

DESCRIPTION

Title of Invention

FILM FOR FORMING PROTECTION FILM

Technical Field

[0001]

The present invention relates to a protective film-forming film used, for example, for protecting the back face of a semiconductor chip.

Background Art

[0002]

Conventionally, manufacturing a semiconductor device utilizing a mounting method called a facedown method has been performed. In the facedown method, the chip front face having an electrode such as a bump formed thereon faces to and is joined on a substrate board or the like. On the other hand, since the chip back face is naked, it is protected by a protective film. It is known that the protective film is formed of, for example, a protective film-forming film. As the protective film-forming film, one is known that contains a heat-curable component containing an epoxy resin or the like and a binder polymer component containing an acrylic polymer or the like, for example as illustrated in PTL 1.

[0003]

In the case of using a protective film-forming film, in general, first the protective film-forming film is stuck onto the back face of a semiconductor wafer, the protective film-forming film is cured, and thereafter the semiconductor wafer is diced into individual pieces along with the cured protective film-forming film, thereby producing protective film-attached semiconductor chips. While diced, the semiconductor wafer is held by a dicing sheet or the like stuck onto the back face of the wafer. In general, the individual diced semiconductor chip is pushed up by a needle from the back face side via the dicing sheet or the like, and is picked up with a collet or the like.

Citation List

Patent Literature

[0004]

PTL 1: WO2014/1587426

Summary of Invention

Technical Problem

[0005]

For stably dicing a semiconductor wafer, it is preferable that the wafer is held by a dicing tape with a high adhesion force. However, when the adhesion force of the dicing tape is increased, the pickup force in picking up semiconductor chips would also increase and there may often occur a problem that a needle indentation is formed in the surface of the protective film.

The present invention has been made in consideration of the above-mentioned problems and is intended to provide a protective film-forming film capable of preventing the formation of needle indentation in the surface of a protective film.

Solution to Problem

[0006]

As a result of assiduous studies, the present inventors have found that when the Shore D hardness and the Young's modulus of a protective film-forming film after curing are controlled to be a fixed value or more, a needle indentation to be formed in the protective film in picking up can be prevented, and have completed the present invention. The present invention provides the following (1) to (10).

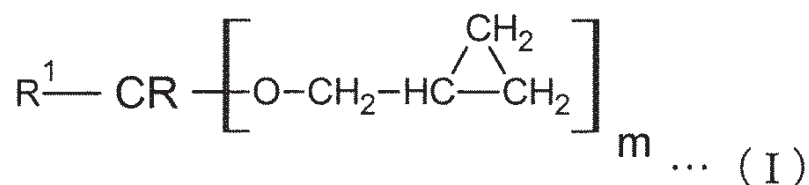
(1) A protective film-forming film for forming a protective film that protects a semiconductor chip, wherein:

the Shore D hardness of the film surface after curing is 55 or more and the Young's modulus (23°C) after curing is 1.0×10^9 Pa or more.

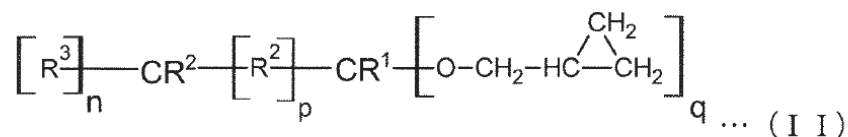
(2) The protective film-forming film according to the above (1), which contains an acrylic polymer (A) and an epoxy curable component (B).

(3) The protective film-forming film according to the above (2), wherein the epoxy curable component (B) contains an epoxy group-having condensed cyclic aromatic compound (b1).

(4) The protective film-forming film according to the above (3), wherein the epoxy group-having condensed cyclic aromatic compound (b1) is a compound represented by the following general formula (I) or (II):



wherein CR represents a condensed polycyclic aromatic hydrocarbon group, R¹ represents a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, and m represents an integer of 2 to 6; and



wherein CR¹ and CR² each represent a condensed polycyclic aromatic hydrocarbon group and these condensed polycyclic aromatic hydrocarbon groups may be the same or different; R² represents a divalent hydrocarbon group and the hydrocarbon group may have a substituent; R³ represents an alkyl group having 1 to 10 carbon atoms, or a glycidyl ether group; n represents an integer of 0 to 3; p represents an integer of 0 to 10, provided that when p is 0 R² is a single bond; and q represents an integer of 1 to 3.

(5) The protective film-forming film according to any of the above (2) to (4), wherein the monomer to constitute the acrylic polymer (A) contains an alkyl (meth)acrylate in which the alkyl group has 1 to 8 carbon atoms.

(6) The protective film-forming film according to any of the above (2) to (5), wherein the monomer to constitute the acrylic polymer (A) contains methyl (meth)acrylate.

(7) The protective film-forming film according to any one of the above (2) to (6), wherein the monomer to constitute the acrylic polymer (A) contains methyl acrylate.

(8) The protective film-forming film according to any one of the above (1) to (7), which contains a filler (C).

(9) A protective film-forming composite sheet including: a support sheet; and a protective film-forming film according to any one of the above (1) to (8) that is provided on the support sheet.

(10) A protective film-attached chip including: a semiconductor chip; and a protective film that is provided on the semiconductor chip and that is formed by

curing the protective film-forming film according to any one of the above (1) to (8).

Advantageous Effects of Invention

[0007]

The present invention provides a protective film-forming film capable of preventing a needle indentation from forming in a protective film in picking up.

Description of Embodiments

[0008]

Hereinafter, the present invention will be specifically described using the embodiments.

Note that, in the present specification, "(meth)acrylic" is used as a term indicating both "acrylic" and "methacrylic", which is the same for other similar terms. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) are polystyrene-equivalent values as measured according to a gel permeation chromatography (GPC) method.

[0009]

[Protective Film-Forming Film]

A protective film-forming film of the present invention is a film for forming a protective film that protects a semiconductor chip, wherein the Shore D hardness of the film surface after curing is 55 or more and the Young's modulus (23°C) after curing is 1.0×10^9 Pa or more.

When the protective film-forming film has the Shore D hardness of less than 55 or the Young's modulus of less than 1.0×10^9 Pa, the protective film may readily undergo plastic deformation. Consequently, when a protective film-attached chip is pushed up with a needle, a needle indentation may readily form in the film surface so that the advantageous effects of the present invention could not be achieved.

[0010]

Preferably, the Shore D hardness of the protective film-forming film is 58 or more and the Young's modulus (23°C) thereof is 2.0×10^9 Pa or more, and more preferably, the Shore D hardness is 62 or more and the Young's modulus (23°C) is 5.0×10^9 Pa or more. In the present invention, the Shore D hardness and the Young's modulus are defined higher as above, so that a needle indentation could hardly form in the surface of the protective film even when a semiconductor chip

is picked up with a high picking-up force.

The upper limit of the Shore D hardness and that of the Young's modulus (23°C) are not specifically limited, but from the viewpoints of preventing the protective film from being brittle and of increasing the reliability of the film, preferably, the Shore D hardness is 90 or less and the Young's modulus (23°C) is 9.0×10^{10} Pa or less, more preferably, the Shore D hardness is 80 or less and the Young's modulus (23°C) is 5.0×10^{10} Pa or less.

[0011]

The material for the protective film-forming film of the present invention is not specifically limited, but generally contains a binder resin and a heat-curable component. The binder resin is a component that imparts flexibility and film formability of the protective film and the protective film-forming film. As the binder resin, an acrylic resin, a polyester resin, a urethane resin, an acrylic urethane resin, a silicone resin, a rubber polymer, a phenoxy resin and the like are usable. One alone or two or more kinds of binder resins may be used either singly or as combined.

The heat-curable component is a component for forming a hard protective film on a semiconductor chip by curing, and generally contains a heat-curable resin and a heat-curing agent for heat-curing the heat-curable resin. The heat-curable resin includes an epoxy resin, a phenolic resin, an amino resin, an unsaturated polyester resin, a polyurethane resin, a silicone resin, a heat-curable polyimide resin, etc. One alone or two or more kinds may be used either singly or as combined for the heat-curable resins and the heat-curing agent, respectively.

[0012]

Preferably, the protective film-forming film of the present invention contains an acrylic polymer (A) (that is, an acrylic resin) as the binder resin, and contains an epoxy curable component (B) as the heat-curable component. In the present invention, when the film contains both the above-mentioned components (A) and (B), both the above-mentioned Shore D hardness and the Young's modulus can be readily controlled to fall within a desired range while increasing the reliability of the protective film. In addition, even when a semiconductor chip is picked up with a high picking-up force, a needle indentation could hardly form in the protective film.

The acrylic polymer (A) and the epoxy curable component (B) are described hereinunder in more detail.

[0013]

<Acrylic Polymer (A)>

The acrylic polymer (A) to constitute the acrylic resin is a polymer that contains at least a (meth)acrylate monomer as the monomer to constitute the acrylic polymer. Specifically, the acrylic polymer (A) is one prepared by polymerization of a monomer that contains at least a (meth)acrylate monomer.

Specific examples of the (meth)acrylate monomer include alkyl (meth)acrylates in which the alkyl group has 1 to 18 carbon atoms such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, n-octyl (meth)acrylate, n-nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, and lauryl (meth)acrylate; (meth)acrylates having a cyclic skeleton such as cycloalkyl (meth)acrylate in which a cycloalkyl group has 1 to about 18 carbon atoms, benzyl (meth)acrylate, isobornyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, and imide (meth)acrylate; hydroxy group-containing (meth)acrylates such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, and 2-hydroxypropyl (meth)acrylate; and epoxy group-containing (meth)acrylates such as glycidyl (meth)acrylate, β -methylglycidyl (meth)acrylate, (3,4-epoxycyclohexyl)methyl (meth)acrylate, and 3-epoxycyclo-2-hydroxypropyl (meth)acrylate.

Further, a monomer other than (meth)acrylate monomers, such as acrylic acid, methacrylic acid, itaconic acid, vinyl acetate, acrylonitrile, styrene, vinyl ether, N-methylolacrylamide and the like may also be used as a monomer to constitute the acrylic polymer (A). One alone or two or more of the above-mentioned monomers may be used either singly or as combined.

[0014]

The monomer to constitute the acrylic polymer (A) preferably contains an alkyl (meth)acrylate among the above-mentioned monomers, and among them, more preferably contains an alkyl (meth)acrylate in which the alkyl group has 1 to 8 carbon atoms. Also preferably, the alkyl (meth)acrylate in which the alkyl group has 1 to 8 carbon atoms accounts for 50% by mass or more of all the monomers constituting the acrylic polymer, more preferably 60 to 95% by mass, even more preferably 70 to 90% by mass. In the alkyl (meth)acrylate in which the alkyl group has 1 to 8 carbon atoms, the carbon number of the alkyl group is

more preferably 1 to 4.

Further, the alkyl (meth)acrylate in which the alkyl group has 1 to 8 carbon atoms preferably contains methyl (meth)acrylate for readily increasing the Shore D hardness and the Young's modulus. More preferably, the content of methyl (meth)acrylate is 50 to 80% by mass of all the monomers constituting the acrylic polymer (A). In addition, the methyl (meth)acrylate is more preferably methyl acrylate from the viewpoint of improving the close-contact properties and tackiness of the protective film-forming film to semiconductor wafers and improving the handleability thereof.

[0015]

Further, the monomer to constitute the acrylic polymer (A) preferably contains a hydroxyl group-containing (meth)acrylate or an epoxy group-containing (meth)acrylate among the above-mentioned monomers, and even more preferably contains both the two. Using these monomers facilitates control of the close-contact properties and tacky characteristics of the protective film-forming film to semiconductor wafers, while maintaining the Shore D hardness and the Young's modulus each to fall within a suitable range.

The hydroxyl group-containing (meth)acrylate preferably accounts for 1 to 30% by mass of all the monomers constituting the acrylic polymer (A), more preferably 5 to 25% by mass, even more preferably 10 to 20% by mass.

The epoxy group-containing (meth)acrylate preferably accounts for 0.1 to 30% by mass of all the monomers constituting the acrylic polymer (A), more preferably 0.5 to 25% by mass, even more preferably 1 to 8% by mass.

[0016]

The weight-average molecular weight (M_w) of the acrylic polymer (A) is preferably 10,000 or more for imparting flexibility and film formability to the protective film-forming film. The weight-average molecular weight is more preferably 15,000 to 1,000,000, even more preferably 20,000 to 500,000.

The glass transition temperature of the acrylic polymer (A) is preferably -60 to 50°C, more preferably -30 to 30°C, even more preferably -20 to 20°C. The glass transition temperature of the acrylic polymer (A) is a theoretical value to be obtained according to a Fox equation. When the glass transition temperature is made to fall within the above range, the Shore D hardness and the Young's modulus can be readily made each to fall within a favorable range while increasing the reliability of the protective film.

The proportion of the acrylic polymer (A) to the total mass (in terms of the solid content) of the protective film-forming film is generally 10 to 80% by mass, preferably 15 to 50% by mass.

[0017]

<Epoxy Curable Component (B)>

The epoxy curable component (B) is generally composed of an epoxy compound (epoxy resin) as a heat-curable resin and a heat-curing agent.

Specific examples of the epoxy compound include epoxy compounds having bi- or more multi-functionality in the molecule, such as a biphenyl compound, a bisphenol A diglycidyl ether and a hydrogenated product thereof, an ortho-cresol novolak epoxy resin, a dicyclopentadiene-type epoxy resin, a biphenyl-type epoxy resin, a bisphenol A-type epoxy resin, a bisphenol F-type epoxy resin, a phenylene skeleton-type epoxy resin, an epoxy group-having condensed cyclic aromatic compound, etc.. These may be used singly or in combination of two or more.

The amount of the epoxy compound is preferably 45 to 150 parts by mass relative to 100 parts by mass of the acrylic polymer (A), more preferably 55 to 120 parts by mass, even more preferably 68 to 110 parts by mass, still more preferably 75 to 100 parts by mass. When the amount of the epoxy compound is made to fall within the above range, the Shore D hardness and the Young's modulus may be more readily controlled each to fall within a desired range while bettering the reliability or the like of the protective film.

[0018]

Among the above-mentioned compounds, the epoxy compound preferably contains an epoxy group-having condensed cyclic aromatic compound (b1). The epoxy group-having condensed cyclic aromatic compound (b1) is a compound having a condensed polycyclic aromatic hydrocarbon group and an epoxy group, in which the epoxy group bonds to the condensed polycyclic aromatic hydrocarbon group directly or via an alkylene ether group. In the condensed cyclic aromatic compound (b1), the total carbon number of the condensed polycyclic aromatic hydrocarbon group is not specifically limited but is preferably 8 to 55, more preferably 12 to 45, even more preferably 16 to 35. The alkylene ether group is a divalent group having an alkylene group and an etheric oxygen atom, and examples thereof include an oxymethylene group, etc.

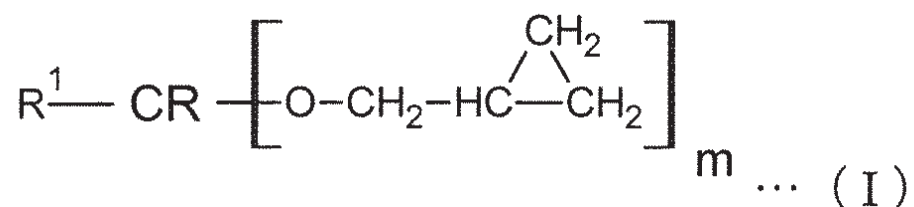
When an epoxy group-having condensed cyclic aromatic compound (b1) is used as the epoxy compound, the Shore D hardness and the Young's modulus of

the protective film-forming film can be readily controlled each to be a high value. In addition, the protective film-forming film can be cured within a short period of time and the protective film can be strengthened, and therefore the reliability of the protective film and the productivity of protective film-attached chips can be readily increased.

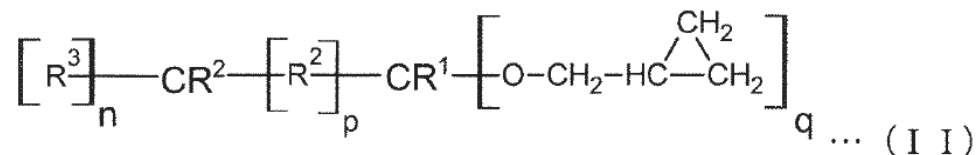
[0019]

Examples of the epoxy group-containing condensed cyclic aromatic compound (b1), as one having a glycidyl ether group bonding to the condensed ring (or an epoxy group bonding thereto via an oxymethylene group), include compounds represented by the following general formula (I) or (II):

[0020]



In the general formula (I), CR represents a condensed polycyclic aromatic hydrocarbon group, R^1 represents a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, and m represents an integer of 2 to 6. When R^1 is an alkyl group, the carbon number thereof is preferably 1 to 6. m is preferably 2 to 4.



In the general formula (II), CR^1 and CR^2 each represent a condensed polycyclic aromatic hydrocarbon group and these condensed polycyclic aromatic hydrocarbon groups may be the same or different; R^2 represents a divalent hydrocarbon group and the hydrocarbon group may have a substituent a; R^3 represents an alkyl group having 1 to 10 carbon atoms, or a glycidyl ether group; n represents an integer of 0 to 3; p represents an integer of 0 to 10, provided that when p is 0 R^2 is a single bond; and q represents an integer of 1 to 3. The carbon number of R^2 is preferably 1 to 6. When R^3 is an alkyl group, the carbon number thereof is preferably 1 to 6. n is preferably 1 to 2, p is preferably 0 to 4, q is preferably 1 to 2, and among them p is more preferably 1.

[0021]

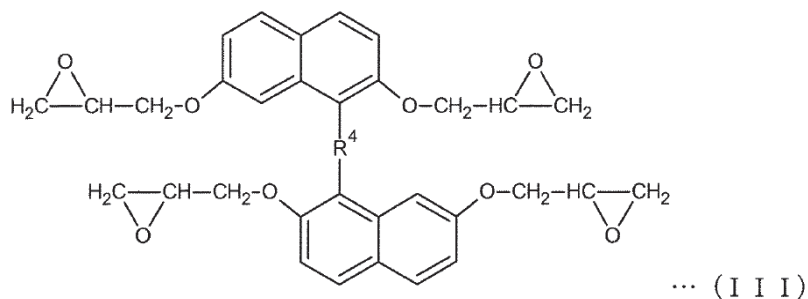
Examples of the substituent a for R^2 in the general formula (II) include a phenyl group, a phenyl group having a substituent b, etc. Examples of the substituent b include an alkyl group having 1 to 6 carbon atoms, a glycidyl ether group, etc., and is preferably an alkyl group having 1 to 4 carbon atoms.

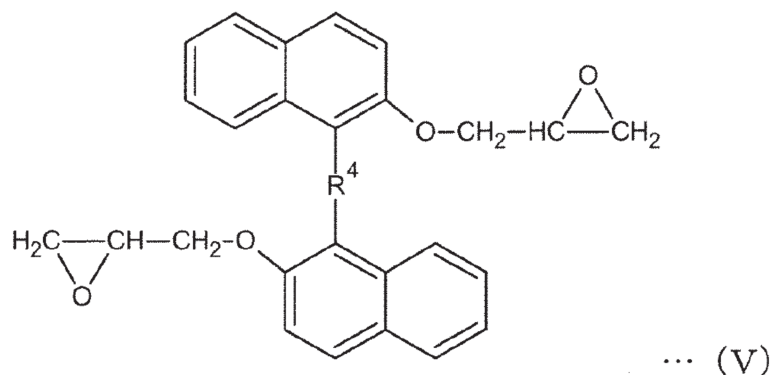
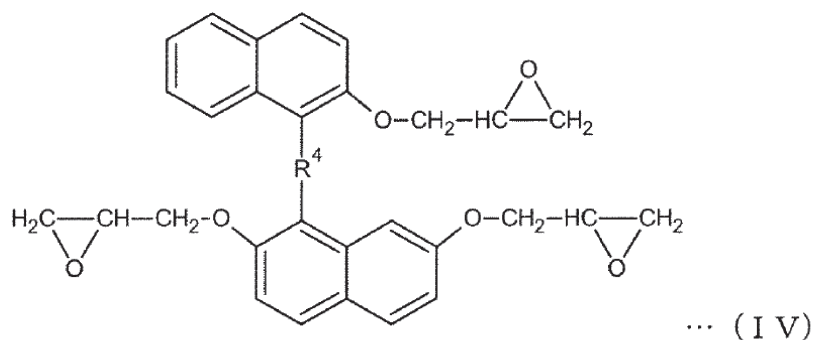
The condensed polycyclic aromatic hydrocarbon group is one in which two or more aromatic rings are condensed, and the carbon number of the condensed polycyclic aromatic hydrocarbon group in the above-mentioned general formula (I) or (II) is preferably independently 8 to 22, more preferably 10 to 20. Specific examples of the condensed polycyclic aromatic hydrocarbon group include a hydrocarbon group composed of a naphthalene ring, an anthracene ring, a phenanthrene ring, a 3,4-benzopyrene ring, or the like, and among these, a naphthalene ring is preferred from the viewpoint of the curability of the protective film-forming film.

[0022]

The epoxy group-containing condensed cyclic aromatic compound is preferably a compound represented by the general formula (II) among those mentioned above, and is more preferably a compound represented by the general formula (II) and having a naphthalene ring. Specific examples of the compound represented by the general formula (II) and having a naphthalene ring include a compound such as 1,1-bis(2,7-diglycidyloxy-1-naphthyl)alkane or the like represented by the following general formula (III), a compound such as 1-(2,7-diglycidyloxy-1-naphthyl)-1-(2-glycidyloxy-1-naphthyl)alkane or the like represented by the following general formula (IV), a compound such as 1,1-bis(2-glycidyloxy-1-naphthyl)alkane or the like represented by the following general formula (V), etc.

[0023]

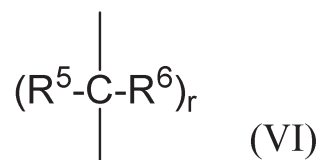




In the general formulae (III) to (V), R^4 represents a single bond or a divalent hydrocarbon group, and the hydrocarbon group may have a substituent. In the case where two or more kinds of the compounds represented by the general formulae (III) to (V) are used as combined, R^4 in each compound may be the same as or different from each other.

[0024]

R^4 in the general formulae (III) to (V) is more preferably a divalent hydrocarbon group optionally having a substituent and represented by the following formula (VI).



In the general formula (VI), the upper and lower chemical bonds from the carbon each bond to the naphthalene ring, and R^5 and R^6 each independently represent a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a phenyl group or a phenyl group having a substituent c . In the case where R^5 and R^6 each are a phenyl group having a substituent c , examples of the substituent c

include an alkyl group having 1 to 10 carbon atoms, a glycidyl ether group, and so on, and the substituent c is preferably an alkyl group having 1 to 6 carbon atoms. R^5 and R^6 are especially preferably hydrogen atoms from the viewpoint of the curability of the protective film-forming film. In the above formula (VI), r is an integer of 0 to 4, and is preferably 0 to 3, more preferably 1. When r is 0, the structure of the formula (VI) is a single bond.

Among the compounds represented by the general formulae (III) to (V), the compound represented by the general formula (III) is preferred, and the compound of the general formula (III) where R^4 is methylene ($-\text{CH}_2-$) is especially preferred.

[0025]

The epoxy equivalent of the epoxy group-having condensed cyclic aromatic compound (b1) is preferably 120 to 250 g/eq, more preferably 130 to 180 g/eq. By controlling the epoxy equivalent to fall within the above range, the curability of the protective film-forming film is bettered and the Shore D hardness and the Young's modulus can be readily controlled to be a favorable value.

[0026]

The glass transition temperature of the cured product of the epoxy group-having condensed cyclic aromatic compound (b1) is preferably 220°C or more, more preferably 220 to 350°C, even more preferably 240 to 345°C, still more preferably 300 to 330°C. By controlling the glass transition temperature of the cured product of the compound (b1) to fall within the above-mentioned range, the curability of the protective film-forming film is bettered, and the strength thereof is increased. Further, the Shore D hardness and the Young's modulus can be readily controlled to fall within a favorable range.

The glass transition temperature of the cured product of the compound (b1) and that of the other epoxy compound (b2) to be mentioned below is measured by adding a curing agent to the compound (b1) or (b2) then curing it and thereafter analyzing the resultant cured product with a viscoelastometer. The detailed measurement conditions are as described in the section of Examples to be given hereinunder.

[0027]

The softening point of the epoxy group-having condensed cyclic aromatic compound is preferably 60 to 110°C, more preferably 70 to 100°C, even more preferably 80 to 97°C. By controlling the softening point of the epoxy

group-having condensed cyclic aromatic compound to fall within the above-mentioned range, the curability of the protective film-forming film is improved and the Shore D hardness and the Young's modulus can be readily made to have a favorable value. The softening point is one measured according to a ring-and-ball method according to JISK2207:2006, and specifically it is measured according to the method described in the section of Examples to be given hereinafter.

[0028]

The melt viscosity of the epoxy group-having condensed cyclic aromatic compound is preferably 1.0 to 25.0 dPa·s, and is more preferably more than 2.0 dPa·s and 15.0 dPa·s or less, even more preferably 2.5 to 7.0 dPa·s. By controlling the melt viscosity of the epoxy group-having condensed cyclic aromatic compound to fall within the above range, the curability of the protective film-forming film can be improved. The melt viscosity is a viscosity measured with a capillary rheometer at a measurement temperature of 150°C and at a measurement frequency of 1 Hz.

[0029]

The number-average molecular weight (M_n) of the epoxy group-having condensed cyclic aromatic compound (b1) is preferably 200 to 1000, more preferably 300 to 900, even more preferably 400 to 800, still more preferably 450 to 750. By controlling the number-average molecular weight (M_n) of the epoxy group-having condensed cyclic aromatic compound to fall within the above range, the curability of the protective film-forming film can be improved, and the Shore D hardness and the Young's modulus can be readily controlled to be a preferable value.

[0030]

Preferably, the protective film-forming film contains any other epoxy compound (b2) along with the epoxy group-having condensed cyclic aromatic compound (b1). Examples of the other epoxy compound (b2) to be used in combination include the above-listed epoxy compounds except the epoxy group-having condensed cyclic aromatic compound (b1), and among these, using at least any of a bisphenol A-type epoxy resin and a dicyclopentadiene-type epoxy resin is preferred, and using both of these is more preferred.

[0031]

In the case where the epoxy group-having condensed cyclic aromatic

compound (b1) and the other epoxy compound (b2) are used, the ratio by mass of the condensed cyclic aromatic compound (b1) to the other epoxy compound (b2) (b1/b2) is preferably 1/3 to 1/15, more preferably 1/5 to 1/10. By using the two or more kinds of epoxy compounds as combined in the above-mentioned ratio by mass, the Shore D hardness and the Young's modulus can be readily controlled to fall within a desired range while increasing the strength, the curability and the reliability of the protective film-forming film.

[0032]

The number-average molecular weight of the other epoxy compound (b2) is not specifically limited, but is, from the viewpoint of curability of an adhesive and the strength and the heat resistance after curing, preferably 250 to 10000, more preferably 300 to 3000. The epoxy equivalent of the other epoxy compound (b2) is preferably 100 to 1000 g/eq, more preferably 150 to 800 g/eq.

The glass transition temperature of the cured product of the other epoxy compound (b2) is, for increasing the close-contact properties with semiconductor chips, etc., lower than that of the epoxy group-containing condensed cyclic aromatic compound (b1), and is preferably 150 to 240°C, more preferably 165 to 225°C, even more preferably 170 to 220°C.

[0033]

Examples of the heat-curing agent to be used along with the epoxy compound include a compound having two or more functional groups capable of reacting with an epoxy group in one molecule. Examples of the functional group include a phenolic hydroxyl group, an alcoholic hydroxyl group, an amino group, a carboxyl group, an acid anhydride, etc. Among these, a phenolic hydroxyl group, an amino group and an acid anhydride are preferred, and a phenolic hydroxyl group and an amino group are more preferred.

[0034]

Specific examples of the phenolic curing agent having a phenolic hydroxyl group include a polyfunctional phenolic resin, a biphenol, a novolak-type phenolic resin, a dicyclopentadiene-type phenolic resin, a xyloc-type phenolic resin, and an aralkylphenolic resin. Specific examples of the amine-type curing agent having an amino group include a dicyandiamide. One alone or two or more kinds of these may be used either singly or as combined.

The content of the heat-curing agent in the protective film-forming film is preferably 0.1 to 100 parts by mass relative to 100 parts by mass of the epoxy

compound, more preferably 0.5 to 50 parts by mass, even more preferably 1 to 20 parts by mass.

The proportion of the epoxy curable component (B) (that is, the total amount of the epoxy compound and the heat-curable agent) is generally 5 to 60% by mass relative to the total mass (in terms of the solid content) of the protective film-forming film, but preferably 15 to 40% by mass

[0035]

<Filler (C)>

Preferably, the protective film-forming film further contains a filler (C). With containing a filler (C), the protective film can be given moisture resistance, dimensional stability, or the like, and the reliability of the protective film can be also improved. Further, the Shore D hardness and the Young's modulus can be readily controlled to be a favorable value. Specific examples of the filler (C) include an inorganic filler. Examples of preferred inorganic fillers include a powder of silica, alumina, talc, calcium carbonate, titanium oxide, iron oxide, silicon carbide, boron nitride, and the like, a bead obtained by converting these materials into a spherical shape, single-crystal fiber, and glass fiber. Among these fillers, a silica filler and an alumina filler are preferred, and a silica filler is more preferred. Further, these inorganic fillers can be used singly or in combination of two or more.

The content of the filler (C) is preferably 10 to 70% by mass as a proportion thereof relative to the total mass (in terms of the solid content) of the protective film-forming film, more preferably 40 to 65% by mass.

The mean particle size of the inorganic filler is preferably 0.02 to 20 μm , more preferably 0.05 to 10 μm . The mean particle size of the inorganic filler is a number-average particle size calculated by measuring the major axis diameter of twenty inorganic filler particles randomly selected, with an electronic microscope, followed by averaging the resultant data to give an arithmetic average as the number-average particle size.

[0036]

<Curing Accelerator (D)>

The protective film-forming film may further contain a curing accelerator (D). With containing a curing accelerator (D), the heat-curing rate of the protective film-forming film can be controlled.

Examples of preferred curing accelerators (D) include tertiary amines

such as triethylenediamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol, and tris(dimethylaminomethyl)phenol; imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole, and 2-phenyl-4-methyl-5-hydroxymethylimidazole; organic phosphines such as tributylphosphine, diphenylphosphine, and triphenylphosphine; and tetraphenyl boron salts such as tetraphenylphosphonium tetraphenylborate and triphenylphosphine tetraphenylborate. These curing accelerators may be used singly or in combination of two or more.

The curing accelerator (D) is contained in the protective film-forming film in an amount of preferably 0.01 to 10 parts by mass, more preferably 0.1 to 5 parts by mass, based on 100 parts by mass of the epoxy compound. When the protective film-forming film contains the curing accelerator (D) in an amount in the above range, the protective film-forming film has excellent adhesive properties even when exposed to high temperature and high humidity, thus capable of achieving high reliability even when exposed to severe conditions.

[0037]

<Coloring agent (E)>

The protective film-forming film may further contain a coloring agent (E). With containing a coloring agent (E), the film can block IR rays and the like, and can therefore prevent malfunction of a semiconductor device by IR rays and the like to be generated from the surrounding apparatus. Further, when the protective film is marked by means of laser marking or the like, the marks of letters, signs and others can be more readily recognized.

An organic or inorganic pigment or dye is used as the coloring agent. Any dye including acid dye, reactive dye, direct dye, disperse dye, or cationic dye can be used as the dye. Further, the pigment is also not particularly limited, and may be suitably selected for use from a known pigment. Among these, more preferred is a black pigment, which has good shieldability against electromagnetic waves and infrared rays and can improve the discrimination by the laser marking method. As the black pigment, carbon black, iron oxide, manganese dioxide, aniline black, activated carbon, or the like is used, but it is not limited to these. From the point of view of increasing the reliability of the protective film, carbon black is particularly preferred. The coloring agent (E) may be used singly or in combination of two or more.

The content of the coloring agent (E) is preferably 0.01 to 10% by mass as the proportion thereof relative to the total mass (in terms of the solid content) of the protective film-forming film, more preferably 0.1 to 5% by mass.

[0038]

<Coupling Agent (F)>

The protective film-forming film may further contain a coupling agent. The coupling agent is one having a functional group to react with an inorganic substance and a functional group to react with an organic functional group, and can improve the adhesion and the close-contact properties of the protective film-forming film to an adherend. Further, it can improve the cohesiveness of the protective film. The coupling agent includes a titanate coupling agent, an aluminate coupling agent, a silane coupling agent, etc. Among these, a silane coupling agent is preferred.

As the silane coupling agent, a compound having a group capable of reacting with a functional group that at least one of the above-mentioned binder resin, and the heat-curable resin to constitute the heat-curable component has, is preferably used. Specific examples of the silane coupling agent include γ -glycidoxypentyltrimethoxysilane, γ -glycidoxypentylmethyldiethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -(methacryloxypropyl)trimethoxysilane, γ -aminopropyltrimethoxysilane, N-6-(aminoethyl)- γ -aminopropyltrimethoxysilane, N-6-(aminoethyl)- γ -aminopropylmethyldiethoxysilane, N-phenyl- γ -aminopropyltrimethoxysilane, γ -ureidopropyltriethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, bis(3-triethoxysilylpropyl)tetrasulfane, methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane, vinyltriacetoxysilane, and imidazole silane. These may be used singly or in combination of two or more.

The content of the coupling agent is preferably 0.1 to 10% by mass as the proportion thereof relative to the total mass (in terms of the solid content) of the protective film-forming film, more preferably 0.1 to 3.0% by mass.

[0039]

<Other Additives>

Examples of other additives which may be contained in the protective film-forming film include, but are not particularly limited to, a cross-linking agent, a compatibilizer, a leveling agent, a plasticizer, an antistatic agent, an antioxidant,

an ion scavenger, a gettering agent, a chain transfer agent, an energy-ray polymerizable compound, and a photopolymerization initiator.

The thickness of the protective film-forming film is not specifically limited but is preferably 3 to 300 μm , more preferably 5 to 250 μm , even more preferably 7 to 200 μm .

[0040]

[Protective Film-Forming Composite Sheet]

The protective film-forming composite sheet of the present invention comprises a support sheet, and a protective film-forming film that is provided on the support sheet. The protective film-forming film is releasable from the support sheet.

In the protective film-forming composite sheet, the protective film-forming film may have the same shape as that of the support sheet. Further, the protective film-forming composite sheet may have the structure (hereinafter also referred to as a "pre-shaping structure") in which the protective film-forming film is prepared into a shape that is generally the same shape as that of a wafer or that can include the whole shape of the wafer, and the support sheet has a larger size than the protective film-forming film.

[0041]

The support sheet is a sheet for supporting a protective film-forming film, and comprises a substrate. Examples of the substrate include a polyethylene film, a polypropylene film, a polybutene film, a polybutadiene film, a polymethylpentene film, a polyvinylchloride film, a vinyl chloride copolymer film, a polyethylene terephthalate film, a polyethylene naphthalate film, a polybutylene terephthalate film, a polyurethane film, an ethylene-vinyl acetate copolymer film, an ionomer resin film, an ethylene-(meth)acrylic acid copolymer film, an ethylene-(meth)acrylate copolymer film, a polystyrene film, a polycarbonate film, a polyimide film, and a fluororesin film, and a cross-linking film of these. Furthermore, a laminated film formed of two or more layers of these films as laminated, and a film prepared by coloring these films can also be used. Furthermore, the support sheet may be composed of a substrate only or may have any of various layers besides the substrate.

For example, the support sheet may be a release film that comprises a release agent layer, which is prepared by a release treatment, on the surface of the substrate on the side on which the protective film-forming film is provided.

Examples of the release agent used for the release treatment include an alkyd-based, a silicone-based, a fluorine-based, an unsaturated polyester-based, a polyolefin-based, and a wax-based release agent, and an alkyd-based, a silicone-based, and a fluorine-based release agent are preferred because these release agents have heat resistance.

Further, in the protective film-forming composite sheet, a release film may be attached to the surface of a protective film-forming film opposite to the side on which a support sheet is provided, thus protecting or supporting the protective film-forming film by the release film.

[0042]

Further a pressure sensitive adhesive sheet comprising a substrate and a pressure sensitive adhesive layer that is provided on the substrate may be used as a support sheet. In this case, a protective film-forming film is provided on the pressure sensitive adhesive layer. With such a structure, when a wafer is singulated into chips together with a protective film-forming film or a protective film on a support sheet, the wafer and the chips can be suitably fixed by the support sheet.

Further, it is preferred to have a removable pressure sensitive adhesive layer as the pressure sensitive adhesive layer because it is easy to separate a protective film-forming film or a protective film from the support sheet. A removable pressure sensitive adhesive layer having a weak tackiness, which has an adhesive strength to such a degree as the protective film-forming film can be released, may be used; or a removable pressure sensitive adhesive layer having energy-ray curable properties, in which the adhesive strength is reduced by energy-ray irradiation, may be used. Specifically, the removable pressure sensitive adhesive layer can be formed of various known pressure sensitive adhesives; for example, general-purpose pressure sensitive adhesives such as a rubber-based, an acrylic, a silicone-based, a urethane-based, and a vinyl ether-based pressure sensitive adhesive, pressure sensitive adhesives having surface unevenness, energy ray-curable pressure sensitive adhesives, thermal expansion component-containing pressure sensitive adhesives, and the like.

[0043]

When a protective film-forming composite sheet has the pre-shaping structure in the case where the energy ray-curable removable pressure sensitive adhesive layer is used, a region where a protective film-forming film is laminated

may be previously irradiated with energy rays to reduce tackiness, while other regions may not be irradiated with energy rays to maintain adhesive strength at a high level, for example, for the purpose of adhering to a jig such as a ring flame. In order to prevent only the other regions from being irradiated with energy rays, for example, an energy ray-shielding layer may be provided in a region of a support sheet corresponding to the other regions by printing or the like, and the energy ray irradiation may be performed from the support sheet side. Further, in order to obtain the same effect, it may have a structure in which a removable pressure sensitive adhesive layer having generally the same shape as a protective film-forming film is further laminated on a region of the pressure sensitive adhesive layer of the pressure sensitive adhesive sheet where the protective film-forming film is laminated.

[0044]

When the protective film-forming film does not have a pre-shaping structure, an adhesive layer or a double-coated pressure sensitive adhesive tape may be additionally provided on the peripheral part of the surface (e.g. surface in contact with an adherend) of the protective film-forming film, in order to fix other jigs such as a ring frame. When the protective film-forming film has a pre-shaping structure, an adhesive layer or a double-coated pressure sensitive adhesive tape may be additionally provided on a region in the peripheral part of the support sheet where the protective film-forming film is not laminated, in order to fix other jigs such as a ring frame.

[0045]

The protective film-forming film may be produced by applying a protective film-forming composition prepared by mixing the above-mentioned components in a suitable ratio in a suitable solvent or in the absence of a solvent, onto a support sheet, and then drying it. Alternatively, the protective film-forming film may be produced by applying the protective film-forming composition to a process film other than a support sheet, drying the composition to form a film, and then suitably transferring the film to the support sheet or the like. The process film may be left for use as a release film described above without being removed thereafter.

[0046]

[Method of Using Protective Film-Forming Film]

The protective film-forming film is attached to an adherend such as a

semiconductor wafer or a semiconductor chip, and is then heat-cured and used as a protective film. Here, when the protective film-forming film is attached to an adherend as a protective film-forming composite sheet, a release film may be first peeled off if necessary, and then, a laminate of the protective film-forming film and a support sheet is attached to an adherend in such a manner that the protective film-forming film is in contact with the adherend, and then the support sheet may be peeled off from the protective film-forming film if necessary.

The protective film-forming film may be cured by heating, for example, at 100 to 180°C for 30 to 180 minutes, though not specifically limited thereto.

[0047]

Hereinafter, a method for using the protective film-forming film will be described with an example in which the protective film-forming film is used for protecting the back face of a semiconductor chip and a protective film-attached chip is thus manufactured, but is not limited to the example to be described below.

In the present method, the above protective film-forming film is first laminated to the back face of a semiconductor wafer. For example, when a protective film-forming composite sheet is used, the laminate of the protective film-forming film and the support sheet is attached to the back face of a semiconductor wafer. Subsequently, the protective film-forming film laminated on the semiconductor wafer is heat-cured to form a protective film on the entire surface of the wafer.

The support sheet may be peeled off from the protective film-forming film before heat-curing, but the peeling may be carried out after heat-curing of the protective film or it may be carried out after dicing. In the case where the support sheet is peeled off after dicing, the support sheet can play a role as a dicing sheet. In the case where the support sheet plays a role as a dicing sheet, the sheet is preferably the above-mentioned pressure sensitive adhesive sheet.

[0048]

The semiconductor wafer may be a silicon wafer or may be a compound semiconductor wafer such as gallium arsenide. Further, the semiconductor wafer has a circuit formed on the front face, the back face thereof is grinded or the like as appropriate and a thickness thereof is about 50 to 500 μm .

[0049]

Next, the laminate of the semiconductor wafer and the protective film is diced for each circuit formed on the wafer face. The dicing is performed so as to

cut both the wafer and the protective film, and the laminate of the semiconductor wafer and the protective film is singulated into a plurality of chips by dicing to be semiconductor chips each having a protective film on the back face thereof (protective film-attached chips).

Wafer dicing is carried out according to an ordinary method utilizing a dicing sheet. Here, the support sheet used in forming the protective film may be used as the dicing sheet, as it is not peeled off. In the case where the support sheet has already been peeled off, a known dicing sheet may be stuck onto the surface on the protective film side of the laminate of the semiconductor wafer and the protective film, before dicing.

[0050]

After the dicing, the back face of each singulated protective film-attached chips is pushed up by a needle from the dicing sheet side, and then picked up according to an ordinary means such as a collet, thereby collecting the protective film-attached chips. In the present invention, as described above, the Shore D hardness and the Young's modulus after curing of the protective film-forming film are a predetermined value or more, and therefore in picking up, a picking-up indentation can be prevented from forming in the protective film.

In the above description, an example of heat-curing the protective film-forming film before dicing has been shown, but the protective film-forming film may be heat-cured after dicing the semiconductor wafer but before picking up. In mounting or after mounting the protective film-attached chip according to a face-down process, the film may be heat-cured.

[0051]

[Protective Film-Attached Chip]

The protective film-attached chip of the present invention is obtained, for example, by the above manufacturing method and it has a semiconductor chip and a protective film provided on the semiconductor chip, and the protective film is formed by curing the protective film-forming film as described above. The protective film is generally laminated on the back face of a chip and protects the back face of the chip. A semiconductor device can be manufactured by mounting the protective film-attached chip of the present invention on a substrate board or the like by a facedown method. Further, a semiconductor device can also be manufactured by bonding the protective film-attached chip to another member (onto a chip mounting part) such as a die pad part or another semiconductor chip.

Examples

[0052]

Hereinafter, the present invention will be described further in detail with reference to Examples, but the present invention is not limited to these Examples.

[0053]

The measuring method and the evaluation method in the present invention are as follows.

[Shore D Hardness]

A protective film-forming film were piled to have a thickness of 6 mm or more, and then cured by heating at 130°C for 2 hours. The Shore D hardness of the surface of the cured protective film-forming film was measured at a measurement temperature of 23°C using a constant-pressure loading machine (CL-150, manufactured by Kobunshi Keiki Co., Ltd.).

[Young's Modulus]

A protective film-forming film was cured by heating at 130°C for 2 hours. The Young's modulus of the cured protective film-forming film was measure in an environment at 23°C, at a test speed of 200 mm/min, according to JIS K7127.

[0054]

[Glass Transition Temperature of Epoxy Compound after Curing]

2 g of a curing agent, 2-phenyl-4,5-dihydroxymethylimidazole (Curezol 2PHZ, manufactured by Shikoku Chemicals Corporation) was added to 100 g of an epoxy compound, and the epoxy compound was cured at a curing temperature of 160°C for a curing time of 120 minutes. Next, the cured product of the epoxy compound was cut into strip specimens each having a width of 4.5 mm, a length of 20.0 mm and a thickness of 0.18 mm. Subsequently, using a viscoelastometer (DMAQ800 manufactured by TA Instruments Corporation), $\tan \delta$ (ratio of loss elastic modulus to storage elastic modulus) of the test specimen was measured in a tensile mode, at a frequency of 11 Hz, at a heating rate of 3°C/min in an air atmosphere at 0 to 350°C. Within the temperature range, the temperature showing a maximum value of $\tan \delta$ was read to be the glass transition temperature (T_g) of the cured product of the epoxy compound.

[Softening Point of Epoxy Compound]

According to JISK 2207:2006, a ball having a predetermined weight was put in the center of the support ring in a water or glycerin bath, and the bath

temperature was elevated at a prescribed rate, and then the temperature at which the specimen hanged down by the weight of the ball was read to be the softening point of the specimen (ring-and-ball method).

[Melt Viscosity of Epoxy Compound]

The melt viscosity of an epoxy compound was measured using a capillary rheometer (CFT-100D, manufactured by Shimadzu Corporation), at a measurement temperature of 150°C and at a measurement frequency of 1 Hz.

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

The weight-average molecular weight (Mw) and the number-average molecular weight (Mn) were measured as standard polystyrene-equivalent values, according to a gel permeation chromatography (GPC) method under the following measurement condition.

Measuring apparatus: To a high speed GPC apparatus "HLC-8120GPC" manufactured by Tosoh Corporation, high speed columns "TSK guard column H_{XL}-H", "TSK Gel GMH_{XL}", and "TSK Gel G2000 H_{XL}" (these are all manufactured by Tosoh Corporation) were connected in this order for measurement.

Column temperature: 40°C, Liquid flow rate: 1.0 mL/min, Detector: differential refractometer

[0055]

[Inspection for Needle Indentation in Picking-up]

First, the release film was peeled off from the protective film-forming composite sheet obtained in Examples and Comparative Examples. Using a tape mouter (Adwill RAD-3600F/12, manufactured by Lintec Corporation), the protective film-forming composite sheet was stuck onto a silicon wafer while the exposed protective film-forming film thereof faced to the polished surface of the #2000-polished silicon wafer (200 mm diameter, thickness 280 μm). At this time, the table on which the silicon wafer was put was heated to be at 70°C.

Next, the support sheet was further peeled off from the protective film-forming composite sheet, and then heated at 130°C for 2 hours to cure the protective film-forming film to form a protective film on the silicon wafer. Subsequently, a pressure sensitive adhesive sheet (Adwill D-676H, manufactured by Lintec Corporation) to be a dicing sheet was stuck onto the side of the protective film, and using a dicing machine (DFD651, manufactured by DISCO Inc.), this was diced into a size of 5 mm × 5 mm to thereby singulate the silicon

wafer along with the protective film.

Next, the dicing sheet was irradiated with UV under UV irradiation condition at a lighting intensity of 230 mW/cm² and at an integral light quantity of 170 mJ/cm² to thereby cure the pressure sensitive adhesive layer of the pressure sensitive adhesive sheet, and then tested in a pickup test to check for presence or absence of needle indentations. In the pickup test, a push-pull gauge (MODEL-RE, manufactured by Aikoh Engineering Co., Ltd.) with No. 5 needle set therein was used, and a portion of the dicing sheet in contact with the semiconductor chip to be the pickup object was pushed up by 1.5 mm with the needle from the side of the dicing sheet. Among the tested samples, those with no needle indentation in the protective film were evaluated as A, and those with needle indentations therein were as B.

[0056]

[Protective Film-Forming Composition]

The components to constitute the protective film-forming film in Examples and Comparative Examples are shown below.

(Acrylic Copolymer)

Acrylic polymer 1: Acrylic polymer prepared by copolymerization of 8 parts by mass of butyl acrylate, 70 parts by mass of methyl acrylate, 17 parts by mass of 2-hydroxyethyl acrylate, and 5 parts by mass of glycidyl methacrylate (polymerization-average molecular weight: 300,000, glass transition temperature: 0°C)

Acrylic polymer 2: Acrylic polymer prepared by copolymerization of 15 parts by mass of butyl acrylate, 65 parts by mass of methyl acrylate, 10 parts by mass of 2-hydroxyethyl acrylate and 10 parts by mass of glycidyl acrylate (polymerization-average molecular weight: 400,000, glass transition temperature: -1°C)

Acrylic polymer 3: Acrylic polymer prepared by copolymerization of 55 parts by mass of butyl acrylate, 10 parts by mass of methyl acrylate, 15 parts by mass of 2-hydroxyethyl acrylate and 20 parts by mass of glycidyl acrylate (polymerization-average molecular weight: 800,000, glass transition temperature: -28°C)

(Epoxy Compound)

Epoxy compound 1: 1,1-Bis(2,7-diglycidyoxy-1-naphthyl)methane (glass transition temperature of cured product: 326°C, softening point: 92°C, melt

viscosity: 4.5 dPa·s, number-average molecular weight: 550, epoxy equivalent: 160 g/eq)

Epoxy compound 2: Bisphenol A-type epoxy resin (jER828, manufactured by Mitsubishi Chemical Corporation, glass transition temperature of cured product: 180°C, number-average molecular weight: 370, epoxy equivalent: 184 to 194 g/eq)

Epoxy compound 3: Dicyclopentadiene-type epoxy resin (Epiclon HP-7200HH, manufactured by DIC Corporation, glass transition temperature of cured product: 210°C, softening point: 88°C, melt viscosity: 8 dPa·s, number-average molecular weight: 760, epoxy equivalent: 275 to 280 g/eq)

Heat-Curing Agent: Dicyandiamide (Adeka Hardener 3636AS, manufactured by Adeka Corporation)

Curing Accelerator: 2-Phenyl-4,5-dihydroxymethylimidazole (Curezol 2PHZ, manufactured by Shikoku Chemicals Corporation)

Inorganic Filler: Silica filler (fused quartz filler, mean particle size 8 μm)

Coloring Agent: Carbon black (MA600B, manufactured by Mitsubishi Chemical Corporation)

(Coupling Agent)

Coupling Agent 1: Silane coupling agent (X-41-1056, manufactured by Shin-Etsu Chemical Co., Ltd.)

Coupling Agent 2: Silane coupling agent (KBE-403, manufactured by Shin-Etsu Chemical Co., Ltd.)

Coupling Agent 3: Silane coupling agent (KBM-403, manufactured by Shin-Etsu Chemical Co., Ltd.)

[0057]

Examples 1 to 4, Comparative Examples 1 to 4

In Examples and Comparative Examples, a diluted liquid (solid concentration 61% by mass) prepared by diluting a protective film-forming composition composed of the ingredients shown in Table 1, with methyl ethyl ketone was applied to the release-treated surface of a release film (SP-PET381031, manufactured by Lintec Corporation, thickness: 38 μm), using a knife coater, to form a coating film thereon so that a thickness thereof was made to be 25 μm after drying, and then dried at 120°C for 3 minutes to thereby form a protective film-forming film on the release film.

Next, a support sheet (SP-PET381130, manufactured by Lintec Corporation, thickness: 38 μm) was laminated on the protective film-forming film

to produce a three-layered protective film-forming composite sheet composed of the release film, the protective film-forming film and the support sheet.

[0058]
Table 1

	Example 1		Example 2		Example 3		Example 4		Comparative Example 1		Comparative Example 2		Comparative Example 3		Comparative Example 4	
	part by mass	% by mass	part by mass	% by mass	part by mass	% by mass	part by mass	% by mass	part by mass	% by mass	part by mass	% by mass	part by mass	% by mass	part by mass	% by mass
Acrylic Polymer 1	50	25.5%	50	25.5%	0	0.0%	0	0.0%	50	28.1%	0	0.0%	50	26.7%	0	0.0%
Acrylic Polymer 2	0	0.0%	0	0.0%	50	25.5%	50	25.5%	0	0.0%	50	28.1%	0	0.0%	0	0.0%
Acrylic Polymer 3	0	0.0%	0	0.0%	0	0.0%	0	0.0%	0	0.0%	0	0.0%	0	0.0%	50	26.1%
Epoxy Compound 1	5	2.6%	5	2.6%	5	2.6%	5	2.6%	2	1.1%	2	1.1%	0	0.0%	0	0.0%
Epoxy Compound 2	30	15.3%	25	12.8%	30	15.3%	25	12.8%	15	8.4%	15	8.4%	24	12.8%	27	14.1%
Epoxy Compound 3	5	2.6%	10	5.1%	5	2.6%	10	5.1%	5	2.8%	5	2.8%	8	4.3%	9	4.7%
Heat-Curing Agent	1	0.5%	1	0.5%	1	0.5%	1	0.5%	1	0.6%	1	0.6%	0.8	0.4%	0.8	0.4%
Curing Accelerator	1	0.5%	1	0.5%	1	0.5%	1	0.5%	1	0.6%	1	0.6%	0.8	0.4%	0.8	0.4%
Inorganic Filler	100	51.1%	100	51.1%	100	51.1%	100	51.1%	100	56.3%	100	56.3%	100	53.4%	100	52.3%
Coloring Agent	3	1.5%	3	1.5%	3	1.5%	3	1.5%	3	1.7%	3	1.7%	3	1.6%	3	1.6%
Coupling Agent 1	0.3	0.2%	0.3	0.2%	0.3	0.2%	0.3	0.2%	0.3	0.2%	0.3	0.2%	0.3	0.2%	0.3	0.2%
Coupling Agent 2	0.2	0.1%	0.2	0.1%	0.2	0.1%	0.2	0.1%	0.2	0.1%	0.2	0.1%	0.2	0.1%	0.2	0.1%
Coupling Agent 3	0.2	0.1%	0.2	0.1%	0.2	0.1%	0.2	0.1%	0.2	0.1%	0.2	0.1%	0.2	0.1%	0.2	0.1%
Total	195.7	100%	195.7	100%	195.7	100%	195.7	100%	177.7	100%	177.7	100%	187.3	100%	191.3	100%
Shore D Hardness	68.2		68.8		64.8		65.2		41.5		39.5		45.8		48.2	
Young's Modulus (Pa)	7.0×10^8		7.2×10^8		5.6×10^8		6.0×10^8		5.0×10^8		3.5×10^8		1.2×10^8		8.5×10^8	
Evaluation of Needle Indentations	A		A		A		A		B		B		B		B	

[0059]

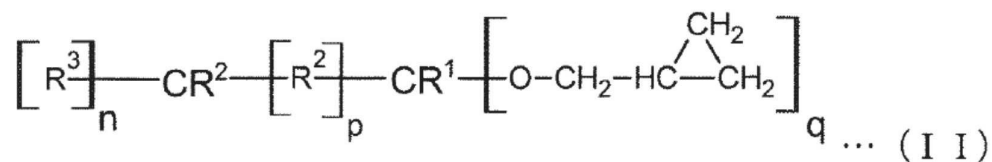
In the above Examples 1 to 4, both the Shore D hardness and the Young's modulus were high values, and therefore in the pickup test, no needle indentations were seen, and protective film-having chips having good quality were produced. As opposed to these, in Comparative Examples 1 to 4, at least one of the Shore D hardness and the Young's modulus was a low value, and therefore in the pickup test, needle indentations were seen, and protective film-having chips having good quality could not be produced.

CLAIMS

[Claim 1]

A protective film-forming film for forming a protective film that protects a semiconductor chip, wherein the Shore D hardness of the film surface after curing is 55 or more and the Young's modulus (23°C) after curing is 1.0×10^9 Pa or more, comprising :

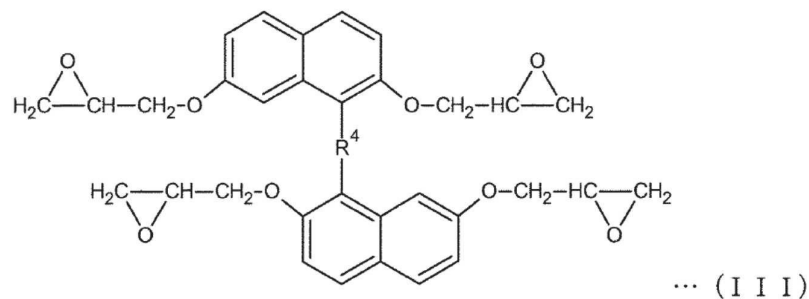
an acrylic polymer (A) and an epoxy curable component (B) containing an epoxy group-having condensed cyclic aromatic compound (b1), and the epoxy group-having condensed cyclic aromatic compound (b1) is a compound represented by the following general formula (II):

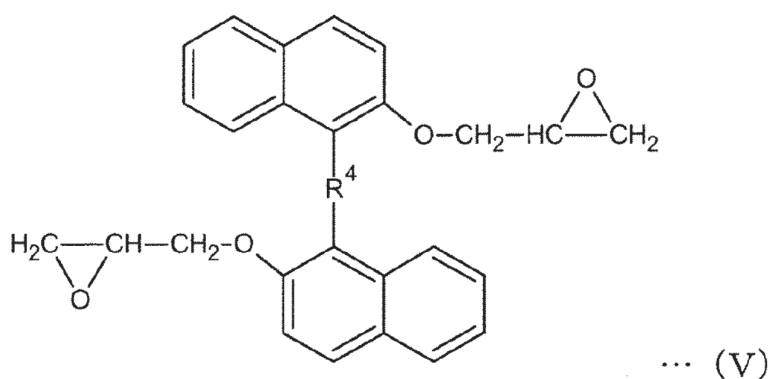
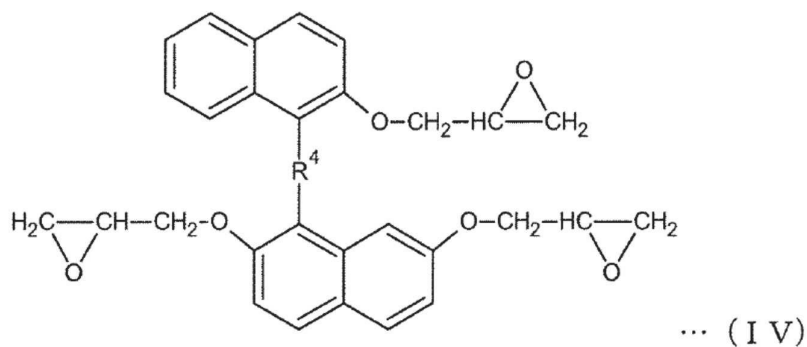


wherein CR^1 and CR^2 each represent a condensed polycyclic aromatic hydrocarbon group; R^2 represents a divalent hydrocarbon group; R^3 represents an alkyl group having 1 to 10 carbon atoms, or a glycidyl ether group; n represents an integer of 0 to 3; p represents an integer of 0 to 10, provided that when p is 0 R^2 is a single bond; and q represents an integer of 1 to 3.

[Claim 2]

The protective film-forming film according to any one of claim 1, wherein the compound represented by the general formula (II) is a compound represented by the following general formula (III), (IV) or (V).





wherein R^4 represents a single bond or a divalent hydrocarbon group, and the hydrocarbon group may have a substituent. In the case where two or more kinds of the compounds represented by the general formulae (III) to (V) are used as combined, R^4 in each compound may be the same as or different from each other.

[Claim 3]

The protective film-forming film according to any one of claims 1 or 2, wherein the epoxy curable component (B) is composed of an epoxy compound and a thermosetting agent, and said epoxy compound is contained in an amount of 45 to 150 parts by mass with respect to 100 parts by mass of the acrylic polymer (A).

[Claim 4]

The protective film-forming film according to any one of claims 1 to 3, wherein the epoxy curable component (B) contains a fused cyclic aromatic compound (b1) having an epoxy group and another epoxy compound (b2) in a mass ratio (b1:b2) of 1:3 to 1:15.

[Claim 5]

The protective film-forming film according to any one of claims 1 to 4, wherein the monomer to constitute the acrylic polymer (A) contains an alkyl (meth) acrylate in which the alkyl group has 1 to 8 carbon atoms.

[Claim 6]

The protective film-forming film according to any one of claims 1 to 5, wherein the monomer to constitute the acrylic polymer (A) contains methyl (meth) acrylate.

[Claim 7]

The protective film-forming film according to any one of claims 1 to 6, wherein the monomer to constitute the acrylic polymer (A) contains methyl acrylate.

[Claim 8]

The protective film-forming film according to any one of claims 1 to 7, comprising a filler (C).

[Claim 9]

A protective film-forming composite sheet comprising: a support sheet; and a protective film-forming film according to any one of claims 1 to 8 that is provided on the support sheet.

[Claim 10]

A protective film-attached chip comprising: a semiconductor chip; and a protective film that is provided on the semiconductor chip and that is formed by curing the protective film-forming film according to any one of claims 1 to 8.