

DESCRIPTION

Title of Invention: ADHESIVE TAPE FOR WORK PROCESSING

Technical Field

[0001]

The present invention relates to a pressure sensitive adhesive tape for work processing, particularly to a pressure sensitive adhesive tape for protecting a semiconductor wafer surface that is used for protecting the surface of semiconductor wafers with bumps.

Background Art

[0002]

In the midst of rapid progress in thickness reduction, size reduction and multi-functionalization of information terminal devices, thickness reduction and density enhancement also in semiconductor apparatuses to be mounted on them are demanded and the thickness reduction of semiconductor wafers is also demanded. In order to meet the demand, the thickness reduction is conventionally carried out by grinding the rear surface of the semiconductor wafers. Further in recent years, in semiconductor wafers, bumps of about 30 to 100 μm in height composed of solder or the like are formed on the wafer surface in some cases. In the case where the rear surface of such semiconductor wafers with bumps is ground, a surface protecting sheet is attached on the wafer surface on which the bumps are formed in some cases in order to protect bump portions.

[0003]

There is conventionally known a surface protecting sheet having a resin layer that has storage elastic moduli at 25°C and 60°C regulated so as to fall in specific ranges (for example, see Patent Literature 1). This surface protecting sheet is provided with the resin layer having a difference in storage elastic modulus between at room temperature (25°C) and a high temperature (60°C), with an intention that when the surface protecting sheet is attached at a high temperature on a wafer surface having irregular portions, the resin layer becomes soft to allow the surface protecting sheet to absorb irregularities on the wafer surface to thereby lessen differences in height on the wafer surface.

[0004]

Further, there is known a surface protecting sheet in which two resin layers having predetermined tensile elastic moduli are provided on a substrate, the resin layer on the attached surface side among these two resin layers being formed of a thermoplastic elastomer such as polystyrene-based elastomer, polyolefin-based elastomer, polyurethane-based elastomer or polyester-based elastomer, with a view to improving the adhesiveness and the peelability (see Patent Literature 2).

[0005]

Further as a surface protecting sheet, there is known a pressure sensitive adhesive tape in which a middle layer and a pressure sensitive adhesive layer are provided on one surface of a substrate. It is disclosed that in this pressure sensitive adhesive tape, the storage elastic modulus at 25°C of the middle layer is made to be about 30 to 1,000 kPa in order to enhance irregularity absorbability, and that the pressure sensitive adhesive layer is formed of an energy ray-curable pressure sensitive adhesive (for example, see Patent Literature 3). As seen in Patent Literature 3, when an energy ray-curable pressure sensitive adhesive is used for a surface protecting sheet, the application workability to and the peelability from semiconductor wafers become good easily. Conventionally, as energy ray-curable pressure sensitive adhesives to be used in surface protecting sheets, acrylic ones are mainly used in view of easiness of regulating the adhesivity and securing the embeddability of bumps.

Citation List

Patent Literature

[0006]

PTL1: JP 4603578 B

PTL2: JP 4918181 B

PTL3: JP 4367769 B

Summary of Invention

Technical Problem

[0007]

In recent years, along with further density enhancement and size reduction of semiconductor apparatuses, the height of bumps is likely to become high and even ones having a height of 200 μm or higher are being studied. However, in

the case where an acryl-based surface protecting sheet described in Patent Literature 3 is used for semiconductor wafers having high bumps and large differences in height, a large number of pressure sensitive adhesive residues (adhesive residues) are sometimes generated on the bumps when the sheet is peeled. This is because the acryl-based energy ray-curable pressure sensitive adhesive is relatively low in the cohesive force and the mechanical strength.

On the other hand, for example, in Patent Literatures 1 and 2, there are studied the uses of materials other than an acryl-based pressure sensitive adhesive, such as polyurethane-based elastomers, on the attached surface of surface protecting sheets. In Patent Literatures 1 and 2, however, applications of those materials to energy ray-curable pressure sensitive adhesives are not studied and further improvements are necessary in order to secure the adhesivity, the peelability, and the embeddability of bumps.

[0008]

The present invention has been made under these circumstances, and an object of the present invention is to provide a pressure sensitive adhesive tape for work processing which has good tackiness to and peelability from works such as semiconductor wafers as well as good conformability of a pressure sensitive adhesive layer to the surface shape of works, represented by the embeddability of bumps, and also leaves little adhesive residue on the work surface even when the surface shape of works to be attached on is not flat.

Solution to Problem

[0009]

As a result of diligent studies, the present inventors have found that the above problem can be solved by using urethane-based pressure sensitive adhesives as pressure sensitive adhesives, and adapt a specific composition for the pressure sensitive adhesive, and have completed the following present invention. The present invention provides the following pressure sensitive adhesive tapes for work processing of (1) to (16).

(1) A pressure sensitive adhesive tape for work processing, having a substrate and a pressure sensitive adhesive layer provided on one surface side of the substrate,

wherein the pressure sensitive adhesive layer comprises a urethane-based resin (A) and an energy ray-curable compound (B); and the energy ray-curable

compound (B) is non-reactive with the urethane-based resin (A), has a photopolymerizable unsaturated bond, and has a molecular weight of 35,000 or lower.

(2) The pressure sensitive adhesive tape for work processing according to the above (1), wherein the energy ray-curable compound (B) is at least one selected from the group consisting of (meth)acrylate monomers (B1) and urethane (meth)acrylates (B2).

(3) The pressure sensitive adhesive tape for work processing according to the above (2), wherein the energy ray-curable compound (B) comprises at least a (meth)acrylate monomer (B1), and the (meth)acrylate monomer (B1) is a polyfunctional (meth)acrylate ester being a complete ester of a polyhydric alcohol with (meth)acrylic acid.

(4) The pressure sensitive adhesive tape for work processing according to any one of the above (1) to (3), wherein the energy ray-curable compound (B) is bi- or more functional in terms of (meth)acryloyl group in one molecule thereof.

(5) The pressure sensitive adhesive tape for work processing according to any one of the above (1) to (4), wherein the urethane-based resin (A) has a photopolymerizable unsaturated bond.

(6) The pressure sensitive adhesive tape for work processing according to any one of the above (1) to (5), wherein the pressure sensitive adhesive layer is formed of a pressure sensitive adhesive composition comprising, at least, a urethane polymer (A'), the energy ray-curable compound (B), and a crosslinking agent (C); and

the urethane-based resin (A) is a crosslinked polymer that the urethane polymer (A') is crosslinked with the crosslinking agent (C).

(7) The pressure sensitive adhesive tape for work processing according to the above (6), wherein the crosslinking agent (C) comprises a crosslinking agent (C1) having a photopolymerizable unsaturated bond.

(8) The pressure sensitive adhesive tape for work processing according to the above (6) or (7), wherein the urethane polymer (A') and the crosslinking agent (C) are bonded through a urethane bond.

(9) The pressure sensitive adhesive tape for work processing according to any one of the above (6) to (8), wherein the pressure sensitive adhesive composition further comprises a compound (D) having a photopolymerizable unsaturated bond and a reactive functional group reactive with the crosslinking agent (C).

- (10) The pressure sensitive adhesive tape for work processing according to the above (9), wherein the compound (D) is a polyfunctional (meth)acrylate ester being a partial ester of a polyhydric alcohol with (meth)acrylic acid.
- (11) The pressure sensitive adhesive tape for work processing according to any one of the above (1) to (10), wherein the pressure sensitive adhesive layer after energy ray irradiation has a breaking stress of 2.5 MPa or higher.
- (12) The pressure sensitive adhesive tape for work processing according to any one of the above (1) to (11), wherein a middle layer is provided between the substrate and the pressure sensitive adhesive layer.
- (13) The pressure sensitive adhesive tape for work processing according to the above (12), wherein the middle layer has a thickness of 10 to 600 μm .
- (14) The pressure sensitive adhesive tape for work processing according to the above (12) or (13), wherein the middle layer has a loss tangent at 50°C of 1.0 or higher as measured at a frequency of 1 Hz.
- (15) The pressure sensitive adhesive tape for work processing according to any one of the above (1) to (14), wherein the pressure sensitive adhesive tape after energy ray irradiation has a peel strength of 2,000 mN/25 mm or lower.
- (16) The pressure sensitive adhesive tape for work processing according to any one of the above (1) to (15), wherein the pressure sensitive adhesive tape is used for protecting a semiconductor wafer surface.

Advantageous Effects of Invention

[0010]

According to present invention, a pressure sensitive adhesive tape for work processing can be provided which has good tackiness and peelability as well as good conformability of a pressure sensitive adhesive layer to the surface shape of works, and also leaves little adhesive residue on the work surface.

Description of Embodiments

[0011]

Hereinbelow, the "weight-average molecular weight (M_w)" is a value in terms of polystyrenes as measured by gel permeation chromatography (GPC), and is specifically a value measured by a method described in Examples.

Herein, for example, a "(meth)acrylate" is intended to indicate both an "acrylate" and a "methacrylate", and the same will apply to other analogous terms.

[0012]

Hereinafter, the present invention will be described by way of embodiments.

The pressure sensitive adhesive tape for work processing (hereinafter, referred to also simply as "pressure sensitive adhesive tape") of the present invention has a substrate and a pressure sensitive adhesive layer provided on one surface side of the substrate. The pressure sensitive adhesive tape may further have a middle layer between the substrate and the pressure sensitive adhesive layer. The pressure sensitive adhesive tape may be constituted of two layers or three layers as above, and may be provided further with one or more other layers. For example, on the pressure sensitive adhesive layer, a release material may be provided.

Hereinafter, each member constituting the pressure sensitive adhesive tape will be described in detail.

[0013]

<Substrate>

The substrate to be used for the pressure sensitive adhesive tape is not especially limited, but is preferably a resin film. The resin film is suitable for workpieces of electronic components because being little in dust creation as compared with paper and nonwoven fabric, and is preferable because being readily available. The substrate may be a monolayer film composed of one resin film, or may be a multi-layer film obtained by laminating a plurality of resin films.

Examples of the resin film to be used as the substrate include polyolefin-based films, vinyl halide polymer-based films, acryl resin-based films, rubber-based films, cellulose-based films, polyester-based films, polycarbonate-based films, polystyrene-based films, polyphenylene sulfide-based films, and cycloolefin polymer-based films.

Among these, polyester-based films are preferable because they are capable of stably holding wafers when the wafers are ground to ultrathin ones, and are also high in thickness accuracy; and among the polyester-based films,

polyethylene terephthalate films are preferable because they are readily available and high in thickness accuracy.

Further the thickness of the substrate is not especially limited, but is preferably 10 to 200 μm , and more preferably 25 to 150 μm .

[0014]

In view of improving the adhesivity of the substrate to the pressure sensitive adhesive layer or the middle layer, there may be used a substrate obtained by further laminating a primer layer or a pressure sensitive adhesive layer on the surface of the resin film. Further the substrate to be used in the present invention may contain a filler, a colorant, an antistatic agent, an antioxidant, an organic lubricant, a catalyst, or the like. Further the substrate may be transparent, or may be colored as required, but preferable is the substrate transmitting energy rays sufficiently to cure the pressure sensitive adhesive layer.

[0015]

<Middle layer>

The pressure sensitive adhesive tape of the present invention may be provided with the middle layer on one surface of the substrate. When the pressure sensitive adhesive tape has the middle layer, protrusions are embedded in the pressure sensitive adhesive layer and the middle layer even in the case where the differences in height of irregularities on the work surface are large, including the case where the work is provided with bumps, and it thereby becomes easy for the pressure sensitive adhesive tape of the present invention to hold flat a surface of the pressure sensitive adhesive tape on the opposite side to a surface attached on the work. The middle layer to be used in the present invention has a loss tangent ($\tan\delta$) (hereinafter, referred to also simply as "loss tangent") at 50°C as measured at a frequency of 1 Hz of preferably 1.0 or higher.

When the loss tangent of the middle layer is such a value, the middle layer sufficiently deforms and can easily conform to the irregularities upon attaching the pressure sensitive adhesive tape for work processing on a work having irregularities, such as a wafer with bumps. In order that the middle layer sufficiently absorbs irregularities such as bumps, for example, to give a good attaching state to the surface of the wafer with bumps, the loss tangent of the middle layer is more preferably 1.5 or higher, still more preferably 1.65 or higher, and further still more preferably 1.8 or higher.

Further in view of regulating the flowability of the middle layer within a suitable range when being heated, the loss tangent of the middle layer is preferably 5.0 or lower, and more preferably 4.0 or lower.

Here, the above-mentioned loss tangent of the middle layer is more specifically a value measured based on a method described in Examples described later.

[0016]

Further the thickness of the middle layer can suitably be regulated according to the state of a surface on which the pressure sensitive adhesive tape is attached, but is preferably 10 to 600 μm , more preferably 25 to 550 μm , and still more preferably 35 to 500 μm , in view of absorbing bumps having relatively large heights.

[0017]

The middle layer is formed of a resin composition for the middle layer. The resin composition for the middle layer contains preferably a urethane (meth)acrylate.

(Urethane (meth)acrylate (X))

A urethane (meth)acrylate (X) is a compound having, at least, a (meth)acryloyl group and a urethane bond, and has a property of being polymerized by energy ray irradiation. Here, the energy rays are rays having energy quanta among electromagnetic waves or charged particle beams, and refer to active rays such as ultraviolet rays or electron beams.

The number of the (meth)acryloyl group in the urethane (meth)acrylate (X) may be one, two, three, or more, but in order to facilitate making the loss tangent to be 1.0 or higher, the resin composition for the middle layer preferably contains a monofunctional urethane (meth) acrylate. The reason of this is as follows: since the monofunctional urethane (meth) acrylate does not participate in the formation of a three-dimensional network structure in a polymerized structure, it becomes difficult for a three-dimensional network structure to be formed in the middle layer to thereby tend to result in an increased loss tangent.

[0018]

The urethane (meth)acrylate (X) to be used for the resin composition for the middle layer can be obtained, for example, by reacting an isocyanate-terminated urethane prepolymer obtained by reacting a polyol compound with a

polyisocyanate compound, with a compound having a (meth)acryloyl group. The urethane (meth)acrylate (X) may be used singly or in combination of two or more. [0019]

[Polyol compound]

The polyol compound is not especially limited as long as it is a compound having two or more hydroxy groups.

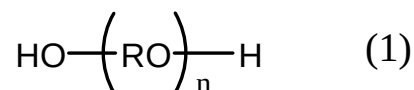
Specific examples of the polyol compound include alkylene diols, polyether-type polyols, polyester-type polyols and polycarbonate-type polyols.

Among these, polyether-type polyols are preferable.

Here, the polyol compound may be any of bifunctional diols, trifunctional triols, and tetra- or more functional polyols. In view of availability, versatility, reactivity and the like, bifunctional diols are preferable, and polyether-type diols are more preferable.

[0020]

The polyether-type diols are preferably compounds represented by the following formula (1).



[0021]

In the above formula (1), R is a divalent hydrocarbon group, and is preferably an alkylene group, and more preferably an alkylene group having 1 to 6 carbon atoms. Among alkylene groups having 1 to 6 carbon atoms, preferable are an ethylene group, a propylene group and a tetramethylene group, and more preferable are a propylene group and a tetramethylene group.

Further, n is the number of repeating units of an alkylene oxide, and is preferably 10 to 250, more preferably 25 to 205, and still more preferably 40 to 185. When n is in the above range, it becomes easy to provide a proper urethane-bond concentration of an obtained urethane (meth)acrylate and to prepare the middle layer that satisfies the above requirement for the loss tangent.

Among compounds represented by the above formula (1), preferable are polyethylene glycol, polypropylene glycol and polytetramethylene glycol, and more preferable are polypropylene glycol and polytetramethylene glycol.

The isocyanate-terminated urethane prepolymer in which ether-bond moieties $[-(\text{R}-\text{O})_n-]$ are introduced is produced by a reaction of a polyether-type diol with a polyisocyanate compound. By using such a polyether-type diol, a

urethane (meth)acrylate contains constitutional units derived from the polyether-type diol.

[0022]

The polyester-type polyol is obtained by polycondensating a polyol component with a polybasic acid component. The polyol component includes various types of known glycols such as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, pentanediol, 3-methyl-1,5-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, hexanediol, octanediol, 2,2-diethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 1,4-cyclohexanedimethanol and ethylene glycol or propylene glycol adducts of bisphenol A.

As the polybasic acid component to be used for production of the polyester-type polyol, there can be used compounds generally known as polybasic acid components of polyesters.

Specific examples of the polybasic acid component include dibasic acids such as adipic acid, maleic acid, succinic acid, oxalic acid, fumaric acid, malonic acid, glutaric acid, pimelic acid, azelaic acid, sebacic acid and suberic acid; aromatic polybasic acids including dibasic acids such as phthalic acid, isophthalic acid, terephthalic acid and 2,6-naphthalenedicarboxylic acid, and polybasic acids such as trimellitic acid and pyromellitic acid; and anhydrides corresponding thereto and derivatives thereof, and dimer acids and hydrogenated dimer acids. Among these, aromatic polybasic acids are preferable in view of forming a coated film having a proper hardness. For the esterification reaction to produce the polyester-type polyols, various types of known catalysts may be used, if needed.

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

[0023]

The number-average molecular weight of the polyol compound as calculated from the hydroxyl value thereof is preferably 1,000 to 10,000, more preferably 2,000 to 9,000, and still more preferably 3,000 to 7,000. When the number-average molecular weight is 1,000 or higher, it is preferable because such a situation can be avoided that the control of the viscoelastic properties of the middle layer becomes difficult due to formation of an excessive amount of urethane bonds. On the other hand, when the number-average molecular

weight is 10,000 or lower, it is preferable because excessive softening of an obtained middle layer can be prevented.

Here, the number-average molecular weight of the polyol compound as calculated from a hydroxyl value thereof is a value calculated from [the number of functional groups of the polyol] $\times 56.11 \times 1,000$ / [the hydroxyl value (unit: mgKOH/g)].

[0024]

[Polyisocyanate compound]

Examples of the polyisocyanate compound include aliphatic polyisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate and trimethylhexamethylene diisocyanate; alicyclic diisocyanates such as isophorone diisocyanate, norbornane diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, dicyclohexylmethane-2,4'-diisocyanate and ω,ω' -diisocyanate dimethylcyclohexane; and aromatic diisocyanates such as 4,4'-diphenylmethane diisocyanate, tolylene diisocyanate, xylylene diisocyanate, tolidine diisocyanate, tetramethylene xylylene diisocyanate and naphthalene-1,5-diisocyanate.

Among these, preferable are isophorone diisocyanate, hexamethylene diisocyanate and xylylene diisocyanate, in view of the handleability.

[0025]

{Compound having a (meth)acryloyl group}

The compound having a (meth)acryloyl group includes (meth)acrylates having a hydroxy group. The (meth)acrylate having a hydroxy group is not especially limited as long as it is a compound having, at least, a hydroxy group and a (meth)acryloyl group in one molecule thereof.

Specific examples of the (meth)acrylate having a hydroxy group include hydroxyalkyl (meth)acrylates such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 4-hydroxycyclohexyl (meth)acrylate, 5-hydroxycyclooctyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, pentaerythritol tri(meth)acrylate, polyethylene glycol mono(meth)acrylate and polypropylene glycol mono(meth)acrylate; hydroxy group-containing (meth)acrylamides such as N-methylol(meth)acrylamide; and reaction products obtained by reacting a diglycidyl ester of vinyl alcohol, a diglycidyl ester of vinylphenol or a diglycidyl ester of bisphenol A with (meth)acrylic acid.

Among these, hydroxyalkyl (meth)acrylates are preferable and 2-hydroxyethyl (meth)acrylate is more preferable.

[0026]

The weight-average molecular weight of the urethane (meth)acrylate (X) for the resin composition for the middle layer thus obtained 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 weight-average molecular weight is 1,000 or higher, it is preferable because a proper hardness is imparted to the middle layer due to the intermolecular force between structures originated from the urethane (meth)acrylate in a polymerized substance of a urethane (meth)acrylate with a polymerizable monomer described later.

The amount of the urethane (meth)acrylate (X) blended in the resin composition for the middle layer is, based on the total amount of the composition, preferably 20 to 70% by mass, more preferably 25 to 60% by mass, still more preferably 30 to 50% by mass, and further still more preferably 33 to 47% by mass. When the amount of the urethane (meth)acrylate blended is in such a range, it is easy to form the middle layer high in the loss tangent.

[0027]

The resin composition for the middle layer contains, in addition to the urethane (meth)acrylate (X), further, for example, a thiol group-containing compound (Y) or a polymerizable monomer (Z), and preferably contains both thereof.

(Thiol group-containing compound (Y))

The thiol group-containing compound (Y) is not especially limited as long as it is a compound having at least one thiol group in the molecule. But it is preferably a polyfunctional thiol group-containing compound, and more preferably a tetrafunctional thiol group-containing compound, in view of facilitating raising of the loss tangent.

Specific examples of the thiol group-containing compound (Y) include nonylmercaptan, 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-mercaptopbutyrate) and 1,3,5-tris(3-mercaptopbutyloxyethyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione.

Here, these thiol group-containing compounds (Y) may be used singly or in combination of two or more.

[0028]

The molecular weight of the thiol group-containing compound (Y) is preferably 200 to 3,000, and more preferably 300 to 2,000. When the molecular weight is in the above range, the compatibility with the urethane (meth)acrylate (X) becomes good and the film formability can be made good.

The amount of the thiol group-containing compound (Y) blended is, with respect to 100 parts by mass of the total of the urethane (meth)acrylate (X) and the polymerizable monomer (Z) described later, preferably 1.0 to 4.9 parts by mass, and more preferably 1.5 to 4.8 parts by mass.

When the amount blended is 1.0 part by mass or larger, it is easy to form the middle layer having a high loss tangent and the bump absorbability can be thus improved. On the other hand, when the amount blended is 4.9 parts by mass or smaller, exudation and the like of the middle layer when the tape is taken up in a roll form can be prevented.

[0029]

[Polymerizable monomer (Z)]

The resin composition for the middle layer to be used in the present invention preferably further contains the polymerizable monomer (Z) in view of improving the film formability. The polymerizable monomer (Z) is a polymerizable compound other than the above urethane (meth)acrylate (X), and is polymerizable with other components by irradiation of energy rays. It should be noted that resin components are excluded from the polymerizable monomer (Z). The polymerizable monomer (Z) is preferably a compound having at least one (meth)acryloyl group.

Herein, "resin components" refers to oligomers or polymers having a repeated structure in their structure and having a weight-average molecular weight of 1,000 or higher.

[0030]

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 hydroxyl group, an amido group, an amino group or an

epoxy group, (meth)acrylates having an alicyclic structure, (meth)acrylates having an aromatic structure, (meth)acrylates having a heterocyclic structure, and vinyl compounds such as styrene, hydroxyethyl vinyl ether, hydroxybutyl vinyl ether, N-vinylformamide, N-vinylpyrrolidone, N-vinylcaprolactam, and allyl glycidyl ether.

[0031]

Examples of the alkyl (meth)acrylates having an alkyl group having 1 to 30 carbon atoms include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, tridecyl (meth)acrylate, tetradecyl (meth)acrylate, hexadecyl (meth)acrylate, octadecyl (meth)acrylate and eicosyl (meth)acrylate.

[0032]

Examples of the (meth)acrylates having a functional group include hydroxyl group-containing (meth)acrylates such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and hydroxybutyl (meth)acrylate; amido group-containing compounds such as (meth)acrylamide, N,N-dimethyl(meth)acrylamide, N-butyl(meth)acrylamide, N-methylol(meth)acrylamide, N-methylolpropane(meth)acrylamide, N-methoxymethyl(meth)acrylamide and N-butoxymethyl(meth)acrylamide; amino group-containing (meth)acrylates such as primary amino group-containing (meth)acrylates, secondary amino group-containing (meth)acrylates and tertiary amino group-containing (meth)acrylates; and epoxy group-containing (meth)acrylates such as glycidyl (meth)acrylate and methylglycidyl (meth)acrylate.

[0033]

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

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

[0034]

Among these, (meth)acrylates having a relatively bulky group are preferable in view of the compatibility with the above urethane (meth)acrylate (X); and more specifically, preferable are (meth)acrylates having an alicyclic structure, (meth)acrylates having an aromatic structure and (meth)acrylates having a heterocyclic structure, and more preferable are (meth)acrylates having an alicyclic structure. Further in view of facilitating providing a loss tangent of 1.0 or higher, the polymerizable monomer preferably contains a (meth)acrylate having a functional group and a (meth)acrylate having an alicyclic structure, and more preferably contains a (meth)acrylate having a hydroxyl group and isobornyl (meth)acrylate.

[0035]

The amount of the (meth)acrylate having an alicyclic structure blended in the resin composition for the middle layer is, preferably 32 to 53% by mass, more preferably 35 to 51% by mass, still more preferably 37 to 48% by mass, and further still more preferably 40 to 47% by mass, based on the total amount of the composition, from the above viewpoints.

The amount of the (meth)acrylate having an alicyclic structure with respect to the total amount of the polymerizable monomer (Z) contained in the resin composition for the middle layer is, from the above viewpoints, preferably 52 to 87% by mass, more preferably 55 to 85% by mass, still more preferably 60 to 80% by mass, and further still more preferably 65 to 77% by mass. When the amount of the (meth)acrylate having an alicyclic structure blended is in such a range, it is easy to provide a loss tangent of 1.0 or higher.

[0036]

Further, the amount of the polymerizable monomer (Z) blended in the resin composition for the middle layer is preferably 30 to 80% by mass, more preferably 40 to 75% by mass, still more preferably 50 to 70% by mass, and further still more preferably 53 to 67% by mass. When the amount of the polymerizable monomer (Z) blended is in such a range, the middle layer is likely to become flexible since the motion of moieties formed by the polymerization of the polymerizable monomer (Z) in the middle layer is high; and therefore, it becomes

easier to form the middle layer whose loss tangent satisfies the above requirement.

Further from the similar viewpoint, the mass ratio of the urethane (meth)acrylate (X) to the polymerizable monomer (Z), urethane (meth)acrylate (X)/polymerizable monomer, in the resin composition for the middle layer is preferably 20/80 to 60/40, more preferably 30/70 to 50/50, and still more preferably 35/65 to 45/55.

[0037]

(Energy ray polymerization initiator (R))

The resin composition for the middle layer preferably further comprises an energy ray polymerization initiator (R). The incorporation of the energy ray polymerization initiator (R) enables the resin composition for the middle layer to be easily cured by energy rays such as ultraviolet rays. The energy ray polymerization initiator (R) is commonly also called a "photopolymerization initiator", and therefore is also simply called a "photopolymerization initiator" hereinafter.

Examples of the photopolymerization initiator include photopolymerization initiators such as benzoin compounds, acetophenone compounds, acylphosphinoxide compounds, titanocene compounds, thioxanthone compounds and peroxide compounds, and photosensitizers such as amines and quinones; and more specific examples thereof include 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether and 2,2-dimethoxy-1,2-diphenylethan-1-one.

These photopolymerization initiators may be used singly or in combination of two or more.

The amount of the photopolymerization initiator blended is, with respect to 100 parts by mass of the total of the urethane (meth)acrylate and the polymerizable monomer, 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.

[0038]

(Other additives)

The resin composition for the middle layer may contain other additives as long as they do not impair the advantage of the present invention. Examples of the other additives include crosslinking agents, antioxidants, softening agents (plasticizers), fillers, rust preventives, pigments and dyes. In the case where

these other additives are blended, the amount thereof is, with respect to 100 parts by mass of the total of the urethane (meth)acrylate and the polymerizable monomer, preferably 0.01 to 6 parts by mass, and more preferably 0.1 to 3 parts by mass.

The resin composition for the middle layer may contain, in addition to the urethane (meth)acrylate, the resin components other than the urethane (meth)acrylate as long as they do not impair the advantage of the present invention, but preferably comprises the urethane (meth)acrylate only as the resin components.

The content of the resin components other than the urethane (meth)acrylate contained in the resin composition for the middle layer is preferably 5% by mass or lower, more preferably 1% by mass or lower, still more preferably 0.1% by mass or lower, and further still more preferably 0% by mass. [0039]

Further the middle layer may be formed of a resin composition for the middle layer containing other resin components in place of the urethane (meth)acrylate (X). The middle layer may be formed of, for example, a curable composition containing a non-reactive urethane polymer or oligomer and a polymerizable monomer, or may be formed by using a composition containing an ethylene- α -olefin copolymer. As the non-reactive urethane polymer or oligomer, a known one may be used; and as the polymerizable monomer, the same one as described before can be used. Such a curable composition may contain the above-mentioned energy ray polymerization initiator. [0040]

The ethylene- α -olefin copolymer is obtained by polymerizing ethylene with an α -olefin monomer. The α -olefin monomer includes propylene, 1-butene, 2-methyl-1-butene, 2-methyl-1-pentene, 1-hexene, 2,2-dimethyl-1-butene, 2-methyl-1-hexene, 4-methyl-1-pentene, 1-heptene, 3-methyl-1-hexene, 2,2-dimethyl-1-pentene, 3,3-dimethyl-1-pentene, 2,3-dimethyl-1-pentene, 3-ethyl-1-pentene, 2,2,3-trimethyl-1-butene, 1-octene and 2,2,4-trimethyl-1-octene. These α -olefin monomers can be used singly or in combination of two or more.

Further the ethylene- α -olefin copolymer may be one obtained by polymerizing ethylene and an α -olefin monomer with other monomers. Examples of the other monomer components include vinyl compounds such as vinyl acetate, styrene, acrylonitrile, methacrylonitrile and vinyl ketone;

unsaturated carboxylic acids such as acrylic acid and methacrylic acid;
unsaturated carboxylate esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, methyl methacrylate, ethyl methacrylate and n-propyl methacrylate;
and unsaturated carboxylic acid amides such as acrylamide and methacrylamide.
These monomers can be used singly or in combination of two or more.

[0041]

<Pressure sensitive adhesive layer>

The pressure sensitive adhesive layer is provided on the substrate, and in the case where the middle layer is provided, it is provided on the middle layer. The pressure sensitive adhesive layer in the present invention comprises, at least, a urethane-based resin (A), and an energy ray-curable compound (B) being non-reactive with the urethane-based resin (A) and having a molecular weight of 35,000 or lower.

In the present invention, since the cohesive force and the mechanical strength of the pressure sensitive adhesive layer become high by incorporating the urethane-based resin (A) in the pressure sensitive adhesive layer, it becomes difficult for the adhesive residue to be generated in the work surface having bumps and the like when the pressure sensitive adhesive tape is peeled off a work after energy ray curing. Further the incorporation of at least the energy ray-curable compound (B) makes the pressure sensitive adhesive layer to be energy ray-curable. Hence, the peeling performance when the pressure sensitive adhesive tape is peeled off a work becomes good. Further, since the energy ray-curable compound (B) is non-reactive as described later, the storage elastic modulus of the pressure sensitive adhesive layer becomes low to thereby facilitate securing the conformability to irregularities on the work surface.

[0042]

The pressure sensitive adhesive layer preferably has a breaking stress after energy ray irradiation of 2.5 MPa or higher. When the breaking stress is 2.5 MPa or higher, the mechanical strength becomes a sufficient value and the reduction of generation of the above-mentioned adhesive residue becomes easy. Further in order to easily improve the embeddability of protrusions, and the adhesivity and the peelability of the pressure sensitive adhesive layer while suppressing the generation of the adhesive residue, the breaking stress is preferably 2.8 to 30 MPa, and more preferably 3.0 to 25 MPa. Here, the

breaking stress is that measured by a method described in Examples described later.

Here, the breaking stress can be regulated by altering the kind of the urethane-based resin (A). Further the breaking stress can be regulated also by the amount of photopolymerizable unsaturated bonds described later; when the amount of photopolymerizable unsaturated bonds contained in the pressure sensitive adhesive layer is large, the breaking stress is likely to become high, and when the amount thereof is small, the breaking stress is likely to become low. Similarly, the breaking stress can be regulated also by the amount of a crosslinking agent component described later; when the amount of the crosslinking agent component is large, the breaking stress is likely to become high, and when the amount thereof is small, the breaking stress is likely to become low.

[0043]

Since the pressure sensitive adhesive layer is energy ray-curable, the layer can be relatively soft before energy ray irradiation, and thus it is easy for the pressure sensitive adhesive layer to conform to irregularities formed on the work surface. Further the pressure sensitive adhesive tape is irradiated with energy rays and cured to be thereby reduced in the peel strength, and it becomes easy for the pressure sensitive adhesive tape to be peeled off a work.

In view of suppressing the generation of the adhesive residue when the pressure sensitive adhesive tape is peeled, the peel strength of the pressure sensitive adhesive tape after energy ray irradiation is preferably 2,000 mN/25 mm or lower. Particularly in the case where the pressure sensitive adhesive tape of the present invention having the middle layer is attached on a work having large protrusions (for example, 200 μm or higher in height) such as bumps on the surface, the protrusions are in the state of being absorbed by the middle layer of the pressure sensitive adhesive tape attached on the work surface. Hence, on peeling the pressure sensitive adhesive tape, the adhesive residue is easily generated; but the peel strength to be 2,000 mN/25 mm or lower facilitates prevention of such generation of the adhesive residue. The peel strength of the pressure sensitive adhesive tape after energy ray irradiation is preferably 50 to 1,750 mN/25 mm, and more preferably 100 to 1,500 mN/25 mm.

[0044]

Further the peel strength of the pressure sensitive adhesive tape before energy ray irradiation is, for example, higher than 2,000 mN/25 mm, and preferably 3,000 to 30,000 mN/25 mm, and more preferably 3,500 to 9,000 mN/25 mm. When the peel strength before energy ray irradiation is in such a range, the adhesivity to the work surface is good and the protection performance of the work becomes good.

Here, the peel strength of the pressure sensitive adhesive tape is measured as follows: the pressure sensitive adhesive layer surface of the pressure sensitive adhesive tape is attached on a silicon mirror wafer, and the pressure sensitive adhesive tape is peeled in an environment of 23°C at a peel angle of 180° at a peel rate of 300 mm/min and measure the peel strength. Specifically, the peel strength is measured by a method described in Examples described later.

The peel strength can be regulated by altering the kinds and the like of the urethane-based resin (A) and the energy ray-curable compound (B). Further the peel strength after energy ray irradiation can be regulated also by the amount of photopolymerizable unsaturated bonds described later; when the amount of photopolymerizable unsaturated bonds contained in the pressure sensitive adhesive composition is large, the peel strength is likely to become low, and when the amount thereof is small, the peel strength is likely to become high. Further also by blending a crosslinking agent (C1) or a compound (D) containing a photopolymerizable unsaturated bond as described later, it becomes easy to lower the peel strength after energy ray irradiation.

[0045]

(Urethane-based resin (A))

The urethane-based resin (A) is a polymer having at least one of urethane bonds and urea bonds. Further the pressure sensitive adhesive layer of the present invention is formed of a urethane-based pressure sensitive adhesive composition (hereinafter, also referred to simply as "pressure sensitive adhesive composition") comprising, at least, a urethane polymer (A') and an energy ray-curable compound (B); and the urethane-based resin (A) is constituted of at least the urethane polymer (A') as a main component. Further the urethane-based pressure sensitive adhesive composition, as required, further comprises a crosslinking agent (C), a compound (D) and the like.

[0046]

The urethane-based resin (A) may be the one crosslinked with the crosslinking agent (C). Further, the urethane-based pressure sensitive adhesive composition may contain, in addition to the crosslinking agent (C), a compound bonding directly or indirectly with the urethane polymer (A') and constituting the urethane-based resin (A) as one body in the pressure sensitive adhesive layer, like the compound (D) or the like as described above.

Here, like the crosslinking agent (C) and the compound (D), compounds bonding directly or indirectly with the urethane polymer (A') and constituting the urethane-based resin (A) as one body in the pressure sensitive adhesive layer together with the urethane polymer (A') are generically called "compounds reactive to the main component".

In the present invention, the amount of the urethane polymer (A') blended is preferably 30 to 85% by mass, more preferably 35 to 80% by mass, and still more preferably 37 to 77% by mass, with respect to the total amount of the pressure sensitive adhesive composition, in order to secure the tackiness of the pressure sensitive adhesive layer and to blend proper amounts of components (B) to (E) described later. Further the total amount of the compound reactive to the main component and the urethane polymer (A') is, with respect to the total amount of the pressure sensitive adhesive composition, preferably 40 to 95% by mass, more preferably 45 to 94% by mass, and still more preferably 50 to 93% by mass.

[0047]

The urethane-based resin (A) preferably has photopolymerizable unsaturated bonds. When the urethane-based resin (A) has photopolymerizable unsaturated bonds, in the pressure sensitive adhesive layer of the pressure sensitive adhesive tape for work processing, both of the urethane-based resin (A) and the energy ray-curable compound (B) come to have photopolymerizable unsaturated bonds. Hence, by irradiating the pressure sensitive adhesive layer with energy rays, bonds are formed between the urethane-based resin (A) and the energy ray-curable compound (B) by the polymerization reaction, facilitating more reducing the peel strength of the pressure sensitive adhesive tape after the energy ray irradiation and making good the peelability when the pressure sensitive adhesive tape is peeled off a work. Further, the generation of the adhesive residue when the pressure sensitive adhesive tape is peeled off the work is enabled to be more reduced. Further, as compared with the case where curing

of the pressure sensitive adhesive layer by energy ray irradiation is caused depending on the energy ray-curable compound (B) alone, the strength of the pressure sensitive adhesive layer after the energy ray irradiation is likely to become higher, and the suppression of the generation of the adhesive residue is easier.

[0048]

A method of introducing the photopolymerizable unsaturated bonds in the urethane-based resin (A) is not especially limited. For example, in the case where the urethane polymer (A') before the introduction of the photopolymerizable unsaturated bonds has hydroxyl groups, the photopolymerizable unsaturated bonds can be introduced by reacting a compound having a functional group reactive with a hydroxyl group and a functional group having a photopolymerizable unsaturated bond, with the hydroxyl groups. Examples of the compound having a functional group reactive with a hydroxyl group and a functional group having a photopolymerizable unsaturated bond include methacryloyloxyethyl isocyanate. Such a compound may be reacted previously with the urethane polymer (A'), or may be incorporated previously in the pressure sensitive adhesive layer, and reacted with the urethane polymer (A') in the pressure sensitive adhesive layer formation time.

Further as described later, the photopolymerizable unsaturated bonds may be introduced in the urethane-based resin (A) by using a crosslinking agent (C1) having a photopolymerizable unsaturated bond as the crosslinking agent (C) to crosslink the urethane polymer (A'). Further, the photopolymerizable unsaturated bonds may be introduced in the urethane-based resin (A) by using the compound (D) described later.

[0049]

<Urethane polymer (A')>

The urethane polymer (A') includes ones having at least one of urethane bonds and urea bonds, and specifically includes polyurethane polyols whose terminals have hydroxyl groups obtained by reacting a polyol and a polyisocyanate compound. Further as the urethane polymer (A'), there may be used a urethane polymer whose terminals are isocyanate obtained by reacting a polyol and a polyisocyanate compound.

[0050]

The polyol to be used for the urethane polymer (A') includes polyester polyols and polyether polyols.

As the polyester polyols, known ones are used. The polyester polyols are esters of an acid component and at least one of a glycol component and a polyol component; the acid component includes terephthalic acid, adipic acid, azelaic acid, sebacic acid, phthalic anhydride, isophthalic acid and trimellitic acid. The glycol component includes ethylene glycol, propylene glycol, diethylene glycol, butylene glycol, 1,6-hexaneglycol, 3-methyl-1,5-pentanediol, 3,3'-dimethylolheptane, polyoxyethylene glycols, polyoxypropylene glycols, 1,4-butanediol, neopentylglycol and butylethylpentanediol; and the polyol component includes glycerol, trimethylolpropane and pentaerythritol.

The polyester polyols may additionally be ones obtained by ring-opening polymerizing lactones such as polycaprolactone, poly(β -methyl-valerolactone) and polyvalerolactone.

[0051]

Further as the polyether polyols, known ones are used. There are used, for example, polyether polyols obtained by using, as an initiator, a low-molecular weight polyol such as water, propylene glycol, ethylene glycol, glycerol or trimethylolpropane, and polymerizing an oxirane compound such as ethylene oxide, propylene oxide, butylene oxide or tetrahydrofuran, specifically, polyether polyols having two or more functional groups, such as polypropylene glycol, polyethylene glycol and polytetramethylene glycol.

[0052]

The polyisocyanate compounds include known aromatic polyisocyanates, aliphatic polyisocyanates, araliphatic polyisocyanates and alicyclic polyisocyanates. The aromatic polyisocyanates include 1,3-phenylene diisocyanate, 4,4'-diphenyl diisocyanate, 1,4-phenylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-toluidine diisocyanate, 2,4,6-triisocyanatotoluene, 1,3,5-triisocyanatobenzene, dianisidine diisocyanate, 4,4'-diphenyl ether diisocyanate and 4,4',4''-triphenylmethane triisocyanate.

[0053]

The aliphatic polyisocyanates include trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, pentamethylene diisocyanate, 1,2-propylene diisocyanate, 2,3-butylene diisocyanate, 1,3-butylene

diisocyanate, dodecamethylene diisocyanate and 2,4,4-trimethylhexamethylene diisocyanate.

[0054]

The araliphatic polyisocyanates include ω,ω' -diisocyanato-1,3-dimethylbenzene, ω,ω' -diisocyanato-1,4-dimethylbenzene, ω,ω' -diisocyanato-1,4-diethylbenzene, 1,4-tetramethylxylylene diisocyanate and 1,3-tetramethylxylylene diisocyanate.

[0055]

The alicyclic polyisocyanates include 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, 1,3-cyclopentane diisocyanate, 1,3-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, methyl-2,4-cyclohexane diisocyanate, methyl-2,6-cyclohexane diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), 1,4-bis(isocyanatomethyl)cyclohexane and 1,4-bis(isocyanatomethyl)cyclohexane.

Further the above polyisocyanate compound can be used concurrently with a trimethylolpropane adduct of the above polyisocyanate compound, a biuret as a product thereof with water, a trimer thereof having an isocyanurate ring, or the like.

The polyisocyanate compound is preferably 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate) or the like.

[0056]

Further the polyurethane polyol may be one obtained by reacting, in addition to a polyol and a polyfunctional isocyanate, further a diamine such as ethylene diamine, N-aminoethylethanolamine, isophoronediamine or xylylenediamine. Further as the polyol, there may be used, in addition to the above-mentioned polyester polyol or polyether polyol, ethylene glycol, 1,4-butanediol, neopentyl glycol, butylethylpentanediol, glycerol, trimethylolpropane, pentaerythritol or the like.

Here, the reaction of a polyol with a polyisocyanate compound is usually carried out in the presence of a catalyst such as a tertiary amine-based compound or an organometallic compound.

[0057]

The urethane polymer (A') is not limited to the above, and may be, for example, a Michael addition-type urethane polymer.

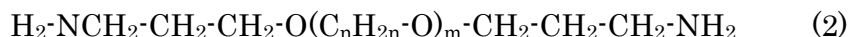
The Michael addition-type urethane polymer includes, for example, ones like the following (1) and (2).

(1) A urethane polymer obtained by reacting a urethane prepolymer obtained by reacting the above polyol with the above polyisocyanate compound and having isocyanate groups (-NCO) on its terminals, with an amino compound obtained by Michael-addition reacting a polyamine with an unsaturated compound.

(2) A urethane polymer obtained by Michael-addition reacting a polyurethaneurea obtained by reacting, in addition to the above polyol and the above polyisocyanate compound, a polyamine and having primary or secondary amino groups on its terminals, with an unsaturated compound.

[0058]

As the polyamine to be used for the Michael addition-type urethane polymer, known ones can be used; the polyamines specifically include aliphatic polyamines such as ethylenediamine, propylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, triethylenetetramine, diethylenetriamine, triaminopropane, 2,2,4-trimethylhexamethylenediamine, tolylenediamine, hydrazine and piperazine, alicyclic polyamines such as isophoronediamine and dicyclohexylmethane-4,4'-diamine, and aromatic polyamines such as phenylenediamine and xylylenediamine. Further, there can also be used diamines having a hydroxyl group in their molecules, such as 2-hydroxyethylethylenediamine, N-(2-hydroxyethyl)propylenediamine, (2-hydroxyethylpropylene)diamine, (di-2-hydroxyethylethylene)diamine, (di-2-hydroxyethylpropylene)diamine, (2-hydroxypropylethylene)diamine and (di-2-hydroxypropylethylene)diamine, dimer diamines obtained by converting carboxyl groups of dimer acids to amino groups, and polyoxyalkylene glycol diamines having propoxyamines on both terminals thereof and represented by the following general formula (2).



wherein n denotes any integer of 2 to 4, and m denotes any integer of 2 to 50.

Further as the polyamines, there can be used dendrimers having primary or secondary amino groups on their terminals.

Among the polyamines described above, isophoronediamine, 2,2,4-trimethylhexamethylenediamine and hexamethylenediamine are preferable from the point of easiness in control of the reaction.

[0059]

Further, the unsaturated compound to be used for the Michael addition-type urethane polymer is used for the purpose of modifying a urethane polymer. Therefore, the kind of the unsaturated compound to be used can optionally be selected according to the purpose of the modification. Examples of the unsaturated compound include (meth)acryl-based unsaturated compounds, amido-based unsaturated compounds, fatty acid vinyl ester-based unsaturated compounds, vinyl ether-based unsaturated compounds, α -olefin-based unsaturated compounds, allyl-based unsaturated compounds, allyl acetate-based unsaturated compounds, vinyl cyanide-based unsaturated compounds and styrene or vinylbenzene-based unsaturated compounds.

Although the kind of the unsaturated compound to be used can arbitrarily be selected according to the purpose of the modification, the selection is carried out preferably by paying attention to functional groups the unsaturated compound has. As the functional groups such unsaturated compounds have, there can be exemplified an alkyl group, a polyalkylene glycol group, an alkoxy group, a phenoxy group, a hydroxyl group, a carboxyl group, a perfluoroalkyl group, an alkoxysilyl group, an epoxy group, and nitrogen-containing groups such as an amido group, a dialkylamino group and a quaternary ammonium base, but in order to incorporate a hydroxyl group in the urethane polymer (A') as described above, preferably, the unsaturated compound has a hydroxyl group.

Here, as a specific example of the unsaturated compound, there is used, for example, one described in JP 2002-121256 A (EP1146061 A1).

[0060]

The weight-average molecular weight of the urethane polymer (A') to be used in the present invention is preferably 10,000 to 300,000, and more preferably 30,000 to 150,000. By making the weight-average molecular weight to be 10,000 or higher, the cohesive force of the pressure sensitive adhesive layer is improved and a larger effect of suppressing generation of the adhesive residue is attained. Further, making the weight-average molecular weight to be 300,000 or lower has an advantage of hardly bring about such a viscosity rise that affects the process suitability even when the pressure sensitive adhesive composition is diluted with a solvent or melted by heating when the pressure sensitive adhesive layer is formed from the pressure sensitive adhesive composition.

[0061]

(Energy ray-curable compound (B))

The energy ray-curable compound (B) to be used in the present invention is the one being non-reactive with the urethane-based resin (A) and having a photopolymerizable unsaturated bond.

Here, the "non-reactive" means that the energy ray-curable compound (B) has no functional group, excluding the "photopolymerizable unsaturated bond", reactive with not only the urethane polymer (A') but also the compound reactive to the main component; and the compound (B) is a compound not reacting on the urethane-based resin (A) in the pressure sensitive adhesive layer.

That is, the energy ray-curable compound (B), when the pressure sensitive adhesive layer is formed by the reaction of the urethane polymer (A') and the crosslinking agent (C), and other components (for example, the (D) component) to be used as required, is a compound not reacting with these (A'), (C) and (D) components.

[0062]

Thus, the energy ray-curable compound (B) results in being present as a component not constituting the urethane-based resin (A) in the pressure sensitive adhesive layer. When used singly, the urethane polymer hardly embeds protrusions such as bumps on the work surface, since it is generally high in the cohesive force and also high in the storage elastic modulus. However, in the present invention, since the energy ray-curable compound (B), which does not constitute the urethane polymer chains, is blended therewith, the storage elastic modulus of the pressure sensitive adhesive layer is lowered to thereby facilitate securing the embeddability of the bumps.

Here, in the present invention, the "photopolymerizable unsaturated bond" means an unsaturated bond to react by energy ray irradiation, and is usually an ethylenic double bond, and preferably a carbon-carbon double bond contained in a (meth)acryloyl group.

[0063]

The molecular weight of the energy ray-curable compound (B) is made to be 35,000 or lower. When the molecular weight is higher than 35,000, reduction of the storage elastic modulus of the pressure sensitive adhesive layer becomes difficult and securing of the embeddability of the bumps becomes difficult. Further, there arises a risk of deterioration of the compatibility with the urethane-based resin (A). The molecular weight of the energy ray-curable compound (B) is preferably 150 to 35,000, and more preferably 200 to 34,000.

Here, the "molecular weight" means, in the case where the formula weight can be identified, a formula weight, and in the case where the formula weight cannot be identified, a weight-average molecular weight.

The amount of the energy ray-curable compound (B) blended is, though depending on the compound to be used, with respect to 100 parts by mass of the urethane-based resin (A) (that is, meaning 100 parts by mass of the total of the urethane polymer (A') and the compound reactive to the main component. The same shall apply hereinafter), usually 1 to 120 parts by mass, preferably 2 to 100 parts by mass, and more preferably 4 to 90 parts by mass. Such a range of the amount of the energy ray-curable compound (B) facilitates providing the pressure sensitive adhesive layer simultaneously satisfying both the conformability to the work surface and the suppression of generation of the adhesive residue.

[0064]

Specific compounds of the energy ray-curable compound (B) include compounds having a (meth)acryloyl group(s). The number of (meth)acryloyl groups (photopolymerizable unsaturated bonds) in one molecule of the energy ray-curable compound (B) suffices if being mono- or more functional, but is preferably bi- or more functional, and more preferably bifunctional to dodecafunctional.

Further, specific examples of the energy ray-curable compound (B) to be used in the present invention include at least one selected from the group consisting of (meth)acrylate monomers (B1) and urethane (meth)acrylates (B2).

[0065]

The (meth)acrylate monomers (B1) are compounds having a (meth)acryloyl group(s) in their molecule; and the number of the (meth)acryloyl groups is preferably bi- or more functional, and more preferably tri- to hexa-functional. Particularly in the case where the urethane-based resin (A) has no photopolymerizable unsaturated bonds, it is preferable that the pressure sensitive adhesive layer contain a (meth)acrylate monomer (B1) in which the number of (meth)acryloyl groups is tetra- or more functional so that the peel strength of the pressure sensitive adhesive tape can easily be reduced after the energy ray irradiation to the pressure sensitive adhesive layer.

Examples of the (meth)acrylate monomer (B1) include polyfunctional (meth)acrylate esters being complete esters in which all hydroxyl groups of a polyhydric alcohol form esters with (meth)acrylic acid. Here, the number of

carbon atoms of the polyhydric alcohol is preferably 4 to 10. Further the molecular weight of the (meth)acrylate monomer (B1) is preferably 150 to 1,000, and more preferably 200 to 800.

Specific compounds of the polyfunctional (meth)acrylate esters include trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, 1,4-butylene glycol di(meth)acrylate and 1,6-hexanediol di(meth)acrylate, but among these, pentaerythritol tetra(meth)acrylate is preferable.

Here, the structure of the (meth)acrylate monomer (B1) can be identified and the molecular weight means a formula weight.

[0066]

The (meth)acrylate monomer (B1) is preferable because even in a small amount thereof blended, the generation of the adhesive residue can be prevented while the peel strength can suitably be reduced by energy ray irradiation.

The amount of the (meth)acrylate monomer (B1) blended is, specifically, with respect to 100 parts by mass of the urethane-based resin (A), preferably 1 to 20 parts by mass, more preferably 2 to 15 parts by mass, and still more preferably 3 to 10 parts by mass. When the energy ray-curable compound (B) is blended in such amounts, the generation of the adhesive residue of the pressure sensitive adhesive layer can suitably be prevented and the peel strength of the pressure sensitive adhesive layer can suitably be reduced by energy ray irradiation.

[0067]

The urethane (meth)acrylate (B2) has a urethane bond, and has (meth)acryloyl groups on its terminals. The urethane (meth)acrylate (B2) includes compounds obtained by producing an isocyanate-terminated urethane polymer by a reaction of a polyol compound with a polyisocyanate compound, and reacting the functional groups of the terminals with a compound having a (meth)acryloyl group. Such a urethane (meth)acrylate (B2) has energy ray curability by the action of the (meth)acryloyl group.

Here, the polyol compound, the polyisocyanate compound and the compound having a (meth)acryloyl group to be used in order to obtain the urethane (meth)acrylate (B2) are suitably selected, respectively, from the polyol compounds, the polyisocyanate compounds and the compounds having a

(meth)acryloyl group to be used for the urethane (meth)acrylate (X) of the middle layer described above, and used; so their specific descriptions will be omitted.

[0068]

The urethane (meth)acrylate (B2) has (meth)acryloyl groups; and the number of (meth)acryloyl groups in one molecule is preferably bi- or more functional, more preferably bi- to dodeca-functional, and still more preferably bi- to deca-functional. Thus making the polyfunctionality facilitates reduction of the peel strength by energy ray curing.

Further the molecular weight of the urethane (meth)acrylate (B2) is made to be 35,000 or lower, but is preferably 2,000 to 35,000, and more preferably 5,000 to 34,000. Here, the molecular weight of the urethane (meth)acrylate (B2) means a weight-average molecular weight thereof. Making the molecular weight of the urethane (meth)acrylate in such a range reduces the storage elastic modulus of the pressure sensitive adhesive layer and facilitates securing the conformability to irregularities on the work surface. Further the migration of the urethane (meth)acrylate (B2) in the pressure sensitive adhesive layer is suppressed and the stability with time of the pressure sensitive adhesive tape is improved.

[0069]

In the case where the energy ray-curable compound (B) is the urethane (meth)acrylate (B2), the amount of the urethane (meth)acrylate (B2) blended is, with respect to 100 parts by mass of the urethane-based resin (A), preferably 30 to 120 parts by mass, more preferably 40 to 100 parts by mass, and still more preferably 50 to 90 parts by mass. The amount of the urethane (meth)acrylate (B2) blended in such a range facilitates maintaining good the tackiness performance of the pressure sensitive adhesive layer and securing the embeddability. Further, such an amount blended facilitates sufficient reduction of the peel strength and further, reduction of the adhesive residue, by the energy ray curing.

[0070]

(Crosslinking agent (C))

The pressure sensitive adhesive composition of the present invention preferably further comprises the crosslinking agent (C). The crosslinking agent (C) is an agent to react with the urethane polymer (A') to crosslink the urethane polymer (A'). The incorporation of the crosslinking agent (C) in the pressure

sensitive adhesive composition facilitates formation of the pressure sensitive adhesive layer high in the crosslinking density and high in the mechanical strength, and further facilitates also preventing the generation of the adhesive residue and the like when the pressure sensitive adhesive tape is peeled.

The crosslinking agent (C) is, in the case where the urethane polymer (A') has hydroxyl groups, preferably a crosslinking agent having two or more isocyanate groups so that the isocyanate groups can react with the hydroxyl groups. By the way, the pressure sensitive adhesive composition, in the case of containing a crosslinking agent, is usually crosslinked by being heated after being coated.

[0071]

Conversely, the urethane polymer (A') may have isocyanate groups and the crosslinking agent (C) may have hydroxyl groups. Since it is common from the standpoint of the production method that the urethane polymer (A') has hydroxyl groups or isocyanate groups, it is preferable that the urethane polymer (A') and the crosslinking agent (C) be bonded through urethane bonds.

[0072]

As the crosslinking agent (C) usable in the present invention, there is preferably used a crosslinking agent (C1) having photopolymerizable unsaturated bonds.

Further the crosslinking agent (C1) having photopolymerizable unsaturated bonds is preferably a compound having two or more isocyanate groups and (meth)acryloyl groups, and more preferably, a urethane (meth)acrylate having at least two isocyanate groups is used.

The weight-average molecular weight of the urethane (meth)acrylate is preferably 500 to 2,000, and more preferably 700 to 1,000. Further in the case where one molecule of the crosslinking agent (C1) has two or more photopolymerizable unsaturated bonds, the photopolymerizable unsaturated bonds in the same molecule of the crosslinking agent (C1) are likely to be polymerized. Hence, the reaction of photopolymerizable unsaturated bonds the crosslinking agent (C1) has and photopolymerizable unsaturated bonds other molecules have is hardly caused and there is small in some cases the effect of reducing the peel strength of the pressure sensitive adhesive tape by the energy ray irradiation on the pressure sensitive adhesive layer. Therefore, a preferable crosslinking agent (C1) is one having one photopolymerizable unsaturated bond

in one molecule thereof. Examples of the urethane (meth)acrylate to be used as the crosslinking agent (C1) include "EBECRYL 4150", manufactured by Daicel-Allnex Ltd.

In the present embodiment, the use of the crosslinking agent (C1) having a photopolymerizable unsaturated bond results in that the urethane-based resin (A) in the pressure sensitive adhesive layer has photopolymerizable unsaturated bonds.

[0073]

Examples of crosslinking agents having hydroxyl groups and photopolymerizable unsaturated bonds include acryl polymers having hydroxyl groups and (meth)acryloyl groups on their side chains. In this case, the urethane-based resin (A) crosslinked with the crosslinking agent (C1) becomes a so-called acrylic urethane resin, but the urethane-based resin (A) of the present invention is regarded as including also such an acrylic urethane resin.

[0074]

The amount of the crosslinking agent (C1) having photopolymerizable unsaturated bonds blended is, with respect to 100 parts by mass of the urethane-based resin (A), preferably 5 to 60 parts by mass, more preferably 10 to 50 parts by mass, and still more preferably 15 to 45 parts by mass. The crosslinking agent (C1) blended in such an amount enables a suitable amount of photopolymerizable unsaturated bonds to be introduced in the urethane-based resin (A), while providing a good crosslinking density of the pressure sensitive adhesive layer.

[0075]

Further the pressure sensitive adhesive composition may contain a crosslinking agent (C2) having no photopolymerizable unsaturated bonds as the crosslinking agent (C). As the crosslinking agent (C2), in the case where the urethane polymer (A') has hydroxyl groups, a polyisocyanate compound can be used by being suitably selected from the above-cited polyisocyanate compounds used for the synthesis of the urethane polymer (A'). Further in the case where the polymer (A') before crosslinking has isocyanate groups, a known polyol can be used as the crosslinking agent (C2). The incorporation of the crosslinking agent (C2) in the pressure sensitive adhesive composition enables the crosslinking density of the pressure sensitive adhesive layer to be made sufficiently high.

[0076]

The whole of the crosslinking agent (C) may be the crosslinking agent (C1) having photopolymerizable unsaturated bonds, or may be the crosslinking agent (C2) having no photopolymerizable unsaturated bonds, but the crosslinking agent (C) preferably contains the crosslinking agent (C1) having photopolymerizable unsaturated bonds, and more preferably contains both the crosslinking agent (C1) and the crosslinking agent (C2).

[0077]

The amount of the crosslinking agent (C2) having no photopolymerizable unsaturated bonds blended is, with respect to 100 parts by mass of the urethane-based resin (A), preferably 0.2 to 15 parts by mass, and more preferably 0.5 to 10 parts by mass. Further as described above, in the case of the concurrent use with the crosslinking agent (C1), the amount of the crosslinking agent (C2) having no photopolymerizable unsaturated bonds may be even relatively small, and is, with respect to 100 parts by mass of the urethane-based resin (A), preferably 0.2 to 5 parts by mass, and more preferably 0.5 to 2 parts by mass.

[0078]

(Compound (D))

The pressure sensitive adhesive composition, in the case of comprising the crosslinking agent (C), preferably further comprises the compound (D) having a photopolymerizable unsaturated bond and a reactive functional group reactive with the crosslinking agent (C). The compound (D) having a reactive functional group reacts with the crosslinking agent (C) when the urethane polymer (A) reacts with the crosslinking agent (C) to form the urethane polymer chains.

When the pressure sensitive adhesive composition comprises the compound (D), the photopolymerizable unsaturated bonds result in being introduced in the urethane-based resin (A) through the compound (D). Hence, when the pressure sensitive adhesive layer is cured by energy rays, the reduction of the peel strength of the pressure sensitive adhesive layer becomes easy and the prevention of generation of the adhesive residue and the like becomes easy. Further there is also attained such an effect that the stabilization with time of the performance of the pressure sensitive adhesive tape becomes easy.

[0079]

The reactive functional group contained in the compound (D) includes an isocyanate group and a hydroxyl group. Further the compound (D) includes (meth)acrylate monomers having hydroxyl groups and (meth)acryloyl groups.

The number of (meth)acryloyl groups (that is, photopolymerizable unsaturated bonds) in one molecule of the compound (D) is preferably bi- or more functional and more preferably bi- to penta-functional, in one molecule thereof.

The molecular weight of the (meth)acrylate monomer to be used as the component (D) is preferably 150 to 3,000, and more preferably 200 to 2,000.

The (meth)acrylate monomer to be used as the component (D) includes polyfunctional (meth)acrylate esters being partial esters of a polyhydric alcohol with (meth)acrylic acid. Here, the number of carbon atoms of the polyhydric alcohol is preferably 4 to 10. As specific compounds thereof, there are exemplified pentaerythritol tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate and dipentaerythritol penta(meth)acrylate, but among these, pentaerythritol tri(meth)acrylate is preferable.

[0080]

The amount of the compound (D) blended is, with respect to 100 parts by mass of the urethane-based resin (A), preferably 1 to 30 parts by mass, more preferably 2 to 20 parts by mass, and still more preferably 3 to 15 parts by mass. Blending the compound (D) in such a range, not adversely affecting the tackiness performance of the pressure sensitive adhesive layer, facilitates reducing the peel strength by energy ray curing and also facilitates preventing generation of the adhesive residue. In the case where the energy ray-curable compound (B) contains the (meth)acrylate monomer (B1), the compound (D) is preferably usually used. Thus, the concurrent use of the compound (D) and the (meth)acrylate monomer (B1) facilitates more exhibiting the advantage of the present invention.

[0081]

(Energy ray photopolymerization initiator (E))

The pressure sensitive adhesive composition preferably further comprises an energy ray photopolymerization initiator (E). The incorporation of the energy ray photopolymerization initiator (E) in the pressure sensitive adhesive layer enables the pressure sensitive adhesive layer to be easily cured by energy ray irradiation. The energy ray photopolymerization initiator (E) can be used by being suitably selected from the above-cited photopolymerization initiators usable in the resin composition for the middle layer.

The amount of the energy ray photopolymerization initiator (E) blended is, with respect to 100 parts by mass of the total of the urethane polymer (A') having

photopolymerizable unsaturated bonds, and compounds having photopolymerizable unsaturated bonds such as the crosslinking agent (C1), the energy ray-curable compound (B) and the compound (D), preferably 0.05 to 25 parts by mass, more preferably 0.1 to 20 parts by mass, and still more preferably 0.3 to 15 parts by mass.

[0082]

Here, the pressure sensitive adhesive composition may contain other additives conventionally used for urethane-based pressure sensitive adhesives, and may contain fillers such as calcium carbonate and titanium oxide, colorants, antioxidants, defoaming agents, light stabilizers and the like.

The thickness of the pressure sensitive adhesive layer can suitably be regulated according to the surface condition of adherend surfaces on which the pressure sensitive adhesive tape is attached, including the bump height on the wafer surface, but is preferably 2 to 150 μm , more preferably 5 to 100 μm , and still more preferably 8 to 50 μm .

[0083]

<Release material>

As the release material provided on the pressure sensitive adhesive layer, and a release material to be used in a step of a production method described later, there is used a release sheet whose one surface has been subjected to a releasing treatment, a release sheet whose both surfaces have been subjected to a releasing treatment, or the like, and there is included a substrate for a release material on which a release agent has been applied, or the like.

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

Examples of the release agents include silicone-based resins, olefin-based resins, rubber-based elastomers such as isoprene-based resins and butadiene-based resins, and long-chain alkyl-based resins, alkyd-based resins and fluororesins.

Further the thickness of the release material is not especially limited, but is preferably 5 to 200 μm , and more preferably 10 to 120 μm .

[0084]

[Production method of the pressure sensitive adhesive tape]

A production method of the pressure sensitive adhesive tape of the present invention is not especially limited, and the pressure sensitive adhesive tape can be produced by known methods.

The middle layer can be formed, for example, by coated a solution of the resin composition for the middle layer directly on one surface of the substrate to form a coated film, thereafter, as required, drying the resultant, and subjecting the resultant to a curing treatment. Alternatively, the middle layer may be formed by coating a solution of the resin composition for the middle layer on the releasing-treated surface of the release material to form a coated film, as required, drying the resultant, and subjecting the resultant to a semi-curing treatment to form a semi-cured layer on the release material, attaching the semi-cured layer on the substrate, and completely curing the semi-cured layer. In this time, the release material may suitably be removed before or after the complete curing of the semi-cured layer. The curing of the middle layer is preferably carried out by irradiating the coated film with energy rays for polymerization curing. The energy rays are preferably ultraviolet rays. Further in the case where the middle layer is formed using an olefin-based material, the middle layer may be formed by extrusion or the like.

[0085]

Then, the pressure sensitive adhesive layer is preferably formed by coating the pressure sensitive adhesive composition, thereafter heating and crosslinking the pressure sensitive adhesive composition, and as required, drying the resultant. In this time, the pressure sensitive adhesive composition may be coated directly on the middle layer or the substrate, or may be formed by coating the pressure sensitive adhesive composition on the releasing-treated surface of the release material to form the pressure sensitive adhesive layer, and thereafter attaching the pressure sensitive adhesive layer on the middle layer or the substrate. The release material disposed on the pressure sensitive adhesive layer may be separated as required.

[0086]

When the middle layer or the pressure sensitive adhesive layer is formed, there may be used a diluted liquid of the resin composition for the middle layer or the pressure sensitive adhesive composition made by further blending an organic solvent to the resin composition for the middle layer or the 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 these organic solvents, there may be used the organic solvents, as they are, used in the synthesis of the each component contained in the resin composition for the middle layer or the pressure sensitive adhesive composition, or there may be added one or more solvents other than these organic solvents thereto.

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

[0087]

[Using method of the pressure sensitive adhesive tape]

The pressure sensitive adhesive tape of the present invention is attached on various types of works, and is used when the works are processed; and use thereof by being attached on work surfaces having irregularities or protrusions is preferable.

Further, it is more preferable that the pressure sensitive adhesive tape be attached on a semiconductor wafer surface, particularly a wafer surface on which bumps are formed, and be thus used as a pressure sensitive adhesive tape for protecting a semiconductor wafer surface. Further, it is still more preferable that the pressure sensitive adhesive tape be attached on a semiconductor wafer surface, and be thus used as a back grind tape to protect circuits formed on the wafer surface when the rear surface of the wafer is ground. In the case where the pressure sensitive adhesive tape of the present invention has the middle layer, since the embeddability is good even when the wafer surface has differences in height due to bumps and the like, the protection performance of the wafer surface becomes good. In this case, the temperature of the pressure sensitive adhesive tape when the pressure sensitive adhesive tape is attached on a semiconductor wafer surface is, for example, about 40 to 80°C, and preferably 50 to 70°C.

[0088]

In the present invention, the pressure sensitive adhesive layer is of an energy ray-curing type, and the pressure sensitive adhesive tape attached on a

work surface of a semiconductor wafer or the like is cured with energy rays by energy ray irradiation, and thereafter peeled off the work surface. Therefore, since the pressure sensitive adhesive tape is peeled off after the peel strength has been reduced, the peelability becomes good. Further, the adhesive residue results in being hardly generated when the pressure sensitive adhesive tape after being cured is peeled as described above.

Then, the pressure sensitive adhesive tape, in the case of being used for a semiconductor wafer, is not limited in its use to a back grind sheet, but is allowed to be used for other applications. The pressure sensitive adhesive tape may be used, for example, as a dicing sheet to hold a wafer when the pressure sensitive adhesive tape is attached on the wafer rear surface and then, the wafer is diced. The wafer in this case may be one in which protrusions such as bumps and irregularities are formed on the wafer rear surface, including ones in which through electrodes are formed.

Examples

[0089]

Hereinafter, the present invention will be described in more detail based on Examples, but the present invention is not limited to these Examples.

[0090]

Measurement methods and evaluation methods in the present invention were as follows.

[Weight-average molecular weight (Mw), Number-average molecular weight (Mn)]

For the weight-average molecular weight (Mw) and the number-average molecular weight (Mn), there were used values in terms of standard polystyrenes acquired from measurements using a gel permeation chromatograph apparatus (product name: "HLC-8220", manufactured by Tosoh Corp.) under the following condition.

(Measurement condition)

Columns: "TSK guard column HXL-H", "TSK gel GMHXL (×2)", "TSK gel G2000HXL" (any of which was manufactured by Tosoh Corp.)

Column temperature: 40°C Developing solvent: tetrahydrofuran Flow rate: 1.0 mL/min

[0091]

[Loss tangent ($\tan\delta$)]

The each resin composition for a middle layer used in Examples and Comparative Examples was coated on a polyethylene terephthalate film-based release film (manufactured by Lintec Corp., product name: "SP-PET381031", thickness: 38 μm) by a fountain die method to form a coated film. Then, the coated film was irradiated with ultraviolet rays from the coated film side to form a semi-cured layer.

Here, the ultraviolet ray irradiation was carried out by using, as a ultraviolet irradiation apparatus, a belt conveyer-type ultraviolet ray irradiation apparatus (manufactured by Eye Graphics Co., Ltd., product name: "ECS-4011GX"), and by using, as a ultraviolet ray source, a high-pressure mercury lamp (manufactured by Eye Graphics Co., Ltd., product name: "H04-L41"), and under the irradiation condition of an illuminance at a light wavelength of 365 nm of 112 mW/cm^2 and a quantity of light thereat of 177 mJ/cm^2 (as measured by a ultraviolet ray actinometer "UVPF-A1", manufactured by Eye Graphics Co., Ltd.).

The polyethylene terephthalate film-based release film (manufactured by Lintec Corp., product name: "SP-PET381031", thickness: 38 μm) was attached on the formed semi-cured layer, which was then irradiated with ultraviolet rays (by using the above ultraviolet ray irradiation apparatus and ultraviolet ray source, and under the irradiation condition of an illuminance of 271 mW/cm^2 and a quantity of light of 1,200 mJ/cm^2) to completely cure the semi-cured layer to form a middle layer having a thickness of 200 μm on both of which the release films were attached.

Five of the middle layers thus formed were prepared; and the PET-based release films were separated and the five middle layers were successively laminated by putting releasing surfaces thereof together to prepare a middle layer laminate (thickness: 1,000 μm).

Then, the obtained middle layer laminate was punched out into a circle of 10 mm in diameter to obtain a sample for measuring the viscoelasticity. The storage elastic moduli (G') at -50 to 150°C were measured by applying a strain of a frequency of 1 Hz on the sample at a temperature-rise rate of $4^\circ\text{C}/\text{min}$ by using a viscoelasticity measuring apparatus (manufactured by TA Instruments Inc., product name: "ARES") to acquire a loss tangent ($\tan\delta$) at 50°C .

[0092]

[Breaking stress]

A pressure sensitive adhesive layer (thickness: 200 μm) on whose both surfaces polyethylene terephthalate film-based release films (manufactured by Lintec Corp., product name: "SP-PET381031") were attached was prepared. Here, the pressure sensitive adhesive layer was formed on one release film by altering the thickness of the pressure sensitive adhesive layer to 40 μm by the same method in Examples and Comparative Examples; thereafter, another release film was attached on the pressure sensitive adhesive layer. Five sheets of such pressure sensitive adhesive layers interposed between the release films were prepared; and surfaces of the pressure sensitive adhesive layers exposed by separating the one release film are faced and laminated. This procedure was repeated to obtain the pressure sensitive adhesive layer having a thickness of 200 μm in which five layers of the pressure sensitive adhesive layers were laminated. The laminate of the pressure sensitive adhesive layers interposed between two sheets of the release films was irradiated with ultraviolet rays at an illuminance of 220 mW/cm^2 at an irradiation speed of 15 mm/sec by using a UV irradiation apparatus "RAD-2000m/12", manufactured by Lintec Corp.; thereafter, the cured material of the pressure sensitive adhesive layer was cut out into 15 $\text{mm} \times 150 \text{ mm}$. Then, labels for stretching the film were attached on both-end 25-mm portions of the cut-out sheet to fabricate a sample of a strip-form whose measurement-objective portion was 15 $\text{mm} \times 100 \text{ mm}$. There was measured the breaking stress when being measured at a tensile rate of 200 mm/min by using an "Autograph AG-IS500N", manufactured by Shimadzu Corp. [0093]

[Peel strength before energy ray irradiation]

The each pressure sensitive adhesive tape of Examples and Comparative Examples was cut equally into 25-mm widths; and one cut pressure sensitive adhesive tape was tentatively placed on a silicon mirror wafer being an adherend; a roll having a weight of 1 kg was once reciprocated thereon to attach the pressure sensitive adhesive tape by the dead load. After the attaching, the resultant was stored in an environment of 23°C and a relative humidity of 50% for 1 hour; and thereafter, there was measured the peel strength when the pressure sensitive adhesive tape was peeled at a peel angle of 180° at a peel rate of 300 mm/min by using a tensile tester (manufactured by Orientec Co., Ltd., product name: "Tensilon").

[Peel strength after energy ray irradiation]

The each pressure sensitive adhesive tape of Examples and Comparative Examples was cut equally into 25-mm widths; and one cut pressure sensitive adhesive tape was tentatively placed on a silicon mirror wafer being an adherend; a roll having a weight of 1 kg was once reciprocated thereon to attach the pressure sensitive adhesive tape by the dead load. After the attaching, the resultant was stored in an environment of 23°C and a relative humidity of 50% for 1 hour; the resultant was irradiated with ultraviolet rays from the pressure sensitive adhesive tape side at an illuminance of 220 mW/cm² at an irradiation rate of 15 mm/sec by using a UV irradiation apparatus "RAD-2000m/12", manufactured by Lintec Corp.; thereafter, the resultant was left in an environment of 23°C and a humidity of 50% for 5 min; and thereafter, there was measured the peel strength when the pressure sensitive adhesive tape was peeled at a peel angle of 180° at a peel rate of 300 mm/min by using a tensile tester (manufactured by Orientec Co., Ltd., product name: "Tensilon").

[0094]

[Embeddability evaluation]

The each pressure sensitive adhesive tape fabricated in Examples and Comparative Examples was attached on a wafer (manufactured by Waltz Co., Ltd., 8-inch wafer, bump specification: Sn/Ag/Cu = 96.5/3/0.5% by mass, wafer surface material: SiO₂) with spherical bumps of 250 μm in bump height and 300 μm in diameter in plan view at a pitch of 500 μm by using a laminator "RAD-3510F/12", manufactured by Lintec Corp. When the tape was attached, a laminate table and a laminate roll of the apparatus were set at 60°C. After the attaching, the resultant was irradiated with ultraviolet rays from the pressure sensitive adhesive tape side at an illuminance of 220 mW/cm² at an irradiation rate of 15 mm/sec by using a UV irradiation apparatus "RAD-2000m/12", manufactured by Lintec Corp. The thus-obtained wafer for evaluation on which the pressure sensitive adhesive tape was attached was observed by using a digital microscope (manufactured by Keyence Corp., product name: "VHX-1000"), and the diameter of a circular void generated on the bump periphery was measured from the substrate side and the embeddability was calculated by the following expression.

$$\text{Embeddability} = \text{a void diameter} / \text{a bump diameter} \times 100 [\%]$$

The case where a calculated embeddability of 110% or higher and lower than 130%, which exhibited a suitable void, was taken as best, and the embeddability was evaluated according to the following evaluation criteria.

A: embeddability = 110% or higher and lower than 130%

B: embeddability = 130% or higher and lower than 140%

C: embeddability = lower than 110%, or 140% or higher

[0095]

[Evaluation of the adhesive residue on bumps]

From a wafer for evaluation on which the pressure sensitive adhesive tape was attached, fabricated similarly to the above embeddability evaluation test, the pressure sensitive adhesive tape was peeled off in an environment of 23°C and a relative humidity of 50%, at a tensile rate of 120 mm/min by using a tensile tester (manufactured by Orientec Co., Ltd., product name: "Tensilon"). After the peeling, the bump portions of the wafer was observed by an electron microscope "VE-9800", manufactured by Keyence Corp., and the presence/absence of the adhesive residues was checked.

[0096]

[Fabrication of a substrate with a middle layer]

There were blended 40 parts by mass of a monofunctional urethane acrylate, 45 parts by mass of isobornyl acrylate (IBXA), 15 parts by mass of hydroxypropyl acrylate (HPA), 3.5 parts by mass of pentaerythritol tetrakis(3-mercaptopbutylate)(manufactured by Showa Denko K.K., product name: "Karenz MTPE1", 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 (manufactured by BASF, product name: "Darocur 1173", solid content concentration: 100% by mass) as a photopolymerization initiator to prepare a resin composition for a middle layer. The resin composition for a middle layer was coated on a polyethylene terephthalate film-based release film (manufactured by Lintec Corp., product name: "SP-PET381031", thickness: 38 µm) by a fountain die method to form a coated film.

Then, the resultant was irradiated with ultraviolet rays from the coated film side to form a semi-cured layer. Here, the ultraviolet ray irradiation was carried out by using, as a ultraviolet irradiation apparatus, a belt conveyer-type ultraviolet ray irradiation apparatus (manufactured by Eye Graphics Co., Ltd.,

product name: "ECS-401GGX"), and by using, as a ultraviolet ray source, a high-pressure mercury lamp (manufactured by Eye Graphics Co., Ltd., product name: "H04-L41"), and under the irradiation condition of an illuminance at a light wavelength of 365 nm of 112 mW/cm² and a quantity of light thereat of 177 mJ/cm² (as measured by a product name "UVPF-A1", manufactured by Eye Graphics Co., Ltd.).

On the formed semi-cured layer, there was laminated a substrate composed of a polyethylene terephthalate (PET)-based film (manufactured by Toyobo Co., Ltd., product name: Cosmoshine A4100", thickness: 50 μm); and further ultraviolet ray irradiation (using the above ultraviolet ray irradiation apparatus and ultraviolet ray source and under the irradiation condition of an illuminance of 271 mW/cm² and a quantity of light of 1,200 mJ/cm²) was carried out from the PET film side for complete curing to form a middle layer of 300 μm in thickness on the PET film as the substrate to obtain a substrate with a middle layer.

The loss tangent (tanδ) at 50°C of the middle layer as measured at a frequency of 1 Hz was 1.92.

In the following Examples and Comparative Examples, "parts by mass" in the case of being diluted with a thinner indicated "parts by mass" in terms of solid content.

[0097]

[Example 1]

As a urethane polymer (A'), there was prepared a polyurethane polyol (manufactured by Toyochem Co., Ltd., product name "SH-101", weight-average molecular weight: 100,000) having a urethane skeleton and a plurality of hydroxyl groups; to 100 parts by mass of the urethane polymer (A'), there were added 32 parts by mass of a urethane acrylate (manufactured by Daicel-Allnex Ltd., product name: "EBECRYL 4150", weight-average molecular weight: 1,040) having a plurality of isocyanate groups as a crosslinking agent (C1), 17 parts by mass of a mixture (mass ratio (B : D) = 40 : 60)(manufactured by Shin-Nakamura Chemical Co., Ltd., product name: "A-TMM-3LM-N") of pentaerythritol tetraacrylate (formula weight: 352) as an energy ray-curable compound (B) with pentaerythritol triacrylate (formula weight: 298) as a compound (D), 5 parts by mass of 2,2-dimethoxy-1,2-diphenylethan-1-one (manufactured by BASF, product name: "Irgacure 651") as an energy ray polymerization initiator (E), and 1 part by mass of a polyisocyanate compound (manufactured by Toyochem Co., Ltd., "T-

501B") as a crosslinking agent (C2), and the mixture was stirred for 10 min and diluted with toluene to prepare a pressure sensitive adhesive composition having a solid content concentration of 40% by mass.

Then, the prepared pressure sensitive adhesive composition was coated on a polyethylene terephthalate-based release film (manufactured by Lintec Corp., product name: "SP-PET381031", thickness: 38 μm), and heated at 100°C for 2 min and dried to form a pressure sensitive adhesive layer of 10 μm in thickness on the release film.

Thereafter, the release film on the substrate with the middle layer fabricated before was removed; and on the exposed middle layer, the pressure sensitive adhesive layer on the release film was attached, and thereafter, unnecessary portions of ends in the width direction were cut and removed to obtain a pressure sensitive adhesive tape provided with the substrate, the middle layer, the pressure sensitive adhesive layer and the release film in this order. The evaluation results of this pressure sensitive adhesive tape are shown in Table 1.

[0098]

[Example 2]

A pressure sensitive adhesive tape was fabricated by the same procedure as in Example 1, except for preparing a pressure sensitive adhesive composition by altering the urethane polymer (A) to a urethane polymer (A') (manufactured by Toyochem Co., Ltd., product name: "SP-205", weight-average molecular weight: 98,000).

[0099]

[Example 3]

A pressure sensitive adhesive tape was fabricated by the same procedure as in Example 1, except for preparing a pressure sensitive adhesive composition by altering 17 parts by mass of "A-TMM-3LM-N" to 100 parts by mass of a urethane acrylate (manufactured by Negami Chemical Industrial Co., Ltd., product name: "UN-6200", bifunctional, weight-average molecular weight: 6,270) as an energy ray-curable compound (B).

[0100]

[Example 4]

A pressure sensitive adhesive tape was fabricated by the same procedure as in Example 3, except for preparing a pressure sensitive adhesive composition

by altering the urethane polymer (A') to a urethane polymer (A')(manufactured by Toyochem Co., Ltd., product name: "SP-205").

[0101]

[Example 5]

A pressure sensitive adhesive tape was fabricated by the same procedure as in Example 1, except for altering 17 parts by mass of "A-TMM-3LM-N" to 100 parts by mass of a urethane acrylate (hexafunctional, weight-average molecular weight: 33,000) as an energy ray-curable compound (B).

[0102]

[Comparative Example 1]

There was prepared a methacryloyl group-added acryl copolymer (weight-average molecular weight: 900,000, solid content: 35% by mass) obtained by adding 2-isocyanatoethyl methacrylate ((manufactured by Showa Denko K.K., product name: "Karenz MOI") to an acryl copolymer obtained by polymerizing 94 parts by mass of 2-ethylhexyl acrylate with 6 parts by mass of 2-hydroxyethyl acrylate so that the addition ratio in terms of molar number of the 2-isocyanatoethyl methacrylate to hydroxyl groups in the acryl copolymer became 50%. To 100 parts by mass of the copolymer, there were added 3 parts by mass of 1-hydroxycyclohexyl phenyl ketone (manufactured by BASF, product name: "Irgacure 184") as a photopolymerization initiator, and 0.8 part by mass of a polyisocyanate compound (manufactured by Toyochem Co., Ltd., product name: "BHS-8515") as a crosslinking agent, and the mixture was stirred for 30 min to prepare an acryl-based pressure sensitive adhesive composition. The obtained acryl-based pressure sensitive adhesive composition was coated on a polyethylene terephthalate-based release film (manufactured by Lintec Corp., product name: "SP-PET381031", thickness: 38 μm), and dried to form a pressure sensitive adhesive layer of 10 μm in thickness.

The release film on the substrate with the middle layer fabricated before was removed; and on the exposed middle layer, the pressure sensitive adhesive layer on the release film was attached, and thereafter, unnecessary portions of ends in the width direction were cut and removed to obtain a pressure sensitive adhesive tape provided with the substrate, the middle layer, the pressure sensitive adhesive layer and the release film in this order. The evaluation results of this pressure sensitive adhesive tape are shown in Table 1.

[0103]

[Comparative Example 2]

There was prepared a methacryloyl group-added acryl copolymer (weight-average molecular weight: 1,000,000, solid content: 25% by mass) obtained by adding 2-isocyanatoethyl methacrylate (manufactured by Showa Denko K.K., product name: "Karenz MOI") to an acryl copolymer obtained by polymerizing 90 parts by mass of 2-ethylhexyl acrylate with 10 parts by mass of 4-hydroxybutyl acrylate so that the addition ratio in terms of molar number of the 2-isocyanatoethyl methacrylate to hydroxyl groups in the acryl copolymer became 65%. To 100 parts by mass of the copolymer, there were added 3 parts by mass of 1-hydroxycyclohexyl phenyl ketone (manufactured by BASF, product name: "Irgacure 184") as a photopolymerization initiator, and 1.1 parts by mass of a polyisocyanate compound (manufactured by Toyochem Co., Ltd., product name: "BHS-8515") as a crosslinking agent, and the mixture was stirred for 30 min to prepare an acryl-based pressure sensitive adhesive composition. Except for the above, a pressure sensitive adhesive tape was fabricated by the same procedure as in Comparative Example 1.

[0104]

[Comparative Example 3]

There was prepared a methacryloyl group-added acryl copolymer (weight-average molecular weight: 1,000,000, solid content: 25% by mass) obtained by adding 2-isocyanatoethyl methacrylate (manufactured by Showa Denko K.K., product name: "Karenz MOI") to an acryl copolymer obtained by polymerizing 90 parts by mass of 2-ethylhexyl acrylate with 10 parts by mass of 4-hydroxybutyl acrylate so that the addition ratio in terms of molar number of the 2-isocyanatoethyl methacrylate to hydroxyl groups in the acryl copolymer became 75%.

To 100 parts by mass of the copolymer, there were added 5 parts by mass of 1-hydroxycyclohexyl phenyl ketone (manufactured by BASF, product name: "Irgacure 184") as a photopolymerization initiator, and 1.2 parts by mass of a polyisocyanate compound (manufactured by Toyochem Co., Ltd., product name: "BHS-8515") as a crosslinking agent, and the mixture was stirred for 30 min to prepare an acryl-based pressure sensitive adhesive composition. Except for the above, a pressure sensitive adhesive tape was fabricated by the same procedure as in Comparative Example 1.

[0105]

[Comparative Example 4]

A pressure sensitive adhesive tape was fabricated by the same procedure as in Example 1, except for not adding "A-TMM-3LM-N".

[0106]

Table 1

	Breaking Stress [MPa]	Peel Strength [mN/25 mm]		Embeddability	Adhesive Residue
		Before Ultraviolet Ray Irradiation	After Ultraviolet Ray Irradiation		
Example 1	9.7	7700	620	A	absent
Example 2	17.3	22000	1300	B	absent
Example 3	3.4	5000	750	A	absent
Example 4	3.9	9200	670	B	absent
Example 5	13.6	3800	540	B	absent
Comparative Example 1	0.59	4800	880	A	present
Comparative Example 2	1.28	4500	780	A	present
Comparative Example 3	1.23	4200	780	A	present
Comparative Example 4	5.8	900	250	C	unevaluable

[0107]

In Examples 1 to 5 hitherto, since the pressure sensitive adhesive composition was urethane-based and contained the energy ray-curable compound (B) non-reactive with the urethane-based resin (A), the embeddability of bumps (conformability of the pressure sensitive adhesive layer to the work surface shape) became good and the breaking stress became high, whereby generation of the adhesive residue in the peeling time could be prevented. Further since the peel strength before the energy ray curing could be made high and the peel strength after the curing could be made sufficiently low, the peelability and the adhesivity were excellent.

By contrast, in Comparative Examples 1 to 3, since the pressure sensitive adhesive composition was acryl-based, the breaking stress was low, whereby generation of the adhesive residue could not be prevented. Further in Comparative Example 4, since the pressure sensitive adhesive composition, though being urethane-based, contained no energy ray-curable compound (B), the

flexibility of the pressure sensitive adhesive layer was inferior and the embeddability was not sufficient.

CLAIMS

[Claim 1]

A pressure sensitive adhesive tape for work processing, comprising: a substrate and a pressure sensitive adhesive layer provided on one surface side of the substrate,

wherein the pressure sensitive adhesive layer comprises a urethane-based resin (A) and an energy ray-curable compound (B); and the energy ray-curable compound (B) is non-reactive with the urethane-based resin (A), has a photopolymerizable unsaturated bond, and has a molecular weight of 35,000 or lower.

[Claim 2]

The pressure sensitive adhesive tape for work processing according to claim 1, wherein the energy ray-curable compound (B) is at least one selected from the group consisting of (meth)acrylate monomers (B1) and urethane (meth)acrylates (B2).

[Claim 3]

The pressure sensitive adhesive tape for work processing according to claim 2, wherein the energy ray-curable compound (B) comprises at least a (meth)acrylate monomer (B1); and the (meth)acrylate monomer (B1) is a polyfunctional (meth)acrylate ester being a complete ester of a polyhydric alcohol with (meth)acrylic acid.

[Claim 4]

The pressure sensitive adhesive tape for work processing according to any one of claims 1 to 3, wherein the energy ray-curable compound (B) is bi- or more functional in terms of (meth)acryloyl group in one molecule thereof.

[Claim 5]

The pressure sensitive adhesive tape for work processing according to any one of claims 1 to 4, wherein the urethane-based resin (A) has a photopolymerizable unsaturated bond.

[Claim 6]

The pressure sensitive adhesive tape for work processing according to any one of claims 1 to 5, wherein the pressure sensitive adhesive layer is formed of a pressure sensitive adhesive composition comprising, at least, a urethane polymer (A'), the energy ray-curable compound (B), and a crosslinking agent (C); and

the urethane-based resin (A) is obtained by crosslinking the urethane polymer (A') with the crosslinking agent (C).

[Claim 7]

The pressure sensitive adhesive tape for work processing according to claim 6, wherein the crosslinking agent (C) comprises a crosslinking agent (C1) having a photopolymerizable unsaturated bond.

[Claim 8]

The pressure sensitive adhesive tape for work processing according to claim 6 or 7, wherein the urethane polymer (A') and the crosslinking agent (C) are bonded through a urethane bond.

[Claim 9]

The pressure sensitive adhesive tape for work processing according to any one of claims 6 to 8, wherein the pressure sensitive adhesive composition further comprises a compound (D) having a photopolymerizable unsaturated bond and a reactive functional group reactive with the crosslinking agent (C).

[Claim 10]

The pressure sensitive adhesive tape for work processing according to claim 9, wherein the compound (D) is a polyfunctional (meth)acrylate ester being a partial ester of a polyhydric alcohol with (meth)acrylic acid.

[Claim 11]

The pressure sensitive adhesive tape for work processing according to any one of claims 1 to 10, wherein the pressure sensitive adhesive layer after energy ray irradiation has a breaking stress of 2.5 MPa or higher.

[Claim 12]

The pressure sensitive adhesive tape for work processing according to any one of claims 1 to 11, wherein a middle layer is provided between the substrate and the pressure sensitive adhesive layer.

[Claim 13]

The pressure sensitive adhesive tape for work processing according to claim 12, wherein the middle layer has a thickness of 10 to 600 μm .

[Claim 14]

The pressure sensitive adhesive tape for work processing according to claim 12 or 13, wherein the middle layer has a loss tangent at 50°C of 1.0 or higher as measured at a frequency of 1 Hz.

[Claim 15]

The pressure sensitive adhesive tape for work processing according to any one of claims 1 to 14, wherein the pressure sensitive adhesive tape after energy ray irradiation has a peel strength of 2,000 mN/25 mm or lower.

[Claim 16]

The pressure sensitive adhesive tape for work processing according to any one of claims 1 to 15, wherein the pressure sensitive adhesive tape is used for protecting a semiconductor wafer surface.