though the substrate may be transparent or may be colored, if desired, it is preferably one which transmits an energy ray to a degree sufficient for curing the pressure sensitive adhesive layer.

[0015]

<Pressure Sensitive Adhesive Layer>

The pressure sensitive adhesive layer is provided on the substrate, and in the case where an intermediate layer is provided, the pressure sensitive adhesive layer is provided on the intermediate layer. The pressure sensitive adhesive layer is formed of a pressure sensitive adhesive composition. The pressure sensitive adhesive composition contains a polymer (A) and a polymer (B), and a crosslinking agent (C) and a crosslinking agent (D). These respective components are hereunder described in detail.

[0016]

[Polymers (A) and (B)]

The polymer (A) has a reactive functional group (A1). In addition, the polymer (B) has a reactive functional group (B1) that is a functional group different from the reactive functional group (A1), and an energy ray-polymerizable group (B2). The reactive functional group (A1) of the polymer (A) undergoes a crosslinking reaction preferentially with the crosslinking agent (C) without undergoing a crosslinking reaction with the crosslinking agent (D). In addition, the reactive functional group (B1) of the polymer (B) undergoes a crosslinking reaction preferentially with the crosslinking agent (D) without undergoing a crosslinking reaction with the crosslinking agent (C).

[0017]

The reactive functional group (A1) and the reactive functional group (B1) are not particularly limited and may be each selected from a hydroxy group, a carboxy group, an amino group, an epoxy group, and so on. Among them, a carboxy group and a hydroxy group are preferred.

It is more preferred that either one of the reactive functional group (A1) or the reactive functional group (B1) is a carboxy group, with the other being a hydroxy group. According to this, the polymer (A) reacts with the crosslinking agent (C), and the polymer (B) reacts with the crosslinking agent (D), whereby

separate network structures are readily formed.

Here, though the reactive functional group (A1) may be a hydroxy group, with the reactive functional group (B1) being a carboxy group, it is more preferred that not only the reactive functional group (A1) is a carboxy group, but also the reactive functional group (B1) is a hydroxy group. When the reactive functional group (B1) of the polymer (B) is a hydroxy group, it becomes easy to react with an energy ray-polymerizable group-containing compound (S) as mentioned later.

[0018]

The polymer (A) is a compound not having an energy ray-polymerizable group, and therefore, it is a non-energy ray-curable compound which is not cured even upon irradiation with an energy ray. On the other hand, the polymer (B) has the energy ray-polymerizable group (B2), and therefore, it is an energy ray-curable compound which is cured upon irradiation with an energy ray. When the pressure sensitive adhesive layer formed of the pressure sensitive adhesive composition is irradiated with an energy ray, the polymer (B) is cured, so that the adhesive strength is lowered.

The energy ray means one having an energy quantum in electromagnetic waves or charged particle beams, and examples thereof include an ultraviolet ray and an electron beam. Above all, it is preferred to cure the pressure sensitive adhesive layer with an ultraviolet ray.

Examples of the energy ray-polymerizable group (B2) include those having a carbon-carbon double bond, such as a (meth)acryloyl group, a vinyl group, and an acryl group, with a (meth)acryloyl group being preferred.

[0019]

In view of the fact that the polymer (A) has the reactive functional group (A1), and the polymer (B) has the reactive functional group (B1) different from the reactive functional group (A1), the polymer (A) is crosslinked with the crosslinking agent (C), and the polymer (B) is crosslinked with the crosslinking agent (D) different from the crosslinking agent (C), respectively. For that reason, in the pressure sensitive adhesive layer, a three-dimensional network structure constituted of the polymer (A) and the crosslinking agent (C) (hereinafter also referred to as "first network") and a three-dimensional network structure constituted of the polymer (B) and the crosslinking agent (D) (hereinafter also referred to as "second network") are formed. In addition, in the second network, the energy ray-polymerizable group (B2) is contained in the polymer (B), and

therefore, it may be assumed that when irradiated with an energy ray, it becomes a denser network, whereby it becomes a stiff and brittle structure. On the other hand, in view of the fact that the first network is constituted of the polymer (A) and the crosslinking agent (C), it may be assumed that the first network takes a flexible and readily elongated structure as compared with the second network.

In the pressure sensitive adhesive layer, after irradiation with an energy ray, a so-called double network in which as mentioned above, the stiff second network becomes tangled into the flexible first network is formed. For that reason, breaking characteristics of the pressure sensitive adhesive layer after irradiation with an energy ray, such as breaking strength, elongation at break, and breaking energy are easy to become favorable, and when the pressure sensitive adhesive sheet is released from a work, such as a semiconductor wafer, the adhesive residue is hardly generated.

[0020]

The polymer (A) and the polymer (B) are each a pressure sensitive adhesive component (pressure sensitive adhesive resin) capable of revealing pressure sensitive adhesiveness in the pressure sensitive adhesive layer, and for example, it is selected from an acrylic polymer, a urethane polymer, a rubber-based polymer, and a polyolefin. Above all, the polymer (A) and the polymer (B) are each preferably selected from an acrylic polymer and a urethane polymer, with an acrylic polymer being more preferred.

As for the polymer (A) and the polymer (B), from the viewpoint of compatibility and so on, it is preferred to use polymers of the same kind as each other. That is, in the case where the polymer (A) is an acrylic polymer, it is preferred that the polymer (B) is an acrylic polymer, too. In addition, in the case where the polymer (A) is a urethane polymer, it is preferred that the polymer (B) is a urethane polymer, too.

[0021]

In the pressure sensitive adhesive layer, when the weight average molecular weight of the polymer (A) becomes high, the first network readily takes a more flexible and elongated structure, whereas when the weight average molecular weight of the polymer (B) becomes low, the second network readily takes a more stiff and brittle structure. Furthermore, the second network readily becomes tangled into the flexible first network, and a double network is readily formed. From these viewpoints, it is preferred that the weight average molecular

weight of the polymer (A) is higher than the weight average molecular weight of the polymer (B).

[0022]

In the pressure sensitive adhesive composition, the content of the polymer (B) is preferably 10 to 100 parts by mass, more preferably 20 to 80 parts by mass, and still more preferably 30 to 70 parts by mass based on 100 parts by mass of the polymer (A).

By regulating the content of the polymer (B) to the aforementioned lower limit value or more, it becomes easy to impart appropriate energy ray-curability to the pressure sensitive adhesive layer. In addition, by allowing the content to fall within the aforementioned range, coatability of the pressure sensitive adhesive composition and film formability, etc. of the pressure sensitive adhesive layer readily become favorable. Furthermore, the first network and the second network are formed in well balance, and the breaking characteristics of the pressure sensitive adhesive layer are readily made favorable.

In the pressure sensitive adhesive composition, it is preferred that the polymer (A) and the polymer (B) are a main component. It is meant by the wording "main component" that a total content of the polymer (A) and the polymer (B) is 50% by mass or more on a basis of the whole amount of the pressure sensitive adhesive composition (solid content basis), and the total content is more preferably 70 to 98% by mass, and still more preferably 80 to 95% by mass. In the present invention, the solid content means all components other than an organic solvent and includes ones that are liquid at room temperature (25°C).

[0023]

(Acrylic Polymer)

The case where the aforementioned polymer (A) and polymer (B) are each an acrylic polymer is hereunder described in more detail.

The acrylic polymer constituting the polymer (A) is a polymer containing a structural unit derived from a (meth)acrylate, preferably an acrylic copolymer (A') containing a structural unit derived from a functional group monomer (a1) having the reactive functional group (A1) (hereinafter sometimes referred to simply as "functional group monomer (a1)"), and more preferably an acrylic copolymer (A') containing a structural unit derived from the functional group monomer (a1) and a structural unit derived from an alkyl (meth)acrylate (a2). When the polymer (A) contains the structural unit derived from the alkyl (meth)acrylate (a2), the

pressure sensitive adhesiveness of the pressure sensitive adhesive layer is readily made favorable.

[0024]

The functional group monomer (a1) is a monomer having the aforementioned reactive functional group (A1), and preferably, a carboxy group-containing monomer is exemplified. Examples of the carboxy group-containing monomer include carboxylic acids having an ethylenically unsaturated bond, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, itaconic acid, and citraconic acid. These may be used alone or may be used in combination of two or more thereof. Among them, acrylic acid and methacrylic acid are preferred, with acrylic acid being more preferred.

[0025]

The content of the structural unit derived from the functional group monomer (a1) (for example, a carboxy group-containing monomer) is preferably 0.5 to 15% by mass, more preferably 1 to 8% by mass, and still more preferably 1.5 to 5% by mass on a basis of the acrylic copolymer (A'). When the content of the functional group monomer (a1), such as a carboxy group-containing monomer, falls within the aforementioned range, it becomes easy to impart an appropriate adhesive strength to the pressure sensitive adhesive layer. In addition, it becomes possible to suitably form the first network through crosslinking with the crosslinking agent (C).

[0026]

Examples of the alkyl (meth)acrylate (a2) include alkyl (meth)acrylates in which an alkyl group thereof has 1 to 20 carbon atoms.

Examples of the alkyl (meth)acrylate in which an alkyl group thereof has 1 to 20 carbon atoms include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-decyl (meth)acrylate, n-dodecyl (meth)acrylate, myristyl (meth)acrylate, palmityl (meth)acrylate, and stearyl (meth)acrylate. These may be used alone or may be used in combination of two or more thereof.

Among those mentioned above, from the viewpoint of appropriately exhibiting the pressure sensitive adhesiveness, an alkyl (meth)arylate in which an alkyl group thereof has 1 to 8 carbon atoms is preferred, and an alkyl (meth)arylate in which an alkyl group thereof has 4 to 8 carbon atoms (hereinafter

sometimes referred to as "monomer (α)" is more preferred. Specifically, as the monomer (α), 2-ethylhexyl (meth)acrylate and n-butyl (meth)acrylate are preferred, with n-butyl (meth)acrylate being more preferred.

[0027]

The content of the structural unit derived from the alkyl (meth)acrylate (a2) is preferably 50 to 99.5% by mass, more preferably 60 to 99% by mass, and still more preferably 70 to 98.5% by mass on a basis of the acrylic copolymer (A').

Though it is more preferred to use, as the alkyl (meth)acrylate (a2), the alkyl (meth)acrylate in which an alkyl group thereof has 4 to 8 carbon atoms, namely the monomer (α), as mentioned above, all of the alkyl (meth)acrylates (a2) to be contained in the acrylic copolymer (A') may be the monomer (α), or a part thereof may be the monomer (α).

Specifically, a proportion of the monomer (α) is preferably 70 to 100% by mass, more preferably 80 to 100% by mass, and still more preferably 90 to 100% by mass relative to the whole amount of the alkyl (meth)acrylate (a2).

[0028]

Though the aforementioned acrylic copolymer (A') which is used for the polymer (A) may be a copolymer of the functional group monomer (a1) and the alkyl (meth)acrylate (a2), it may also be a copolymer of the component (a1), the component (a2), and other monomer (a3) than these components (a1) and (a2).

The other monomer (a3) means a copolymerizable monomer other than the aforementioned components (a1) to (a2), and specifically, examples thereof include (meth)acrylates having a cyclic skeleton, such as a cycloalkyl (meth)acrylate in which a cycloalkyl group thereof has 3 to 20 carbon atoms, benzyl (meth)acrylate, and isobornyl (meth)acrylate; vinyl ester compounds, such as vinyl acetate and vinyl propionate; olefins, such as ethylene, propylene, and isobutylene; halogenated olefins, such as vinyl chloride and vinylidene chloride; styrene-based monomers, such as styrene and α -methylstyrene; diene-based monomers, such as butadiene, isoprene, and chloroprene; and nitrile-based monomers, such as acrylonitrile and methacrylonitrile.

In the acrylic copolymer (A'), the other monomer (a3) may be used alone or may be used in combination of two or more thereof.

[0029]

The acrylic polymer constituting the polymer (B) is a polymer containing a structural unit derived from a (meth)acrylate, and preferably a reaction product

obtained by allowing an acrylic copolymer (B') containing a structural unit derived from a functional group monomer (b1) having the reactive functional group (B1) (hereinafter sometimes referred to simply as "functional group monomer (b1)") to react with an energy ray-polymerizable group-containing compound (S) having the energy ray-polymerizable group (B2). The energy ray-polymerizable group-containing compound (S) is a compound which reacts with a part of the reactive functional group (B1) of the acrylic copolymer (B'). In addition, it is more preferred that the acrylic copolymer (B') further contains a structural unit derived from an alkyl (meth)acrylate (b2).

That is, the acrylic polymer constituting the polymer (B) is preferably a reaction product obtained by allowing a part of the reactive functional group (B1) of the acrylic copolymer (B') containing a structural unit derived from the functional group monomer (b1) having the reactive functional group (B1) and a structural unit derived from the alkyl (meth)acrylate (b2) to react with the energy ray-polymerizable group-containing compound (S) having the energy ray-polymerizable group (B2).

[0030]

The functional group monomer (b1) is a monomer having the aforementioned reactive functional group (B1), and preferably, a hydroxy group-containing monomer is exemplified.

Examples of the hydroxy group-containing monomer include hydroxyalkyl (meth)acrylates, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, and 4-hydroxybutyl (meth)acrylate. Above all, from the standpoints of reactivity between the crosslinking agent (D) and the energy ray-polymerizable group-containing compound (S) and copolymerizability with other monomers, 2-hydroxyethyl (meth)acrylate and 4-hydroxybutyl (meth)acrylate are preferred, with 2-hydroxyethyl (meth)acrylate being more preferred.

[0031]

In the acrylic copolymer (B') for forming the polymer (B), the content of the structural unit derived from the functional group monomer (b1) (for example, a hydroxy group-containing monomer) is preferably 10 to 45% by mass, more preferably 15 to 40% by mass, and still more preferably 20 to 35% by mass on a basis of the acrylic copolymer (B'). When the content of the functional group

monomer (b1), such as a hydroxy group-containing monomer, falls within the aforementioned range, it becomes easy to impart an appropriate adhesive strength to the pressure sensitive adhesive layer. In addition, it becomes possible to suitably form a three-dimensional network structure composed of the second network due to crosslinking with the crosslinking agent (D). Furthermore, by allowing the energy ray-polymerizable group-containing compound (S) to react with the reactive functional group (B1), it becomes possible to introduce an appropriate amount of the energy ray-polymerizable group (B2) into the polymer (B).

[0032]

Specific examples of the alkyl (meth)acrylate (b2) include the same compounds which may be selected for the aforementioned component (a2), and those compounds may be used alone or may be used in combination of two or more thereof. In addition, likewise the component (a2), an alkyl (meth)acrylate in which the alkyl group thereof has 1 to 8 carbon atoms is preferred. Furthermore, it is more preferred to use the monomer (α). Suitable compounds as the monomer (α) are also the same, and n-butyl (meth)acrylate is preferred.

The content of the alkyl (meth)acrylate (b2) is preferably 50 to 90% by mass, more preferably 60 to 85% by mass, and still more preferably 65 to 80% by mass on a basis of the acrylic copolymer (B').

Likewise the component (a2), it is also preferred to use the monomer (α) as the alkyl (meth)acrylate (b2); however, all of the alkyl (meth)acrylates (b2) to be contained in the acrylic copolymer (B') may be the monomer (α), or a part thereof may be the monomer (α). Details of the content thereof are the same as those described for the aforementioned polymer (A).

[0033]

Though the acrylic copolymer (B') may be a copolymer of the functional group monomer (b1) and the alkyl (meth)acrylate (b2), it may also be a copolymer of the component (b1), the component (b2), and other monomer (b3) than these components (b1) and (b2). The other monomer (b3) means a copolymerizable monomer other than the aforementioned components (b1) to (b2), and as specific monomers, those enumerated for the monomer (a3) may be suitably selected and used.

[0034]

(Energy Ray-Polymerizable Group-Containing Compound (S))

The energy ray-polymerizable group-containing compound (S) has the energy ray-polymerizable group (B2) and a functional group (B3) capable of reacting with the reactive functional group (B1) (hereinafter sometimes referred to simply as "functional group (B3)"). Though the functional group (B3) has only to be a functional group capable of reacting with the reactive functional group (B1), examples thereof include an isocyanate group, an epoxy group, and a carboxy group.

When the reactive functional group (B1) is a hydroxy group as mentioned above, it is preferred that the functional group (B3) to be contained in the energy ray-polymerizable group-containing compound (S) is an isocyanate group. In addition, when the reactive functional group (B1) is a carboxy group, it is preferred that the functional group (B3) is an epoxy group. Furthermore, when the reactive functional group (B1) is an epoxy group, it is preferred that the functional group (B3) is a carboxy group.

Among them, from the viewpoint of reactivity and so on, it is more preferred that the reactive functional group (B1) is a hydroxy group, and the functional group (B3) is an isocyanate group.

[0035]

A preferred embodiment of the energy ray-polymerizable group (B2) is that mentioned above. In consequence, the energy ray-polymerizable group-containing compound (S) is preferably a compound having an isocyanate group and a (meth)acryloyl group.

Specific examples of the energy ray-polymerizable group-containing compound (S) include compounds having an isocyanate group and a (meth)acryloyl group, such as 2-isocyanatoethyl (meth)acrylate, isocyanatopropyl (meth)acrylate, and 1,1-(bisacryloyloxymethyl)ethyl isocyanate; and compounds having an epoxy group and a (meth)acryloyl group, such as glycidyl (meth)acrylate. Among them, 2-isocyanatoethyl (meth)acrylate is preferred.

[0036]

Here, the energy ray-polymerizable group-containing compound (S) reacts with a part of the reactive functional group (B1) which the acrylic copolymer (B') has. For that reason, in the polymer (B), the reactive functional group (B1) which does not react with the energy ray-polymerizable group-containing compound (S) remains, and according to this, the polymer (B) has both the reactive functional group (B1) and the energy ray-polymerizable group (B2).

An addition ratio of the energy ray-polymerizable group-containing compound (S) is preferably 75 to 97 equivalents, more preferably 80 to 95 equivalents, and still more preferably 85 to 93 equivalents relative to the whole amount (100 equivalents) of the reactive functional group (B1) of the acrylic copolymer (B').

When the addition ratio is allowed to fall within this range while regulating the content of the structural unit derived from the functional group monomer (b1) to the aforementioned preferred range (10 to 45% by mass, more preferably 15 to 40% by mass, and still more preferably 20 to 35% by mass), a fixed amount of the reactive functional group (B1) remains in the polymer (B). For that reason, the polymer (B) is appropriately crosslinked with the crosslinking agent (D), and it becomes easy to regulate the adhesive strength of the pressure sensitive adhesive layer to an appropriate value. Furthermore, it is also possible to introduce an appropriate amount of the energy ray-polymerizable group (B2) into the polymer (B).

[0037]

The acrylic copolymer (A') and the acrylic copolymer (B') may be each either a random copolymer or a block copolymer.

The acrylic copolymer (A') and the acrylic copolymer (B') can be each produced by polymerizing a mixture of monomers constituting each of the copolymers by a usual radical polymerization method. The polymerization can be performed by a solution polymerization method or the like by using a polymerization initiator, if desired. Examples of the polymerization initiator include known azo-based compounds and organic peroxides.

[0038]

In the case where the polymer (A) and the polymer (B) each are an acrylic polymer, it is preferred that not only a weight average molecular weight of the acrylic polymer constituting the polymer (A) is higher than a weight average molecular weight of the acrylic polymer constituting the polymer (B), but also a difference therebetween is 200,000 or more. In this way, when the difference in molecular weight between the both polymers is made large, a difference in characteristics between the first network and the second network is readily revealed, and a double network is readily formed. For that reason, the breaking characteristics become favorable, and the adhesive residue is readily reduced. From such a viewpoint, the aforementioned difference in weight average

molecular weight is more preferably 300,000 or more, and still more preferably 400,000 or more.

Meanwhile, though an upper limit value of the difference in weight average molecular weight is not particularly limited, the foregoing difference is preferably 850,000 or less, more preferably 750,000 or less, and still more preferably 700,000 or less.

[0039]

In the pressure sensitive adhesive composition, it is preferred that not only the weight average molecular weight of the acrylic polymer constituting the polymer (A) is 300,000 to 1,000,000, but also the weight average molecular weight of the acrylic polymer constituting the polymer (B) is 5,000 to 100,000.

Above all, the weight average molecular weight of the acrylic polymer constituting the polymer (A) is more preferably 350,000 to 850,000, and still more preferably 400,000 to 750,000.

Meanwhile, the weight average molecular weight of the acrylic polymer constituting the polymer (B) is more preferably 15,000 to 90,000, and still more preferably 30,000 to 80,000.

[0040]

By regulating the weight average molecular weight of the polymer (A) to the aforementioned lower limit value or more, the structure of the first network readily becomes more flexible and elongated. In addition, the film formability of the pressure sensitive adhesive layer readily becomes favorable, and furthermore, the cohesion of the pressure sensitive adhesive layer readily becomes high, and the adhesive residue is hardly generated. Meanwhile, by regulating the weight average molecular weight of the polymer (A) to the aforementioned upper limit value or less, the coatability, etc. of the pressure sensitive adhesive composition is readily made favorable.

By regulating the weight average molecular weight of the polymer (B) to the aforementioned upper limit value or less, the aforementioned second network readily takes a more stiff and brittle structure, and a suitable double network is readily formed. In addition, by regulating the weight average molecular weight of the polymer (B) to the aforementioned lower limit value or more, the cohesion of the pressure sensitive adhesive layer becomes appropriate, and the adhesive residue is hardly generated.

[0041]

(Urethane Polymer)

Next, the case where the polymer (A) and the polymer (B) are each a urethane polymer is described. The urethane polymer which is used for each of the polymer (A) and the polymer (B) is a polymer containing at least one of a urethane bond and a urea bond.

The urethane polymer constituting the polymer (A) is a polymer having the aforementioned reactive functional group (A1), and examples thereof include a carboxy group-containing polyurethane.

Examples of the urethane polymer constituting the polymer (B) include a reaction product obtained by allowing a part of a hydroxy group of a hydroxy group-containing polyurethane to react with the aforementioned energy ray-polymerizable group-containing compound (S). The hydroxy group-containing polyurethane is preferably one having a hydroxy group at an end thereof. Examples of the polyurethane having a hydroxy group at an end thereof include a polyurethane polyol obtained by allowing a polyol and a polyisocyanate compound to react with each other. As for the polyol and the polyisocyanate compound, various compounds which are conventionally used for a urethane-based pressure sensitive adhesive can be used.

[0042]

In the case where the polymer (A) and the polymer (B) each are a urethane polymer, it is preferred that not only a weight average molecular weight of the polymer (A) is higher than a weight average molecular weight of the polymer (B), but also a difference therebetween is 25,000 or more, and more preferably 50,000 or more. In addition, though an upper limit value of the difference in weight average molecular weight is not particularly limited, the foregoing difference is preferably 230,000 or less, and more preferably 120,000 or less.

A weight average molecular weight of the urethane polymer constituting the polymer (A) is preferably 30,000 to 250,000, and more preferably 40,000 to 150,000.

A weight average molecular weight of the urethane polymer constituting the polymer (B) is preferably 2,000 to 25,000, and more preferably 3,000 to 20,000.

[0043]

[Crosslinking Agents (C) and (D)]

The crosslinking agent (C) is a crosslinking agent which reacts with the reactive functional group (A1) and is used for the purpose of crosslinking the

polymer (A). In addition, the crosslinking agent (D) is a crosslinking agent which reacts with the reactive functional group (B1) and is used for the purpose of crosslinking the polymer (B).

In general, crosslinking with the crosslinking agent (C) and the crosslinking agent (D) is performed by heating the pressure sensitive adhesive composition. That is, as mentioned later, when the pressure sensitive adhesive composition is heated in a state where it has been formed in a thin film by means of coating or the like, the pressure sensitive adhesive composition is crosslinked with the crosslinking agent (C) and the crosslinking agent (D) to form the pressure sensitive adhesive layer.

The crosslinking agent (C) and the crosslinking agent (D) are each selected from, for example, an isocyanate-based crosslinking agent, an epoxy-based crosslinking agent, an amine-based crosslinking agent, a melamine-based crosslinking agent, an aziridine-based crosslinking agent, a hydrazine-based crosslinking agent, an aldehyde-based crosslinking agent, an oxazoline-based crosslinking agent, a metal alkoxide-based crosslinking agent, a metal chelate-based crosslinking agent, a metal salt-based crosslinking agent, and an ammonium salt-based crosslinking agent. As for each of the crosslinking agent (C) and the crosslinking agent (D), these compounds may be used alone or may be used in combination of two or more thereof among those compounds.

[0044]

The crosslinking agent (C) is suitably selected according to the kind of the reactive functional group (A1) which the polymer (A) has, and the crosslinking agent (D) is suitably selected according to the kind of the reactive functional group (B1) which the polymer (B) has. That is, as for the crosslinking agent (C), one which does not undergo a crosslinking reaction with the reactive functional group (B1) but reacts with the reactive functional group (A1) may be selected. In addition, as for the crosslinking agent (D), one which does not undergo a crosslinking reaction with the reactive functional group (A1) but reacts with the reactive functional group (B1) may be selected. In consequence, as for the crosslinking agent (C) and the crosslinking agent (D), compounds which are different from each other in terms of the kind are used.

For example, as mentioned above, in the case where the reactive functional group (A1) is a carboxy group, the crosslinking agent (C) is preferably selected from an epoxy-based crosslinking agent and a metal chelate-based crosslinking

agent, with an epoxy-based crosslinking agent being more preferred. In addition, in the case where the reactive functional group (A2) is a hydroxy group, the crosslinking agent (D) is preferably an isocyanate-based crosslinking agent.

[0045]

Examples of the epoxy-based crosslinking agent include 1,3-bis(N,N'-diglycidylaminomethyl)cyclohexane, N,N,N',N'-tetraglycidyl-m-xylylenediamine, ethylene glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, trimethylolpropane diglycidyl ether, diglycidylaniline, and diglycidylamine. These may be used alone or may be used in combination of two or more thereof. In addition, among them, 1,3-bis(N,N'-diglycidylaminomethyl)cyclohexane is preferred as the epoxy-based crosslinking agent.

[0046]

Examples of the metal chelate-based crosslinking agent include compounds in which acetylacetone, ethyl acetoacetate, tris(2,4-pentanedionate), etc. coordinates to a polyvalent metal, such as aluminum, iron, copper, zinc, tin, titanium, nickel, antimony, magnesium, vanadium, chromium, and zirconium. These may be used alone or may be used in combination of two or more thereof.

[0047]

Examples of the isocyanate-based crosslinking agent include polyisocyanate compounds. Specific examples of the polyisocyanate compound include aromatic polyisocyanates, such as tolylene diisocyanate, diphenylmethane diisocyanate, and xylylene diisocyanate; aliphatic polyisocyanates, such as hexamethylene diisocyanate; and alicyclic polyisocyanates, such as isophorone diisocyanate and hydrogenated diphenylmethane diisocyanate. In addition, examples thereof further include biurets and isocyanurates thereof as well as adducts thereof that are a reaction product with a low molecular weight active hydrogen containing compound, such as ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane, and castor oil.

These may be used alone or may be used in combination of two or more thereof. In addition, among those mentioned above, adducts of a polyhydric alcohol (for example, trimethylolpropane) of an aromatic polyisocyanate, such as tolylene diisocyanate, are preferred.

[0048]

In the crosslinking agent (C), by restraining its content, the first network

readily takes a flexible and elongated structure, and the adhesive residue is readily reduced. For that reason, it is preferred to make the content of the crosslinking agent (C) relatively small. Specifically, though the content of the crosslinking agent (C) in the pressure sensitive adhesive composition varies with the kind and molecular weight, etc. of the polymer (A), it is preferably 0.05 to 5 parts by mass, more preferably 0.1 to 3 parts by mass, and still more preferably 0.1 to 0.3 parts by mass based on 100 parts by mass of the polymer (A).

[0049]

Meanwhile, when a large amount of the crosslinking agent (D) is contained in the pressure sensitive adhesive composition, the second network readily takes a stiff and brittle structure. For that reason, it is preferred to make the content of the crosslinking agent (D) relatively large. It is preferred that the content of the crosslinking agent (D) in the pressure sensitive adhesive composition is larger than the content of the crosslinking agent (C) on a mass basis.

Though the content of the crosslinking agent (D) in the pressure sensitive adhesive composition varies with the kind and molecular weight, etc. of the polymer (B), specifically, it is preferably 2 to 20 parts by mass, more preferably 4 to 16 parts by mass, and still more preferably 5 to 12 parts by mass based on 100 parts by mass of the polymer (B).

[0050]

[Photopolymerization Initiator (E)]

It is preferred that the pressure sensitive adhesive composition contains a photopolymerization initiator (E). In view of the fact that the pressure sensitive adhesive layer contains a photopolymerization initiator (E), it becomes easy to allow energy ray curing of the pressure sensitive adhesive layer with an ultraviolet ray or the like to proceed.

Examples of the photopolymerization initiator (E) include low molecular weight polymerization initiators, such as acetophenone, 2,2-diethoxybenzophenone, 4-methylbenzophenone, 2,4,6-trimethylbenzophenone, Michler's ketone, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzyl diphenyl sulfide, tetramethylthiuram monosulfide, benzyl dimethyl ketal, dibenzyl, diacetyl, 1-chloroanthraquinone, 2-chloroanthraquinone, 2-ethylantraquinone, 2,2-dimethoxy-1,2-diphenylethan-1-one, 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1,

2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, diethyl thioxanthone, isopropyl thioxanthone, and 2,4,6-trimethylbenzoyldiphenyl phosphine oxide; and oligomerized polymerization initiators, such as oligo{2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone}. These may be used alone or may be used in combination of two or more thereof.

[0051]

The content of the photopolymerization initiator (E) is preferably 0.1 to 20 parts by mass, more preferably 0.5 to 15 parts by mass, and still more preferably 2 to 12 parts by mass based on 100 parts by mass of the total amount of the polymer (A) and the polymer (B).

[0052]

The pressure sensitive adhesive layer may contain, as components other than those mentioned above, a tackifier, a dye, a pigment, a degradation inhibitor, an antistatic agent, a flame retardant, a silane coupling agent, a chain transfer agent, a plasticizer, a filler, a resin component other than the aforementioned polymer (A) and polymer (B), and so on within a range where the effects of the present invention are not impaired.

Though the thickness of the pressure sensitive adhesive layer may be suitably regulated according to the surface state of the surface to be attached, on which the pressure sensitive adhesive sheet is attached, such as a bump height of the wafer surface, it is preferably 2 to 150 μm , more preferably 5 to 100 μm , and still more preferably 8 to 50 μm .

[0053]

[Breaking Characteristics of Pressure Sensitive Adhesive Layer]

As mentioned above, the pressure sensitive adhesive layer is cured upon irradiation with an energy ray and is preferred so as to have the following breaking characteristics after energy ray curing.

That is, the pressure sensitive adhesive layer after energy ray curing preferably has a breaking stress of 1.5 MPa or more, an elongation at break of 80% or more, and a break energy of 1.0 MJ/m³ or more. When the breaking stress, the elongation at break, and the breaking energy have relatively high values as mentioned above, the breaking strength of the pressure sensitive adhesive layer becomes favorable, and the adhesive residue is hardly generated. In addition, from the viewpoint of more preventing the adhesive residue from occurring, it is

more preferred that the breaking stress is 1.8 MPa or more, the elongation at break is 100% or more, and the breaking energy is 1.4 MJ/m³ or more; and it is still more preferred that the breaking stress is 2.0 MPa or more, the elongation at break is 180% or more, and the breaking energy is 1.8 J/m³ or more.

Though upper limits of these are not particularly limited, from the standpoint of practical use, it is preferred that the breaking stress is 10 MPa or less, the elongation at break is 400% or less, and the breaking energy is 5.0 MJ/m³ or less; and it is more preferred that the breaking stress is 6 MPa or less, the elongation at break is 300% or less, and the breaking energy is 3.5 MJ/m³ or less.

The breaking stress, the elongation at break, and the breaking energy mean values as measured by performing a tensile test in conformity with JIS K7127:1999, and specifically, are values obtained through the measurement by the methods described in the section of Examples as mentioned later.

[0054]

[Hysteresis Properties]

In the pressure sensitive adhesive layer after energy ray curing, so far as it has the aforementioned double network, when a fixed strain is applied, the second network is broken, whereas the first network remains without being broken. In consequence, in the pressure sensitive adhesive layer after energy ray curing, when after applying a fixed strain, a strain is again applied, the stress-strain characteristics become different from those in the initial stage to be caused due to the matter that the second network is broken. While such properties are called hysteresis properties, the presence or absence and the size of the hysteresis properties may be confirmed according to the following cyclic tensile test.

That is, the cyclic tensile test in which at every time when the number of elongation increases, the elongation (%) is made high, and elongation (strain) and release of a sample are repeated until the sample is broken is performed, thereby preparing a stress-strain curve at every elongation time as shown in Fig. 1. Then, for example, in plural stress-strain curves, by detecting a maximum value (DSmax) of a difference in stress between the curves at the same elongation, the presence or absence and the size of the hysteresis properties can be confirmed.

[0055]

Fig. 1 shows a stress-strain curve at the time of subjecting a sample of a pressure sensitive adhesive layer to be used in Example 1 as mentioned later after energy ray curing to a cyclic tensile test. Fig. 1 is concerned with an example in

which when the maximum elongation at the time of each elongation is increased by 50% in each time period from 50% (first time), and elongation and release are repeated, the sample is broken at 233% at the time of elongation of the fifth time. Here, in Fig. 1, the stress-strain curve at the time of each elongation is shown, and as shown in Fig. 1, the maximum value (DSmax) of a difference in stress is determined from such plural stress-strain curves. In the example of Fig. 1, though the maximum value (DSmax) of a difference in stress was calculated from the curves prepared from the continued two time periods of the fourth time and the fifth time, it may also be calculated from curves prepared from non-continued two time periods of, for example, the third time and the fifth time. The elongation is a value obtained by dividing a length of increase on drawing the sample by an original length and expressed in terms of %.

[0056]

When the double network is appropriately formed, and the higher the hysteresis properties are, the plural stress-strain curves are separated apart from each other, and the larger the aforementioned maximum value (DSmax) of a difference in stress is. From the viewpoint of appropriately forming a double network, the maximum value (DSmax) of a difference in stress is preferably 20% or more, more preferably 25% or more, and still more preferably 35% or more relative to the stress (BS) at the time of breakage in the cyclic tensile test. From the viewpoint of easiness of production or the like, the maximum value (DSmax) of a difference in stress is preferably 90% or less, and more preferably 60% or less.

[0057]

[Release Strength of Pressure Sensitive Adhesive Sheet]

Since the pressure sensitive adhesive layer is energy ray-curable, it can be made relatively soft before irradiation with an energy ray, whereby the pressure sensitive adhesive layer readily follows irregularities formed on the work surface. In addition, when the pressure sensitive adhesive sheet is cured upon irradiation with an energy ray, its adhesive strength is lowered, so that it is readily released from the work.

The adhesive strength of the pressure sensitive adhesive sheet after irradiation with an energy ray is preferably 1,700 mN/25 mm or less. In the case where the pressure sensitive adhesive sheet is attached to a work having protrusions, such as bumps, on the surface thereof, in general, there is revealed a state where the protrusions are embedded by the pressure sensitive adhesive layer,

or the pressure sensitive adhesive layer and the intermediate layer, of the pressure sensitive adhesive sheet. For that reason, when the pressure sensitive adhesive sheet is released therefrom, the adhesive residue is liable to be generated. However, by regulating the adhesive strength to 1,700 mN/25 mm or less, it becomes easy to prevent such generation of adhesive residue from occurring. In addition, it is also possible to easily release the pressure sensitive adhesive sheet from the work. The adhesive strength of the pressure sensitive adhesive sheet after irradiation with an energy ray is preferably 50 to 1,500 mN/25 mm, and more preferably 100 to 1,300 mN/25 mm.

[0058]

Though the adhesive strength of the pressure sensitive adhesive sheet before irradiation with an energy ray is, for example, larger than 1,700 mN/25 mm, it is preferably 1,800 to 20,000 mN/25 mm, and more preferably 1,800 to 9,000 mN/m. When the adhesive strength before irradiation with an energy ray falls within such a range, the adhesive properties to the work surface become favorable, and the protective performance on the work of the pressure sensitive adhesive sheet is readily enhanced.

The adhesive strength of the pressure sensitive adhesive sheet is one measured when the pressure sensitive adhesive layer surface of the pressure sensitive adhesive sheet is attached to a silicon wafer and then released in an environment at 23°C and at a release angle of 180°C and a release rate of 300 mm/min, and specifically, it is one measured by the method described in the section of Examples as mentioned later.

[0059]

It is possible to regulate the adhesive strength by suitably altering the kinds of the polymer (A) and the polymer (B), the blending amounts of these polymers, the kinds of the crosslinking agent (C) and the crosslinking agent (D), the blending amounts of these crosslinking agents, and so on. For example, by using an acrylic polymer for the polymer (A) and the polymer (B) as mentioned above, it becomes easy to obtain a pressure sensitive adhesive sheet having the aforementioned adhesive strength. In addition, by increasing the blending amounts of the crosslinking agent (C) and the crosslinking agent (D), it becomes easy to lower the adhesive strength.

It is also possible to regulate the adhesive strength after irradiation with an energy ray by the amount of the energy ray-polymerizable group (B2) and the

blending amount of the polymer (B). For example, the adhesive strength after irradiation with an energy ray tends to become low by increasing the amount of the energy ray-polymerizable group (B2) to be contained in the pressure sensitive adhesive composition, whereas it tends to become high by decreasing the foregoing amount of the energy ray-polymerizable group (B2).

[0060]

<Intermediate Layer>

In the pressure sensitive adhesive sheet of the present invention, an intermediate layer may be provided on one surface of the substrate. In view of the fact that the pressure sensitive adhesive sheet has an intermediate layer, even in the case where a difference in height of irregularities on the work surface is large, for example, the case where bumps are provided on the work, a convex part is embedded in the pressure sensitive adhesive layer and the intermediate layer. For that reason, the surface of the pressure sensitive adhesive sheet opposite to the surface on which it is attached to the work is easy to be kept flat.

Though the thickness of the intermediate layer can be suitably regulated according to the state of the surface to be attached on which the pressure sensitive adhesive sheet is attached, it is preferably 10 to 600 μm , more preferably 25 to 550 μm . and still more preferably 35 to 500 μm from the viewpoint that it is also possible to absorb relatively high bumps.

The intermediate layer is one formed of a resin composition for intermediate layer. In addition, it is preferred that the resin composition for intermediate layer contains a urethane (meth)acrylate (X).

[0061]

(Urethane (Meth)acrylate (X))

The urethane (meth)acrylate (X) is a compound having at least a (meth)acryloyl group and a urethane bond and has such properties that it is polymerized upon irradiation with an energy ray. Though the (meth)acryloyl group number in the urethane (meth)acrylate (X) may be monofunctional, bifunctional, trifunctional, or more functional, it is preferred that the resin composition for intermediate layer contains a monofunctional urethane (meth)acrylate. Since the monofunctional urethane (meth)acrylate does not participate in the formation of a three-dimensional network structure in the polymerization structure, the three-dimensional network structure is hardly formed in the intermediate layer, and it readily follows irregularities on the work

surface.

The urethane (meth)acrylate (X) can be, for example, obtained through a reaction of an isocyanate-terminated urethane prepolymer obtained by allowing a polyol compound (x1) to react with a polyisocyanate compound (x2), with a compound (x3) having a (meth)acryloyl group.

The urethane (meth)acrylate (X) may be used either alone or in combination of two or more thereof.

[0062]

The polyol compound for forming the urethane (meth)acrylate (X) is not particularly limited so long as it is a compound having two or more hydroxy groups. Specifically, examples of the polyol compound (x1) include an alkylene diol, a polyether-type polyol, a polyester-type polyol, and a polycarbonate-type polyol. Among them, a polyether-type polyol is preferred.

Though the polyol compound (x1) may be any of a bifunctional diol, a trifunctional triol, and a tetrafunctional or more functional polyol, a bifunctional diol is preferred from the viewpoint of easiness of availability, versatility, reactivity, and so on, and a polyether-type diol is more preferred. Preferred specific examples of the polyether-type diol include polyethylene glycol, polypropylene glycol, and polytetramethylene glycol.

[0063]

The polyester-type polyol is obtained through polycondensation of a polyol component and a polybasic acid component. Examples of the polyol component include various alkane diols (preferably alkane diols having approximately 2 to 10 carbon atoms), such as ethylene glycol, diethylene glycol, and butane diol; and various glycols.

As the polybasic acid component which is used for production of a polyester-type polyol, a compound which is generally known as a polybasic acid component of polyester can be used. Specifically, examples thereof include aliphatic dibasic acids having approximately 4 to 20 carbon atoms, such as adipic acid and sebacic acid; aromatic dibasic acids, such as terephthalic acid; aromatic polybasic acids, such as trimellitic acid; anhydrides corresponding thereto and derivatives thereof; as well as dimer acids and hydrogenated dimer acids.

The polycarbonate-type polyol is not particularly limited, and examples thereof include reaction products of a glycol and an alkylene carbonate.

[0064]

Examples of the polyisocyanate compound (x2) include an aliphatic polyisocyanate, an alicyclic polyisocyanate, and an aromatic polyisocyanate. More specifically, for example, the various polyisocyanate compounds exemplified for the crosslinking agent (C) and the crosslinking agent (D) are usable.

Examples of the compound (x3) having a (meth)acryloyl group include (meth)acrylates having a hydroxy group. Though the (meth)acrylate having a hydroxy group is not particularly limited, for example, a hydroxyalkyl (meth)acrylate is preferred. As the hydroxyalkyl (meth)acrylate, the same compounds as those exemplified above for the hydroxy group-containing monomer are usable.

[0065]

A weight average molecular weight of the urethane (meth)acrylate (X) for the resin composition for intermediate layer is preferably 1,000 to 100,000, more preferably 3,000 to 80,000, and still more preferably 5,000 to 65,000. When the foregoing weight average molecular weight is 1,000 or more, an appropriate hardness is imparted to the intermediate layer in a polymerization product between the urethane (meth)acrylate (X) and a polymerizable monomer (Z) as mentioned later.

[0066]

A blending amount of the urethane (meth)acrylate (X) in the resin composition for intermediate layer is preferably 10 to 70% by mass, more preferably 20 to 70% by mass, still more preferably 25 to 60% by mass, and yet still more preferably 30 to 50% by mass on a basis of the whole amount of the resin composition for intermediate layer (solid content basis). When the blending amount of the urethane (meth)acrylate falls within such a range, it is easy to allow the intermediate layer to follow irregularities on the work surface.

[0067]

The resin composition for intermediate layer further contains, for example, preferably at least one selected from the group consisting of a thiol group-containing compound (Y) and a polymerizable monomer (Z), and more preferably the both, in addition to the aforementioned urethane (meth)acrylate (X).

[0068]

(Thiol Group-Containing Compound (Y))

Though the thiol group-containing compound (Y) is not particularly

limited so long as it is a compound having at least one thiol group in a molecule thereof, a polyfunctional thiol group-containing compound is preferred, and a tetrafunctional thiol group-containing compound is more preferred.

Specifically, examples of the thiol group-containing compound (Y) include nonyl mercaptan, 1-dodecanethiol, 1,2-ethanedithiol, 1,3-propanedithiol, triazinethiol, triazinedithiol, triazinetrithiol, 1,2,3-propanetrithiol, tetraethylene glycol-bis(3-mercaptopropionate), trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), dipentaerythritol hexakis(3-mercaptopropionate), tris[(3-mercaptopropionyloxy)-ethyl]-isocyanurate, 1,4-bis(3-mercaptobutyryloxy)butane, pentaerythritol tetrakis(3-mercaptobutyrate), and 1,3,5-tris(3-mercaptobutyloxyethyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione.

These thiol group-containing compounds (Y) may be used either alone or in combination of two or more thereof.

A blending amount of the thiol group-containing compound (Y) is preferably 1.0 to 4.9 parts by mass, and more preferably 1.5 to 4.8 parts by mass based on 100 parts by mass of a sum total of the urethane (meth)acrylate (X) and a polymerizable monomer (Z) as mentioned later.

[0069]

(Polymerizable Monomer (Z))

From the viewpoint of improving the film formability, it is preferred that the resin composition for intermediate layer further contains a polymerizable monomer (Z). The polymerizable monomer (Z) is a polymerizable compound other than the aforementioned urethane (meth)acrylate (X) and is a compound that is polymerizable upon irradiation with an energy ray. However, the polymerizable monomer (Z) means a monomer exclusive of a resin component. The polymerizable monomer (Z) is preferably a compound having at least one (meth)acryloyl group.

In this specification, the wording "resin component" indicates an oligomer or a polymer having a repeating structure in a structure thereof and refers to a compound having a weight average molecular weight of 1,000 or more.

Examples of the polymerizable monomer (Z) include alkyl (meth)acrylates having an alkyl group having 1 to 30 carbon atoms; (meth)acrylates having a functional group, such as a hydroxy group, an amide group, an amino group, and

an epoxy group; (meth)acrylates having an alicyclic structure; (meth)acrylates having an aromatic structure; (meth)acrylates having a heterocyclic structure; and other vinyl compounds.

[0070]

Examples of the (meth)acrylate having a functional group include hydroxyalkyl (meth)acrylates. As the hydroxyalkyl (meth)acrylate, the same compounds as those exemplified above for the hydroxy group-containing monomer are usable.

Examples of the (meth)acrylate having an alicyclic structure include isobornyl (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenylloxy (meth)acrylate, cyclohexyl (meth)acrylate, and adamantane (meth)acrylate.

Examples of the (meth)acrylate having an aromatic structure include phenylhydroxypropyl (meth)acrylate, benzyl (meth)acrylate, and 2-hydroxy-3-phenoxypropyl (meth)acrylate.

Examples of the (meth)acrylate having a heterocyclic structure include tetrahydrofurfuryl (meth)acrylate and morpholine (meth)acrylate.

These may be used alone or may be used in combination of two or more thereof.

As the polymerizable monomer (Z), it is preferred to use at least a (meth)acrylate having an alicyclic structure; it is more preferred to use both a (meth)acrylate having a functional group and a (meth)acrylate having an alicyclic structure; and it is still more preferred to use both a hydroxyalkyl (meth)acrylate and isobornyl (meth)acrylate.

[0071]

A blending amount of the polymerizable monomer (Z) in the resin composition for intermediate layer is preferably 20 to 80% by mass, more preferably 30 to 80% by mass, still more preferably 40 to 75% by mass, and yet still more preferably 50 to 70% by mass on a basis of the whole amount of the resin composition for intermediate layer (solid content basis). When the blending amount of the polymerizable monomer (Z) falls within such a range, since mobility of a portion formed through polymerization of the polymerizable monomer (Z) in the intermediate layer is high, the intermediate layer tends to become flexible, and the intermediate layer readily follows irregularities on the work surface.

A blending amount of the (meth)acrylate having an alicyclic structure is

preferably 52 to 87% by mass, more preferably 55 to 85% by mass, and still more preferably 60 to 80% by mass relative to the whole amount of the polymerizable monomer (Z) to be contained in the resin composition for intermediate layer. When the blending amount of the (meth)acrylate having an alicyclic structure falls within such a range, the intermediate layer readily follows irregularities on the work surface.

From the same viewpoint, a mass ratio of the urethane (meth)acrylate (X) and the polymerizable monomer (Z) in the resin composition for intermediate layer [$\{\text{urethane (meth)acrylate (X)}\}/\{\text{polymerizable monomer (Z)}\}$] is preferably 20/80 to 60/40, more preferably 30/70 to 50/50, and still more preferably 35/65 to 45/55.

[0072]

(Photopolymerization Initiator)

It is preferred that the resin composition for intermediate layer further contains a photopolymerization initiator. When the resin composition for intermediate layer contains the photopolymerization initiator, it becomes possible to easily cure the resin composition for intermediate layer with an energy ray, such as an ultraviolet ray.

As the photopolymerization initiator, for example, one suitably selected from those exemplified above for the photopolymerization initiator (E) is usable. The photopolymerization initiator may be used either alone or in combination of two or more thereof.

A blending amount of the photopolymerization initiator is preferably 0.05 to 15 parts by mass, more preferably 0.1 to 10 parts by mass, and still more preferably 0.3 to 5 parts by mass based on 100 parts by mass of a sum total of the urethane (meth)acrylate (X) and the polymerizable monomer (Z).

[0073]

(Other Additives)

The resin composition for intermediate layer may further contain other additives within a range where the effects of the present invention are not impaired. Examples of the other additives include a crosslinking agent, an antioxidant, a softener (plasticizer), a filler, a rust inhibitor, a pigment, and a dye. In the case of blending such an additive, a blending amount of the other additive is preferably 0.01 to 6 parts by mass, and more preferably 0.1 to 3 parts by mass based on 100 parts by mass of a sum total of the urethane (meth)acrylate (X) and the polymerizable monomer (Z).

The resin composition for intermediate layer may contain, in addition to the urethane (meth)acrylate (X), a resin component other than the urethane (meth)acrylate (X) within a range where the effects of the present invention are not impaired.

The intermediate layer may be formed of a resin composition for intermediate layer containing other resin component, such as an olefin-based resin, in place of the urethane (meth)acrylate (X).

[0074]

<Release Material>

As the release material which is provided on the pressure sensitive adhesive layer and a release material which is used in a process of a production method as mentioned later, a release sheet having been subjected to a single-sided release treatment, a release sheet having been subjected to a double-sided release treatment, and the like are usable, and those obtained by coating a release agent on a substrate for release material and the like are exemplified.

Examples of the substrate for release material include plastic films, such as polyester resin films of a polyethylene terephthalate resin, a polybutylene terephthalate resin, a polyethylene naphthalate resin, or the like; and polyolefin resin films of a polypropylene resin, a polyethylene resin, or the like.

Examples of the release agent include a silicone-based resin, an olefin-based resin, an isoprene-based resin, a rubber-based elastomer, such as a butadiene-based resin, a long-chain alkyl-based resin, an alkyd-based resin, and a fluorine-based resin.

Though a thickness of the release material is not particularly limited, it is preferably 5 to 200 μm , and more preferably 10 to 120 μm .

[0075]

[Production Method of Pressure Sensitive Adhesive Sheet]

The pressure sensitive adhesive sheet of the present invention is not particularly limited with respect to its production method and can be produced by a known method.

The intermediate layer can be, for example, formed by coating the resin composition for intermediate layer directly on one surface of a substrate to form a coating film, and then optionally drying and performing a curing treatment. In addition, the intermediate layer may also be formed by coating the resin composition for intermediate layer on the release treated surface of a release

material to form a coating film, then optionally drying and performing a semi-curing treatment to form a semi-cured layer on the release material, attaching this semi-cured layer on a substrate, and then completely curing the semi-cured layer. On that occasion, the release material may be suitably removed before completely curing the semi-cured layer or after curing it. As for the curing of the intermediate layer, it is preferred to irradiate the coating film with an energy ray to perform polymerization and curing. The energy ray is preferably an ultraviolet ray. In addition, in the case of forming the intermediate layer by using an olefin resin, the intermediate layer may be formed by means of extrusion molding or the like.

[0076]

It is preferred to form the pressure sensitive adhesive layer by coating the pressure sensitive adhesive composition and heating for crosslinking the pressure sensitive adhesive composition, and then optionally drying. On that occasion, the pressure sensitive adhesive composition may be coated directly on the intermediate layer or the substrate, or may be coated on the release treated surface of the release material to form the pressure sensitive adhesive layer, which is then attached on the intermediate layer or the substrate. The release material to be arranged on the pressure sensitive adhesive layer may be released, if desired.

A heating temperature and a heating time of the pressure sensitive adhesive composition may be a temperature and a time, respectively such that not only the polymer (A) is crosslinked with the crosslinking agent (C), but also the polymer (B) is crosslinked with the crosslinking agent (D). The heating temperature is typically 80 to 110°C, and preferably 90 to 100°C. In addition, the heating time is typically 1 to 5 minutes, and preferably 2 to 3 minutes.

[0077]

On forming the intermediate layer or the pressure sensitive adhesive layer, the resin composition for intermediate layer or the pressure sensitive adhesive composition may be further blended with an organic solvent to form a diluted liquid of the resin composition for intermediate layer or pressure sensitive adhesive composition. Examples of the organic solvent to be used include methyl ethyl ketone, acetone, ethyl acetate, tetrahydrofuran, dioxane, cyclohexane, n-hexane, toluene, xylene, n-propanol, and isopropanol.

As for such an organic solvent, the organic solvent which is used at the time of synthesis of the respective components contained in the resin composition

for intermediate layer or the pressure sensitive adhesive composition may be used as it is, or at least one other organic solvent may also be added.

The resin composition for intermediate layer or the pressure sensitive adhesive composition can be coated by a known coating method. Examples of the coating method include a spin coating method, a spray coating method, a bar coating method, a knife coating method, a roll coating method, a blade coating method, a die coating method, and a gravure coating method.

[0078]

[Use Method of Pressure Sensitive Adhesive Sheet]

The pressure sensitive adhesive sheet of the present invention is one to be used when attached on a work of every sort to process a work, such as a semiconductor wafer and is preferably used upon attachment on the work surface with irregularities, protrusions, or the like.

The pressure sensitive adhesive sheet of the present invention is more preferably used as a pressure sensitive adhesive sheet for semiconductor wafer surface protection upon attachment on the semiconductor wafer surface, particularly the wafer surface having bumps formed thereon. In addition, the pressure sensitive adhesive sheet is still more preferably used as a back grinding tape which is attached on the semiconductor wafer surface to protect a circuit formed on the wafer surface at the time of subsequent grinding of the wafer back surface. In the case where the pressure sensitive adhesive sheet of the present invention has an intermediate layer, even when a difference in height to be caused due to, for example, bumps, is present on the wafer surface, its embedding properties are favorable, and therefore, the protective performance of the wafer surface becomes favorable.

[0079]

In the present invention, the pressure sensitive adhesive layer is of an energy ray curing type, and the pressure sensitive adhesive sheet attached on the work surface, such as a semiconductor wafer, is energy ray-cured upon irradiation with an energy ray and then released from the work surface. In consequence, the pressure sensitive adhesive sheet is released after the adhesive strength has been lowered, and therefore, its release properties become favorable. In addition, as mentioned above, on releasing the cured pressure sensitive adhesive sheet, the adhesive residue is hardly generated.

In the case where the pressure sensitive adhesive sheet is used for a

semiconductor wafer, it is not limited to a back grinding sheet but is also usable for other applications. For example, the pressure sensitive adhesive sheet may also be used as a dicing sheet which is attached on the wafer back surface to hold the wafer on dicing the wafer. In this case, the wafer may be one having through-electrodes formed thereon or one having protrusions, such as bumps, irregularities, etc., formed on the wafer back surface.

Examples

[0080]

The present invention is hereunder described in more detail by reference to Examples, but it should be construed that the present invention is by no means limited by these Examples.

[0081]

The measurement methods and evaluation methods in the present invention are as follows.

[Weight Average Molecular Weight (Mw) and Number Average Molecular Weight (Mn)]

The measurement was performed under the following condition by using a gel permeation chromatograph (a product name: "HLC-8220", manufactured by Tosoh Corporation), and values as expressed in terms of standard polystyrene were adopted.

(Measurement Condition)

Column: "TSK guard column HXL-H", "TSK gel GMHXL-L ($\times 2$)", and "TSK gel G2000HXL" (all of which are manufactured by Tosoh Corporation)

Column temperature: 40°C

Eluent: Tetrahydrofuran

Flow rate: 1.0 mL/min

[0082]

[Tensile Test]

The tensile test was performed by the following method in conformity with JIS K7127:1999.

A measurement sample used for the tensile test was prepared as follows. The values obtained through measurement using the measurement sample were defined as a breaking stress, an elongation at break, and a breaking energy of the pressure sensitive adhesive layer, respectively.

(Preparation of Measurement Sample)

A pressure sensitive adhesive layer (thickness: 40 μm) having a polyethylene terephthalate (PET)-based release film (a trade name: "SP-PET381031", manufactured by Lintec Corporation, thickness: 38 μm) attached on the both surfaces thereof was prepared by the same method as in Example 1. In addition, five sheets of pressure sensitive adhesive layer sandwiched by the same release films as those mentioned above were prepared in the same procedures. Subsequently, two sheets of pressure sensitive adhesive layer exposed by releasing one of the release films were prepared, and the surfaces of the pressure sensitive adhesive layers were opposed to each other and laminated. Such procedures were repeated to laminate five layers of pressure sensitive adhesive layers, thereby obtaining a 200 μm -thick pressure sensitive adhesive layer sandwiched by the two sheets of release film.

The obtained laminate was irradiated with an ultraviolet ray by using a UV irradiating device (a product name: "RAD-2000m/12", manufactured by Lintec Corporation) under a condition at an irradiation rate of 15 mm/sec, an illuminance of 220 mW/cm, and a luminous energy of 500 mJ/cm², thereby curing the pressure sensitive adhesive layer. The obtained cured product of pressure sensitive adhesive layer was cut out in a size of 15 mm $\times$ 140 mm, thereby obtaining a measurement sample.

[0083]

(Measurement of Breaking Stress, Elongation at Break, and Breaking Energy of Pressure Sensitive Adhesive Layer)

A film-pulling label was attached in 20-mm portions of the both ends of the aforementioned measurement sample, thereby preparing a sample having a measurement object part of 15 mm $\times$ 100 mm. The sample was measured for a breaking stress and an elongation at break at the time of measurement at a distance between chucks of 100 mm and a tensile rate of 200 mm/min by using a tensile tester (a product name: "Autograph AG-IS 1kN", manufactured by Shimadzu Corporation). In addition, a stress-strain curve at the time of measurement of breaking stress and elongation at break was prepared, and an area of the underside of the curve was calculated to determine a breaking energy.

[0084]

[Cyclic Tensile Test]

A measurement sample was prepared by the same method as in the

aforementioned tensile test. The tensile test in the cyclic tensile test was performed using the foregoing measurement sample under a condition at a tensile rate of 200 mm/min and a release rate of 600 mm/min by using a tensile tester (a product name: "Autograph AG-IS 1kN", manufactured by Shimadzu Corporation).

The cyclic tensile test was performed in such a manner that at every time when the number of elongation increased, the elongation (%) was made high, and elongation (strain) and release of a sample were repeated until the sample was broken. On that occasion, the elongation of each cycle was set such that it increases from the elongation of 0% at intervals of a fixed increase% each time. Specifically, the increase% of elongation was selected from any of 3%, 5%, 8%, 10%, 20%, 30%, 50%, 100%, and $(100 + 100n)$ (n : an integer of 1 or more) such that the sample was broken in 4 to 6 cycles. That is, in the case where the increase% of elongation was 50%, the elongation was increased to 50%, 100%, 150%, 200%, and 250%, respectively.

In the cyclic tensile test, a stress-strain curve was prepared at every elongation, the prepared stress-strain curves were described on the same chart, and a maximum value (DSmax) of the difference in stress between the curves at the same elongation was detected from the obtained plural stress-strain curves.

[0085]

[Adhesive Strength after Irradiation with Energy Ray]

A pressure sensitive adhesive sheet of each of the Examples and Comparative Example was equally cut in a width of 25 mm and temporarily placed on a silicon mirror wafer as an adherend such that the pressure sensitive adhesive layer was located on the adherend side. A roll having a weight of 1 kg was allowed to execute one reciprocating motion on the temporarily placed pressure sensitive adhesive sheet to apply a load due to a own weight of the roll, thereby attaching the pressure sensitive adhesive sheet on the adherend. After the attachment, the resultant was kept in an environment at 23°C and a relative humidity of 50% for 20 minutes and then irradiated with an ultraviolet ray from the pressure sensitive adhesive sheet side by using a UV irradiating device (a product name: "RAD-2000m/12", manufactured by Lintec Corporation) under a condition at an illuminance of 220 mW/cm², a luminous energy of 560 mJ/cm², and an irradiation rate of 15 mm/sec. Subsequently, the resultant was allowed to stand in an environment at 23°C and a relative humidity of 50% for 5 minutes, and thereafter, the pressure sensitive adhesive sheet was released in an environment at 23°C and

a relative humidity of 50% under a condition at a release angle of 180° and a release rate of 300 mm/min by a tensile tester (product name: Tensilon, manufactured by Orientec Corporation). At that time, the adhesive strength was measured.

[Adhesive Strength before Irradiation with Energy Ray]

The adhesive strength was measured in the same manner as that mentioned above, except for omitting the irradiation with an ultraviolet ray and subsequent standing for 5 minutes.

[0086]

[Evaluation of Adhesive Residue]

A wafer with spherical bumps having a bump height of 250 μm , a pitch of 500 μm , and a diameter in a plan view of 300 μm (8-inch wafer, manufactured by Waltz, bump specification: Sn/Ag/Cu = 96.5/3/0.5% by mass, wafer surface material: SiO₂) was prepared as an adherend.

A pressure sensitive adhesive sheet prepared in each of the Examples and Comparative Example was attached on the wafer in a state where the pressure sensitive adhesive layer of the pressure sensitive adhesive sheet faced the bump forming surface of the wafer by using a laminator (a product name: "RAD-3510F/12", manufactured by Lintec Corporation). On attaching, a temperature of each of a laminate table and a laminate roll of the laminator was set to 60°C.

After lamination, an ultraviolet ray was irradiated from the pressure sensitive adhesive sheet side by using a UV irradiating device (a product name: "RAD-2000m/12", manufactured by Lintec Corporation) under a condition at an illuminance of 220 mW/cm², a luminous energy of 560 mJ/cm², and an irradiation rate of 15 mm/sec.

Subsequently, the pressure sensitive adhesive sheet was released from the wafer in an environment at 50°C and a relative humidity of 50% under a condition at a release rate of 120 mm/sec by using a tensile tester (a product name: "Autograph AG-IS 1KN", manufactured by Shimadzu Corporation).

After releasing, the exposed bump forming surface of the wafer was observed by using a digital microscope (a product name: "VHX-1000", manufactured by KEYENCE Corporation), thereby confirming the presence or absence of adhesive residue. In addition, the bump portion of the wafer was observed by using a scanning electron microscope (a product name: "VE-9800",

manufactured by KEYENCE Corporation), thereby confirming the presence or absence of adhesive residue. According to the scanning electron microscope, it is possible to observe a finer adhesive residue as compared with the digital microscope.

The adhesive residue was evaluated according to the following evaluation criteria.

A: The adhesive residue was not observed by any of the microscopes.

B: The adhesive residue was not observed by the digital microscope, but a slight adhesive residue was observed by the scanning electron microscope.

C: The adhesive residue was observed by any of the microscopes.

[0087]

Next, an intermediate layer-provided substrate and a pressure sensitive adhesive sheet were prepared by the following procedures. In the following description, respective mass parts are those expressed in terms of a solid content regarding a material obtained through dilution with a diluent, such as an organic solvent.

[Preparation of Intermediate Layer-provided Substrate]

A resin composition for intermediate layer was prepared by blending 40 parts by mass of monofunctional urethane acrylate, 45 parts by mass of isobornyl acrylate (IBXA), 15 parts by mass of 2-hydroxypropyl acrylate (HPA), 3.5 parts by mass of pentaerythritol tetrakis(3-mercaptopbutyrate) (a product name: "KARENZ MT PE1", manufactured by Showa Denko K.K., a secondary tetrafunctional thiol-containing compound, solid content concentration: 100% by mass), 1.8 parts by mass of a crosslinking agent, and 1.0 part by mass of 2-hydroxy-2-methyl-1-phenyl-propan-1-one (a product name: "DAROCUR 1173", manufactured by BASF SE, solid content concentration: 100% by mass) as a photopolymerization initiator. This resin composition for intermediate layer was coated on a PET-based release film (a product name: "SP-PET381031", manufactured by Lintec Corporation, thickness: 38 μm .) in the fountain die method, thereby forming a coating film.

Then, an ultraviolet ray was irradiated from the coating film side, thereby forming a semi-cured layer. The irradiation with an ultraviolet ray was performed by using a belt conveyor type ultraviolet ray irradiating device (a product name: "ECS-401GGX", manufactured by EYE GRAPHICS Co., Ltd.) as an ultraviolet ray irradiating device and using a high pressure mercury lamp (a product name:

"H04-L41", manufactured by EYE GRAPHICS Co., Ltd.) as an ultraviolet source under an irradiation condition at an illuminance of 112 mW/cm² of a light wavelength of 365 nm and at a luminous energy of 177 mJ/cm² (measured by a product name: "UVPF-A1", manufactured by EYE GRAPHICS Co., Ltd.).

On the formed semi-cured layer, a substrate made of a PET-based film (a product name: "COSMO SHINE A4100", manufactured by Toyobo Co., Ltd., thickness: 50 µm) was laminated, and the laminate was further irradiated with an ultraviolet ray (using the aforementioned ultraviolet ray irradiating device and ultraviolet source under an irradiation condition at an illuminance of 271 mW/cm² and at a luminous energy of 1,200 mJ/cm²) from the PET-based film side, thereby undergoing complete curing to form an intermediate layer having a thickness of 300 µm on the PET-based film as a substrate. There was thus obtained an intermediate layer-provided substrate.

[0088]

[Example 1]

An acrylic polymer (weight average molecular weight: 600,000) obtained through copolymerization of 97 parts by mass of n-butyl acrylate (BA) and 3 parts by mass of acrylic acid (AA) was prepared as a polymer (A).

In addition, an acrylic polymer (weight average molecular weight: 50,000) obtained by adding, to an acrylic copolymer (B') obtained through copolymerization of 70 parts by mass of n-butyl acrylate (BA) and 30 parts by mass of 2-hydroxyethyl acrylate (2HEA), 2-isocyanatoethyl methacrylate (a product name: "KARENZ MOI", manufactured by Showa Denko K.K.) in an addition ratio of 90 equivalents relative to the hydroxy group derived from 2HEA (100 equivalents) was prepared as a polymer (B).

To a mixture of 100 parts by mass of the polymer (A) and 50 parts by mass of polymer (B), 14.9 parts by mass of 2,2-dimethoxy-1,2-diphenylethane-1-one (a product name: "IRGACURE 651", manufactured by BASF SE) as a photopolymerization initiator (E), 4.2 parts by mass of trimethylolpropane adduct tolylene diisocyanate (a product name: "CORONATE L", manufactured by Tosoh Corporation) as a crosslinking agent (D), and 0.19 parts by mass of 1,3-bis(N,N-diglycidylaminomethyl)cyclohexane (a product name: "TETRAD-C", manufactured by Mitsubishi Gas Chemical Company, Inc.) as a crosslinking agent (C) were added, and the mixture was diluted with an organic solvent (methyl ethyl ketone) in a solid content concentration of 20% by mass and stirred for 30 minutes,

thereby preparing a diluted liquid of a pressure sensitive adhesive composition.

Subsequently, the prepared diluted liquid of a pressure sensitive adhesive composition was coated on a PET-based release film (a product name: "SP-PET381031", manufactured by Lintec Corporation, thickness: 38 μm) and heated for drying at 100°C for 2 minutes, thereby forming a pressure sensitive adhesive layer having a thickness of 10 μm on the release film.

The release film on the previously prepared intermediate layer-provided substrate was removed, the exposed intermediate layer was attached to the pressure sensitive adhesive layer on the release film, and unnecessary portions of end portions in the width direction were removed by means of cutting, thereby preparing a pressure sensitive adhesive sheet composed of substrate/intermediate layer/pressure sensitive adhesive layer/release sheet. The obtained pressure sensitive adhesive sheet and the pressure sensitive adhesive layer to be used for the pressure sensitive adhesive sheet were evaluated with respect to the breaking stress, the elongation at break, the breaking energy, the adhesive strength, and the adhesive residue according to the aforementioned evaluation methods. The results are shown in Table 1.

[0089]

The cyclic tensile test was carried out with respect to the pressure sensitive adhesive layer after energy ray curing, which is used in Example 1. Plural stress-strain curves obtained by the cyclic tensile test are shown in Fig. 1. An increase% of elongation of the test is 50%, and the elongation (%) is 50% at the first time, 100% at the second time, 150% at the third time, 200% at the fourth time, and 250% at the fifth time, respectively.

As shown in Fig. 1, in the cyclic tensile test, the sample was broken at an elongation of 233% at the time of the fifth elongation, and the stress at that time was 3.26 MPa.

In addition, a maximum value (DSmax) of a difference in stress between the curves at the same elongation as read out from Fig. 1 was 1.55 MPa, and the DSmax was 48% relative to the stress at the time of breakage in the cyclic tensile test.

[0090]

Similarly, the cyclic tensile test was carried out with respect to the pressure sensitive adhesive layer before energy ray curing, which is used in Example 1, and plural stress-strain curves obtained by the test are shown in Fig. 2.

An increase% of elongation of the test is 100%, and the elongation (%) is 100% at the first time, 200% at the second time, 300% at the third time, and 400% at the fourth time, respectively.

As shown in Fig. 2, before the energy ray curing, the sample was broken at an elongation of 321%, and the stress at that time was 1.41 MPa.

In addition, a maximum value (DSmax) of a difference in stress between the curves at the same elongation as read out from Fig. 2 was 0.20 MPa, and the DSmax was 14% relative to the stress at the time of breakage in the cyclic tensile test.

[0091]

[Example 2]

A pressure sensitive adhesive sheet was prepared by the same procedures as in Example 1, except for changing the use amount of the 1,3-bis(N,N-diglycidylaminomethyl)cyclohexane (a product name: "TETRAD-C", manufactured by Mitsubishi Gas Chemical Company, Inc.) as the crosslinking agent (C) to 0.38 parts by mass.

[0092]

[Example 3]

A pressure sensitive adhesive sheet was prepared by the same procedures as in Example 1, except for changing the use amount of the 1,3-bis(N,N-diglycidylaminomethyl)cyclohexane (a product name: "TETRAD-C", manufactured by Mitsubishi Gas Chemical Company, Inc.) as the crosslinking agent (C) to 0.57 parts by mass.

[0093]

[Comparative Example 1]

To an acrylic copolymer obtained through a copolymerization of 90 parts by mass of 2-ethylhexyl acrylate (2EHA) and 10 parts by mass of 4-hydroxybutyl acrylate (4HBA), 2-isocyanatoethyl methacrylate (a product name: "KARENZ MOI", manufactured by Showa Denko K.K.) was added in an addition ratio of 65 equivalents relative to the hydroxy group derived from 4HBA (100 equivalents), thereby obtaining an acrylic polymer (weight average molecular weight: 1,000,000). To 100 parts by mass of this acrylic polymer, 3 parts by mass of 1-hydroxycyclohexyl phenyl ketone (a product name: "IRGACURE 184", manufactured by BASF SE) as a photopolymerization initiator was added; 1.1 parts by mass of trimethylolpropane adduct tolylene diisocyanate (a product

name: "CORONATE L", manufactured by Tosoh Corporation) as a crosslinking agent was added; and the mixture was diluted with an organic solvent (methyl ethyl ketone) in a concentration of 20% by mass and stirred for 30 minutes, thereby preparing a diluted liquid of a pressure sensitive adhesive composition. Subsequently, the prepared diluted liquid of a pressure sensitive adhesive composition was coated on a PET-based release film (a product name: "SP-PET381031", manufactured by Lintec Corporation, thickness: 38 μm) and heated for drying at 100°C for 2 minutes, thereby forming a pressure sensitive adhesive layer having a thickness of 10 μm on the release film.

The release film on the previously prepared intermediate layer-provided substrate was removed, the exposed intermediate layer and the pressure sensitive adhesive layer were attached to each other, and unnecessary portions of end portions in the width direction were removed by means of cutting, thereby preparing a pressure sensitive adhesive sheet composed of substrate/intermediate layer/pressure sensitive adhesive layer/release sheet. The obtained pressure sensitive adhesive sheet and the pressure sensitive adhesive layer to be used for the pressure sensitive adhesive sheet were evaluated according to the aforementioned evaluation methods. The results are shown in Table 1.

[0094]

The cyclic tensile test was carried out with respect to the pressure sensitive adhesive layer after energy ray curing, which is used in Comparative Example 1. Plural stress-strain curves obtained by the cyclic tensile test are shown in Fig. 3. An increase% of elongation of the test is 5%, and the elongation (%) is 5% at the first time, 10% at the second time, 15% at the third time, and 20% at the fourth time, respectively.

As shown in Fig. 3, in the cyclic tensile test, the sample was broken at an elongation of 20% at the time of the fourth elongation, and the stress at that time was 0.94 MPa.

In addition, as shown in Fig. 3, all of the stress-strain curves at the time of elongation at the first to fourth times overlapped. For that reason, a maximum value (DSmax) of a difference in stress between the curves at the same elongation as read out from the stress-strain curves was 0 MPa, and the DSmax was 0% relative to the stress at the time of breakage in the cyclic tensile test.

[0095]

Table 1

	Breaking stress [MPa]	Elongation at break [%]	Breaking energy [MJ/m ³]	Adhesive strength [mN/25 mm]		Adhesive residue
				Before UV irradiation	After UV irradiation	
Example 1	2.42	228	2.34	7300	1000	A
Example 2	3.32	144	1.46	2500	1100	B
Example 3	4.22	107	1.42	1900	800	B
Comparative Example 1	1.28	30	0.16	4500	780	C

[0096]

Each of the pressure sensitive adhesive compositions of Examples 1 to 3 contained the polymer (A) and the polymer (B), and the crosslinking agent (C) and the crosslinking agent (D) which are capable of crosslinking these polymers, respectively, and the polymer (B) had an energy ray-polymerizable group (B2), and thus, an appropriated double network was formed after irradiation with an energy ray. For that reason, as is clear from Fig. 1, the pressure sensitive adhesive layer exhibited peculiar hysteresis properties and was favorable in breaking characteristics, and when releasing the pressure sensitive adhesive sheet from the work (namely, the bump forming surface of the wafer), the adhesive residue on the work surface could be effectively prevented from occurring. In addition, the values of adhesive strength before and after irradiation with an energy ray were appropriate. As is also clear from Fig. 2, in the pressure sensitive adhesive compositions of the Examples, before irradiation with an energy ray, though the hysteresis properties were exhibited, they were insufficient, and a double network was not appropriately formed.

In contrast, in Comparative Example 1, only one kind of the polymer and one kind of the crosslinking agent for crosslinking the polymer were blended, and therefore, the breaking characteristics did not become favorable, and the adhesive residue could not be appropriately prevented from occurring.

CLAIMS

[Claim 1]

A semiconductor processing pressure sensitive adhesive sheet comprising a substrate and a pressure sensitive adhesive layer provided on one surface of the substrate, the pressure sensitive adhesive layer being formed of a pressure sensitive adhesive composition, wherein

the pressure sensitive adhesive composition contains a polymer (A) having a reactive functional group (A1); a polymer (B) having a reactive functional group (B1) different from the reactive functional group (A1) and an energy ray-polymerizable group (B2); a crosslinking agent (C) that reacts with the reactive functional group (A1); and a crosslinking agent (D) that reacts with the reactive functional group (B1);

the crosslinking agent (C) and the crosslinking agent (D) are different compounds from each other; and

the semiconductor processing pressure sensitive adhesive sheet is used to be attached on a wafer surface having bumps and protect the wafer surface having bumps.

[Claim 2]

The semiconductor processing pressure sensitive adhesive sheet according to claim 1, wherein a weight average molecular weight of the polymer (A) is higher than a weight average molecular weight of the polymer (B).

[Claim 3]

The semiconductor processing pressure sensitive adhesive sheet according to claim 1 or 2, wherein the polymer (A) and the polymer (B) each are an acrylic polymer.

[Claim 4]

The semiconductor processing pressure sensitive adhesive sheet according to claim 3, wherein a weight average molecular weight of the acrylic polymer constituting the polymer (A) is higher than a weight average molecular weight of the acrylic polymer constituting the polymer (B), and a difference therebetween is 200,000 or

more.

[Claim 5]

The semiconductor processing pressure sensitive adhesive sheet according to claim 4, wherein the weight average molecular weight of the acrylic polymer constituting the polymer (A) is from 300,000 to 1,000,000, and the weight average molecular weight of the acrylic polymer constituting the polymer (B) is from 5,000 to 100,000.

[Claim 6]

The semiconductor processing pressure sensitive adhesive sheet according to any one of claims 3 to 5, wherein the acrylic polymer constituting the polymer (A) is an acrylic copolymer (A') containing a structural unit derived from a functional group monomer (a1) having the reactive functional group (A1) and a structural unit derived from an alkyl (meth)acrylate (a2).

[Claim 7]

The semiconductor processing pressure sensitive adhesive sheet according to any one of claims 3 to 6, wherein the acrylic polymer constituting the polymer (B) is a reaction product obtained by allowing a part of the reactive functional group (B1) of an acrylic copolymer (B') containing a structural unit derived from a functional group monomer (b1) having the reactive functional group (B1) and a structural unit derived from an alkyl (meth)acrylate (b2) to react with an energy ray-polymerizable group-containing compound (S) having the energy ray-polymerizable group (B2).

[Claim 8]

The semiconductor processing pressure sensitive adhesive sheet according to any one of claims 1 to 7, wherein the reactive functional group (A1) is a carboxy group, and the reactive functional group (B1) is a hydroxy group.

[Claim 9]

The semiconductor processing pressure sensitive adhesive sheet according to claim 8, wherein the crosslinking agent (C) is an epoxy-based crosslinking agent, and the crosslinking agent (D) is an isocyanate-based crosslinking agent.

[Claim 10]

The semiconductor processing pressure sensitive adhesive sheet according to any one of claims 1 to 9, wherein the content of the crosslinking agent (D) is larger than the content of the crosslinking agent (C) on a mass basis in the pressure sensitive adhesive composition, and the content of the crosslinking agent (D) in the pressure sensitive adhesive composition is from 2 to 20 parts by mass based on 100 parts by mass of the polymer (B).

[Claim 11]

A semiconductor processing pressure sensitive adhesive sheet comprising a substrate and a pressure sensitive adhesive layer provided on one surface of the substrate, the pressure sensitive adhesive layer being formed of a pressure sensitive adhesive composition, wherein

the pressure sensitive adhesive composition contains a polymer (A) having a reactive functional group (A1); a polymer (B) having a reactive functional group (B1) different from the reactive functional group (A1) and an energy ray-polymerizable group (B2); a crosslinking agent (C) that reacts with the reactive functional group (A1); and a crosslinking agent (D) that reacts with the reactive functional group (B1);

the reactive functional group (A1) is a carboxy group, and the reactive functional group (B1) is a hydroxy group; and

the crosslinking agent (C) is an epoxy-based crosslinking agent, and the crosslinking agent (D) is an isocyanate-based crosslinking agent.

[Claim 12]

A semiconductor processing pressure sensitive adhesive sheet comprising a substrate and a pressure sensitive adhesive layer provided on one surface of the substrate, the pressure sensitive adhesive layer being formed of a pressure sensitive adhesive composition, wherein

the pressure sensitive adhesive composition contains a polymer (A) having a reactive functional group (A1); a polymer (B) having a reactive functional group (B1) different from the reactive functional group (A1) and an energy ray-polymerizable group (B2); a crosslinking agent (C) that reacts with the reactive functional group (A1); and a crosslinking agent (D) that reacts with the reactive functional group (B1); and

the content of the crosslinking agent (D) is larger than the content of the crosslinking agent (C) on a mass basis in the pressure sensitive adhesive composition, and the content of the crosslinking agent (D) in the pressure sensitive adhesive composition is from 2 to 20 parts by mass based on 100 parts by mass of the polymer (B).