

## DESCRIPTION

### **PROTECTIVE FILM FOR SEMICONDUCTOR WAFER, AND METHOD FOR MANUFACTURING SEMICONDUCTOR CHIP**

#### TECHNICAL FIELD

[0001]

The present invention relates to a protective film for a semiconductor wafer and a method for manufacturing a semiconductor chip.

#### BACKGROUND ART

[0002]

A flip chip interconnection method has been used for making a mounting area of a semiconductor chip small or reducing a height. In the connecting method, a wafer which has a circuit and a connecting bump on its surface is subjected to dicing to obtain a semiconductor chip, the surface of the chip is faced to the substrate and connected, and then, resin sealing, etc., are carried out to protect the semiconductor chip.

[0003]

In the above-mentioned dicing process, it has been known a sheet for forming a protect film for a chip which is to prevent the chip from damaging by vibration, etc., of the rotary blade (hereinafter referred to as "chipping"), and also acts as a sealing film in place of resin sealing (PATENT LITERATURE 1, PATENT LITERATURE 2).

[0004]

Also, for the purpose of preventing twisting of an IC card, it has been known a card using a reinforcing material having a low linear expansion coefficient (PATENT LITERATURE 3), and a card using a reinforcing material for

preventing cracking of the semiconductor chip in the IC card (PATENT LITERATURE 4).

[0005]

The above-mentioned protect film for a chip has been used by bonding to the back surface of the wafer. Accordingly, in the dicing process, that finally cut by the rotary blade is the protect film. However, the resin components contained in the protect film have a stretching property so that there are problems that it is difficultly cut, and causes clogging of the rotary blade to vibrate the rotary blade, whereby the wafer is damaged.

[0006]

When a reinforcing material having a low linear expansion coefficient is used for preventing twisting of the IC card, and when a twisting or bending stress is applied to the IC card, if the reinforcing material is not distributed to the whole portion, it is possible to relax the stress at the portion at which a semiconductor chip is not present and has a low modulus of elasticity. However, when the reinforcing material is distributed to the whole portion, the thin semiconductor chip is received the twisting or bending stress to cause crack.

[0007]

In the method of attaching a reinforcing material to the semiconductor chip in the IC card, there may occur fluctuation of quality and remarkable lowering in productivity because of a plural number of curing processes, protrusion of an adhesive, fluctuation of reinforcing strength caused by positional deviation or inclination of the reinforcing layer and unevenness of the thickness of the adhesive agent.

CITATION LIST

## PATENT LITERATURES

[0008]

[Patent LITERATURE 1] JP 2002-280329A

[Patent LITERATURE 2] JP 2004-260190A

[Patent LITERATURE 3] JP H10-24686A

[Patent LITERATURE 4] JP 2000-268152A

## Summary of the invention

[0009]

The present invention has been accomplished in view of the above-mentioned circumstances, and an object thereof is to provide a protective film for a semiconductor wafer excellent in cutting characteristics by a dicer and a method for manufacturing a semiconductor chip having high productivity.

## MEANS FOR SOLVING PROBLEM

[0010]

To solve the above-mentioned problems, according to the present invention,

it is provided a protective film for a semiconductor wafer which is a protective film for a semiconductor wafer having a base film, and a protect film formed over the base film, wherein the protect film comprises Components (A) to (E) mentioned below.

(A) 100 parts by mass of at least one selected from the group consisting of a phenoxy resin, a polyimide resin and a (meth)acrylic resin,

(B) 5 to 200 parts by mass of an epoxy resin,

(C) 100 to 400 parts by mass of a filler other than fibrous inorganic fillers,

(D) a catalytic amount of an epoxy resin-curing catalyst, and

(E) 25 to 5,000 parts by mass of a fibrous inorganic filler.

[0011]

Since the protect film of such a protective film for a semiconductor wafer has a fibrous inorganic filler, it can prevent chipping at the time of dicing the semiconductor wafer to obtain a semiconductor chip. Also, the protect film of a protective film for a semiconductor wafer has high bending strength, and can prevent crack of the chip due to bending stress at the time that it is used in the market.

[0012]

In addition, it is preferred that the above-mentioned protect film comprises a reinforcing layer and an adhesive layer,

the adhesive layer contains Components (A) to (D) mentioned below, and the reinforcing layer contains Component (E) mentioned below.

(A) 100 parts by mass of at least one selected from the group consisting of a phenoxy resin, a polyimide resin and a (meth)acrylic resin,

(B) 5 to 200 parts by mass of an epoxy resin,

(C) 100 to 400 parts by mass of a filler other than fibrous inorganic fillers,

(D) a catalytic amount of an epoxy resin-curing catalyst, and

(E) 1000 to 5,000 parts by mass of a fibrous inorganic filler.

[0013]

Thus, when the protect film comprises two layers of a reinforcing layer and an adhesive layer, prevention of chipping and improvement in bending strength of the semiconductor chip are more improved, whereby high

productivity can be realized.

[0014]

Also, it is preferred that the phenoxy resin in the above-mentioned Component (A) is a bisphenol A type phenoxy resin or a bisphenol F type phenoxy resin, and the epoxy resin in the above-mentioned Component (B) is a liquid bisphenol A type epoxy resin or a liquid bisphenol F type epoxy resin.

[0015]

When such a combination of Component (A) and Component (B) is employed, the protective film for a semiconductor wafer becomes more excellent in cutting characteristics by a dicer.

[0016]

In addition, according to the present invention, it is provided a method for manufacturing a semiconductor chip by dicing a semiconductor wafer, which comprises attaching the above-mentioned protective film for a semiconductor wafer to the semiconductor wafer, and dicing the same collectively, to manufacture a semiconductor chip having a protect film with the same size as that of the above-mentioned semiconductor chip at the back surface thereof.

[0017]

Such a method for manufacturing a semiconductor chip is employed, chipping at the time of dicing can be suppressed, and further, bending strength of the protect film provided at the back surface of the semiconductor chip becomes high, whereby high productivity of the semiconductor chip can be realized.

#### EFFECT OF INVENTION

[0018]

The semiconductor wafer protective film of the present invention can be easily cut by a dicer, since the protect film contains a fibrous inorganic filler, and prevention of chipping and bending strength of the semiconductor chip are improved, whereby high productivity can be realized.

#### BRIEF DESCRIPTION OF DRAWINGS

[0019]

Fig. 1 is a sectional view showing an example of the protective film for a semiconductor wafer of the present invention;

Fig. 2 is a sectional view showing another example of the protective film for a semiconductor wafer of the present invention; and

Fig. 3 is a sectional view showing a further different example of the protective film for a semiconductor wafer of the present invention.

#### DESCRIPTION OF EMBODIMENTS

[0020]

The present inventors have earnestly carried out investigations to accomplish the above-mentioned object, and as a result, they have found that

when a protective film for a semiconductor wafer having a base film, and a protect film formed over the base film, wherein the protect film comprises Components (A) to (E) mentioned below, is employed, it becomes a protective film for a semiconductor wafer excellent in cutting characteristics.

(A) 100 parts by mass of at least one selected from the group consisting of a phenoxy resin, a polyimide resin and a (meth)acrylic resin,

- (B) 5 to 200 parts by mass of an epoxy resin,
- (C) 100 to 400 parts by mass of a filler other than fibrous inorganic fillers,
- (D) a catalytic amount of an epoxy resin-curing catalyst, and
- (E) 25 to 5,000 parts by mass of a fibrous inorganic filler.

[0021]

(A) At least one selected from the group consisting of a phenoxy resin, a polyimide resin and a (meth)acrylic resin

The phenoxy resin is a resin derived from epichlorohydrin and bisphenol A or bisphenol F, etc. It is preferably a resin having a weight average molecular weight measured by GPC in terms of a polystyrene of 10,000 to 200,000, more preferably 20,000 to 100,000, most preferably 30,000 to 80,000. If the weight average molecular weight is the above-mentioned lower limit value or more, it is easy to form a film, while if it is the above-mentioned upper limit value or less, sufficient softness along the unevenness of the substrate surface having a fine circuit pattern can be obtained, so that the range is preferred.

[0022]

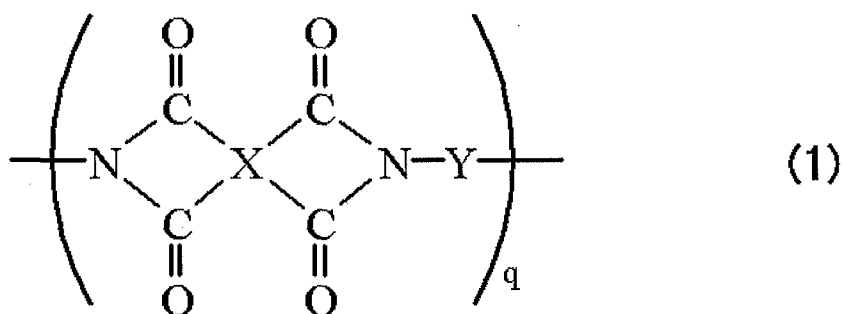
Examples of the phenoxy resin may be mentioned those commercially sold under the trade names of PKHC, PKHH and PKHJ (each available from Tomoe Engineering Co., Ltd.), those which are bisphenol A and bisphenol F mixed type materials and commercially sold under the trade names of Epikote 4250, Epikote 4275 and Epikote 1255HX30 (each available from Nippon Kayaku Co., Ltd.), Epikote 5580BPX40 using a brominated epoxy (each available from Nippon Kayaku Co., Ltd.), bisphenol A type ones commercially sold under the trade names of YP-50, YP-50S, YP-55, YP-70 (each

available from Tohto Kasei Co., Ltd.), commercially sold under the trade names JERE1256, E4250, E4275, YX6954BH30, YL7290BH30 (each available from Japan Epoxy Resin Co., Ltd.), etc. In the point of having the above-mentioned weight average molecular weight, JER E1256 is preferably used. The phenoxy series polymer has an epoxy group(s) at the terminal(s) thereof, and it reacts with Component (B) mentioned later.

[0023]

As the polyimide resin, those containing the following recurring unit may be used,

[Chemical Formula 1]



wherein X represents a tetravalent organic group containing an aromatic ring or an aliphatic ring, Y represents a divalent organic group, and "q" represents an integer of 1 to 300.

[0024]

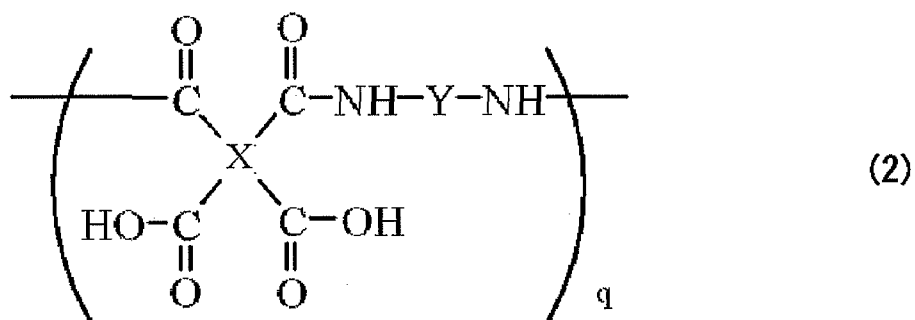
It is preferably having a weight average molecular weight in terms of a polystyrene measured by the GPC of 10,000 to 200,000, more preferably 20,000 to 100,000, most preferably 30,000 to 80,000. If the weight average molecular weight is the above-mentioned lower limit or more, it is easy to form a film, while if it is the above-mentioned upper limit or less, sufficient softness along the unevenness of the substrate surface having a fine circuit pattern can be obtained, so that the range is

preferable.

[0025]

The above-mentioned polyimide resin can be obtained by subjecting the polyamic acid resin having the following recurring unit to dehydration and ring-closure according to the conventional manner,

[Chemical Formula 2]

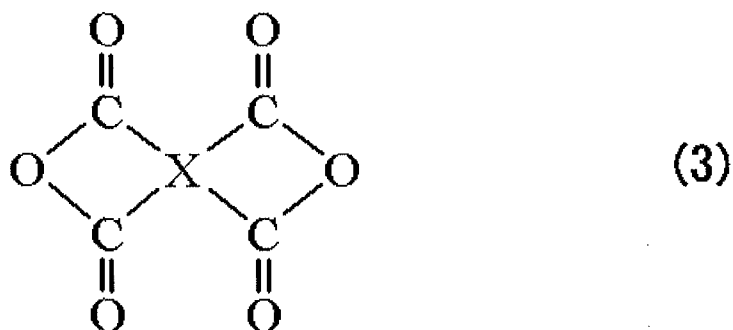


wherein X, Y and "q" have the same meanings as defined above.

[0026]

The polyamic acid resin represented by the above formula can be obtained by reacting a tetracarboxylic acid dianhydride represented by the following structural formula (3),

[Chemical Formula 3]



wherein X has the same meaning as defined above,  
and a diamine represented by the following structural formula (4),



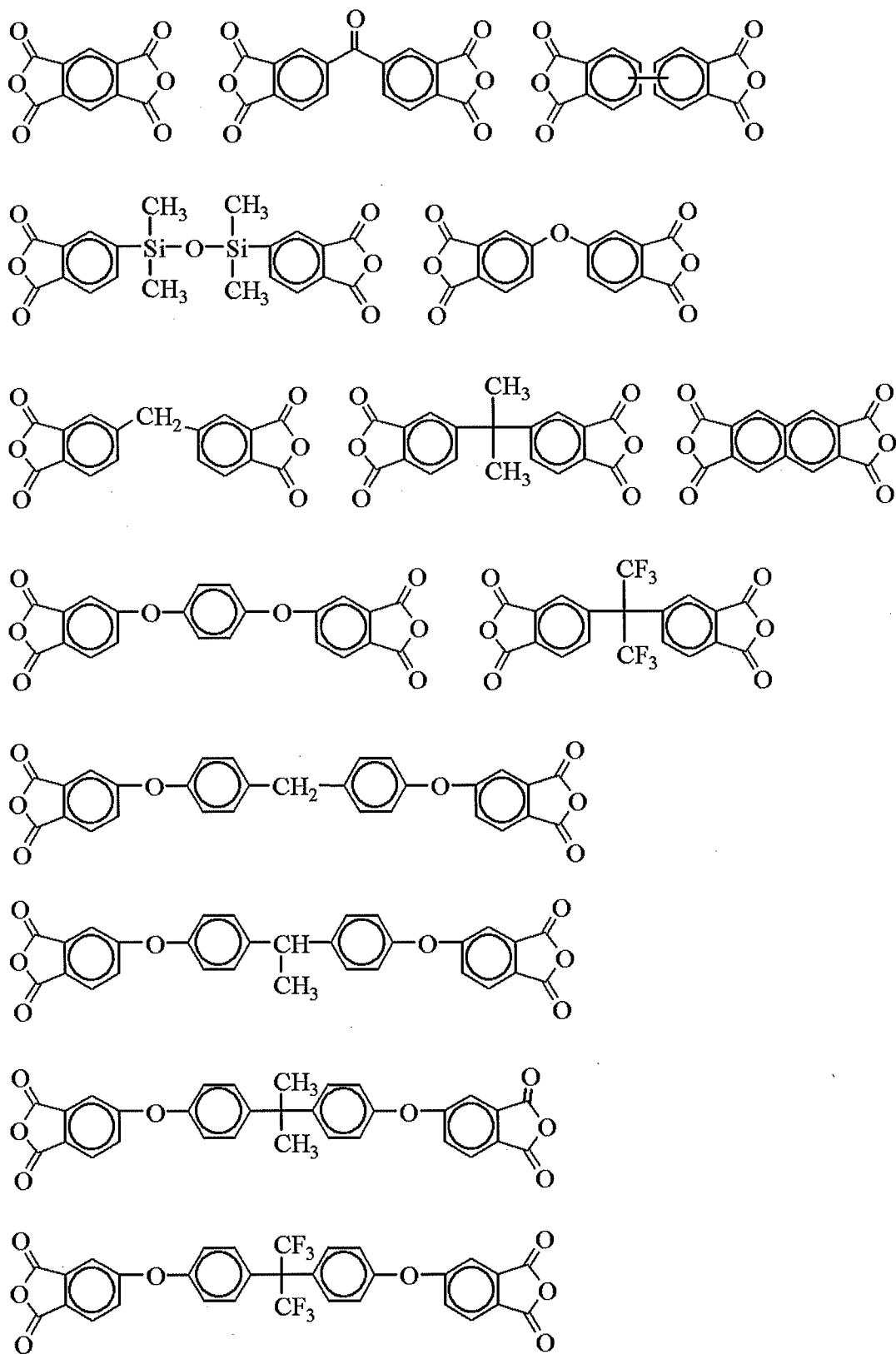
wherein Y has the same meaning as defined above,  
with substantially equimolar amounts in an organic solvent  
according to the conventional manner.

[0027]

Here, examples of the tetracarboxylic acid  
dianhydride represented by the above-mentioned formula (3)  
may be mentioned the following compounds, and these may be  
used in combination.

[0028]

[Chemical Formula 4]



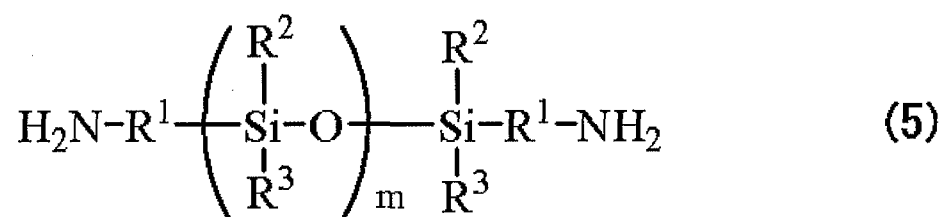
[0029]

Among the diamine represented by the above-mentioned

formula (4), preferably 1 to 80 mole%, more preferably 1 to 60 mole% is desirably a diaminosiloxane compound represented by the below mentioned structural formula (5), in the points of solubility into an organic solvent, adhesiveness to the base film, low elasticity and flexibility.

[0030]

[Chemical Formula 5]



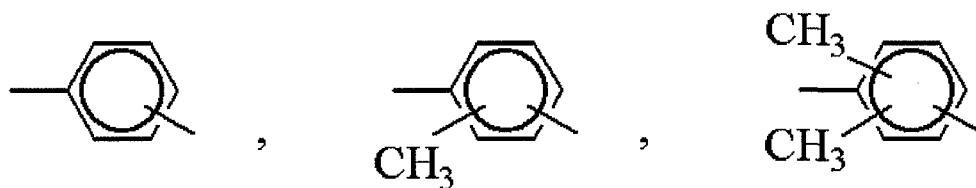
wherein  $\text{R}^1$  each independently represents a divalent organic group having 3 to 9 carbon atoms,  $\text{R}^2$  and  $\text{R}^3$  each independently represents an unsubstituted or substituted monovalent hydrocarbon group having 1 to 8 carbon atoms, and "m" represents an integer of 1 to 200.

[0031]

As the above-mentioned  $\text{R}^1$ , which is the divalent organic group having 3 to 9 carbon atoms, there may be mentioned, for example, an alkylene group such as  $-(\text{CH}_2)_3-$ ,  $-(\text{CH}_2)_4-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ,  $-(\text{CH}_2)_6-$ ,  $-(\text{CH}_2)_8-$ , etc., an arylene group represented by any of the following formulae,

[0032]

[Chemical Formula 6]

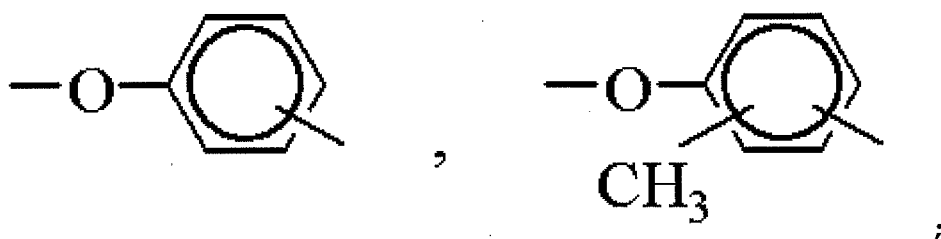


an alkylene-arylene group,

a divalent hydrocarbon group which may contain an ether bond including an oxyalkylene group such as  $-(CH_2)_3-O-$ ,  $-(CH_2)_4-O-$ , etc., an oxyarylene group represented by any of the following formulae,

[0033]

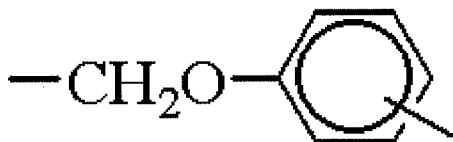
[Chemical Formula 7]



an oxyalkylene-arylene group represented by the following formula,

[0034]

[Chemical Formula 8]



[0035]

$R^2$  or  $R^3$  is preferably mentioned, for example, an alkyl group such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, a tert-butyl group, a hexyl group, a cyclohexyl group, a 2-ethylhexyl group, an octyl group, etc.; an alkenyl group such as an allyl group, a propenyl group, an isopropenyl group, a butenyl group, an isobutenyl group, a hexenyl group, etc.; an aryl group such as a phenyl group, a tolyl group, a xylyl group, etc., an aralkyl group such as a benzyl group, a phenylethyl group, etc.; a part or whole of the hydrogen atom(s)

bonded to a carbon atom(s) of the above hydrocarbon groups is/are substituted by a halogen atom such as fluorine, bromine, chlorine, etc., and other atoms, for example, a halogen-substituted alkyl group such as a chloromethyl group, a bromoethyl group, a 3,3,3-trifluoropropyl group, etc., and among these, a methyl group and a phenyl group are preferred. Two or more kinds of the diaminosiloxane compounds may be used in combination.

[0036]

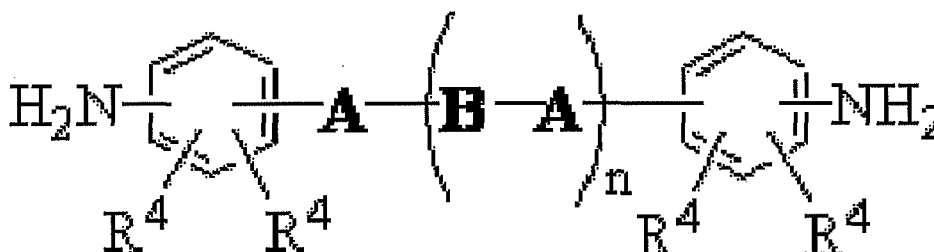
As the diamine represented by the above-mentioned formula (4) which is other than the diaminosiloxane compound represented by the above-mentioned formula (5), there may be mentioned, for example, an aromatic ring-containing diamine such as p-phenylenediamine, m-phenylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, 2,2'-bis(4-aminophenyl)propane, 4,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenylsulfide, 1,4-bis(3-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, 1,4-bis(p-aminophenylsulfonyl)benzene, 1,4-bis(m-aminophenylsulfonyl)benzene, 1,4-bis(p-aminophenyl thioether)benzene, 1,4-bis(m-aminophenyl thioether)benzene, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[3-methyl-4-(4-aminophenoxy)phenyl]propane, 2,2-bis[3-chloro-4-(4-aminophenoxy)phenyl]propane, 1,1-bis[4-(4-aminophenoxy)phenyl]ethane, 1,1-bis[3-methyl-4-(4-aminophenoxy)phenyl]ethane, 1,1-bis[3-chloro-4-(4-aminophenoxy)phenyl]ethane, 1,1-bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]ethane, bis[4-(4-aminophenoxy)phenyl]methane, bis[3-methyl-4-(4-aminophenoxy)phenyl]methane, bis[3-chloro-4-(4-aminophenoxy)phenyl]methane, bis[3,5-dimethyl-4-(4-aminophenoxy)phenyl]methane, bis[4-(4-aminophenoxy)phenyl]sulfone, 2,2-bis[4-(4-

aminophenoxy)phenyl]perfluoropropane, etc., preferably p-phenylenediamine, m-phenylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, 1,4-bis(3-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, 2,2-bis[4-(4-aminophenoxy)phenyl]propane or 2,2-bis[3-methyl-4-(4-aminophenoxy)phenyl]propane, etc.

[0037]

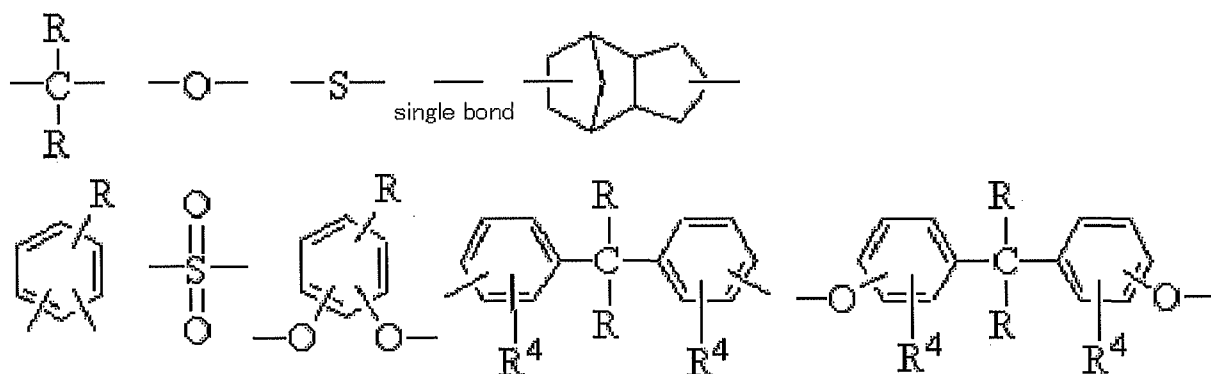
The polyimide resin preferably has a phenolic hydroxyl group in the point of adhesiveness. The phenolic hydroxyl group can be provided by using a material having a phenolic hydroxyl group as the diamine compound, and such a diamine may be mentioned, for example, a material having the following structure,

[Chemical Formula 9]



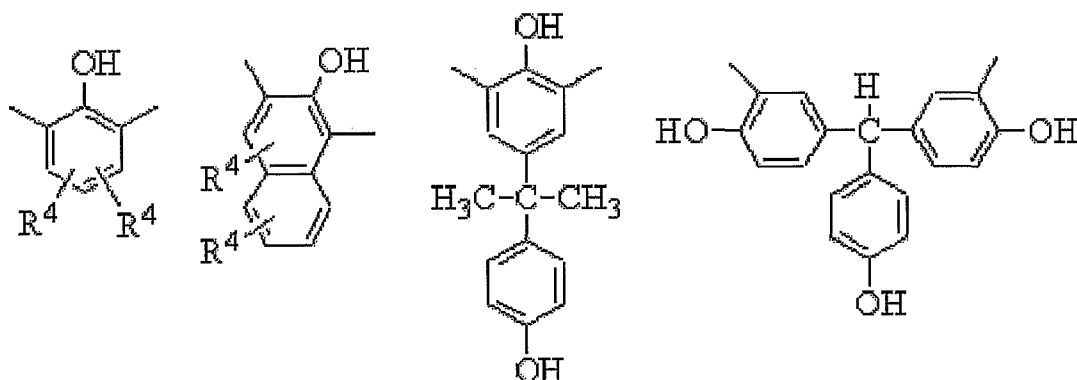
wherein A represents any of the groups mentioned below,

[Chemical Formula 10]



wherein B represents any of the groups mentioned below,

[Chemical Formula 11]



wherein R<sup>4</sup>s each independently represent a hydrogen atom or a halogen atom such as fluorine, bromine, iodine, etc., or an unsubstituted or substituted monovalent hydrocarbon group having 1 to 8 carbon atoms such as an alkyl group, an alkenyl group, an alkynyl group, a trifluoromethyl group, a phenyl group, etc., the substituents attached to each aromatic ring may be different from each other, "n" represents an integer of 0 to 5; A and B may be each one kind alone or may be a combination of two or more kinds; and each R represents a hydrogen atom, a halogen atom or an unsubstituted or substituted monovalent hydrocarbon group.

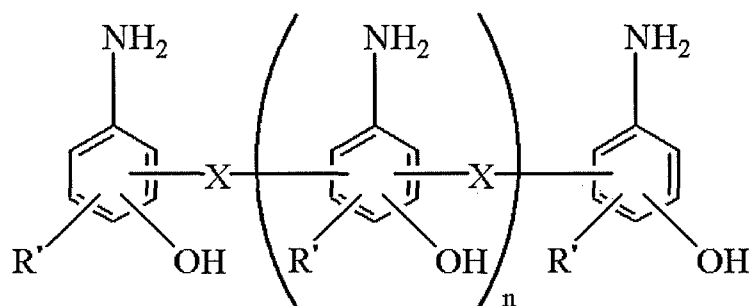
[0038]

The unsubstituted or substituted monovalent hydrocarbon group having 1 to 8 carbon atoms of the above-mentioned R<sup>4</sup> may be mentioned, for example, similar to those specifically exemplified as the above-mentioned R<sup>2</sup> and R<sup>3</sup>, and an alkynyl group such as an ethynyl group, a propynyl group, a butynyl group, a hexynyl group, etc.

[0039]

Also, as the other diamine having a phenolic hydroxyl group, the following may be mentioned,

[Chemical Formula 12]



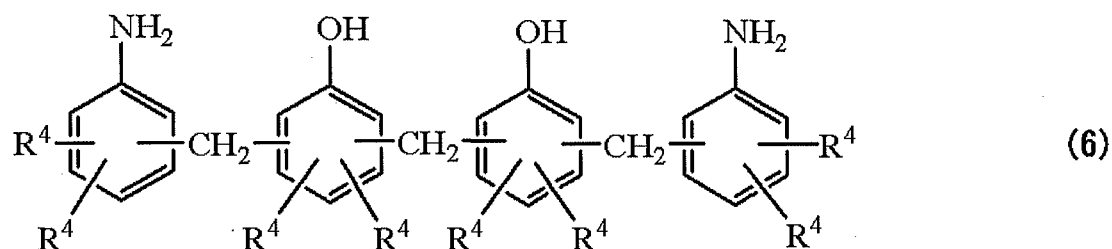
wherein each R' represents a hydrogen atom, a halogen atom such as a fluorine, a bromine, an iodine, etc., or an unsubstituted or a halogen-substituted monovalent hydrocarbon group having 1 to 8 carbon atoms such as an alkyl group, an alkenyl group, an alkynyl group, a trifluoromethyl group, a phenoxy group, etc., the substituents attached to each aromatic ring may be different from each other, each X represents a single bond, a methylene group, or a propylene group; and "n" has the same meaning as defined above.

[0040]

Among the diamine compounds having the phenolic hydroxyl group mentioned above, the diamine compound represented by the following formula (6) is particularly preferred.

[0041]

[Chemical Formula 13]



wherein R<sup>4</sup>s have the same meanings as defined above.

[0042]

A blending amount of the above-mentioned diamine compound having the phenolic hydroxyl group is preferably

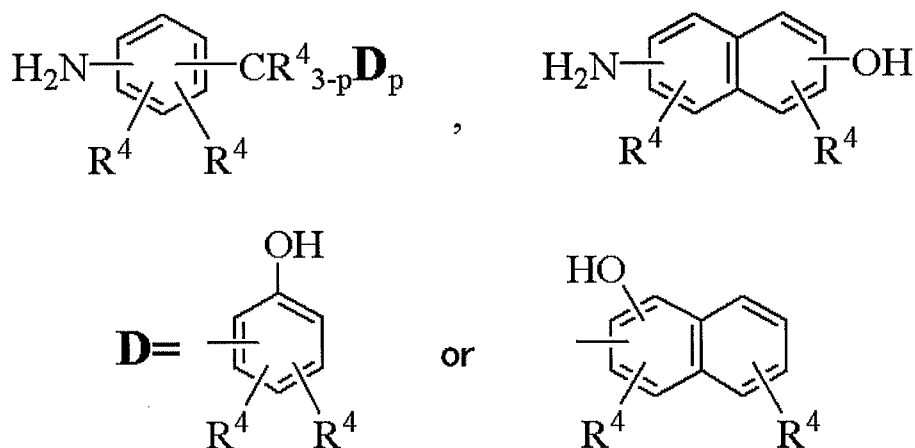
5 to 60 % by mass, particularly 10 to 40 % by mass based on the whole diamine compound. If the polyimide silicone resin is used with the blending amount of the diamine compound within the above range, a composition having high adhesiveness and forming a flexible adhesive layer can be obtained.

[0043]

Incidentally, for introducing the phenolic hydroxyl group, a monoamine having a phenolic hydroxyl group may be used, and an example thereof may be mentioned monoamines having the following structures.

[0044]

[Chemical Formula 14]



wherein  $\text{R}^4$  has the same meaning as mentioned above, and the substituents bonded to the respective aromatic rings may be different from each other, D may be used a single kind alone or may be used in combination of two or more kinds, and "p" represents an integer of 1 to 3.

[0045]

When the monoamine having a phenolic hydroxyl group is used, a blending amount thereof is preferably 1 to 10 mole% based on the whole diamine compound.

[0046]

The polyamic acid resin can be synthesized by

dissolving the above-mentioned respective starting materials in a solvent under an inert atmosphere, and reacting these generally at 80°C or lower, preferably 0 to 40°C. The obtained polyamic acid resin is heated generally at 100 to 200°C, preferably 150 to 200°C, to cause dehydration and ring closure of the acid amide portion of the polyamic acid resin, whereby the objective polyimide resin can be synthesized.

[0047]

The above-mentioned solvent may not be a material which can completely dissolve the above-mentioned starting materials, so long as it is inactive to the polyamic acid to be obtained. There may be mentioned, for example, tetrahydrofuran, 1,4-dioxane, cyclopentanone, cyclohexanone,  $\gamma$ -butyrolactone, N-methylpyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide and dimethylsulfoxide, preferably an aprotic polar solvent, particularly preferably N-methylpyrrolidone, cyclohexanone and  $\gamma$ -butyrolactone. These solvents may be used a single kind alone, or in combination of two or more kinds.

[0048]

To carry out the above-mentioned dehydration and ring closure easier, an azeotropic dehydrating agent such as toluene, xylene, etc., is desirably used. Also, the dehydration and ring closure may be carried out at a low temperature by using an acetic anhydride/pyridine mixed solution.

[0049]

Incidentally, for the purpose of adjusting the molecular weight of the polyamic acid and polyimide resin, a dicarboxylic acid anhydride such as maleic anhydride, phthalic anhydride, etc., and/or monoamines such as aniline, n-butylamine, the monoamine having the phenolic

hydroxyl group mentioned above may be added. However, an amount of the dicarboxylic acid anhydride to be added is generally 0 to 2 parts by mass based on 100 parts by mass of the tetracarboxylic acid dianhydride, and an amount of the monoamine to be added is generally 0 to 2 parts by mass based on 100 parts by mass of the diamine.

[0050]

As the (meth)acrylic resin, there may be mentioned, for example, a (meth)acrylic ester copolymer comprising constitutional units derived from a (meth)acrylic ester monomer(s) and (meth)acrylic acid derivative(s). Here, the (meth)acrylic ester monomer may be used, preferably an alkyl (meth)acrylic ester having a carbon number of the alkyl group of 1 to 18, for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, etc. Also, the (meth)acrylic acid derivative(s) may be mentioned, for example, (meth)acrylic acid, glycidyl (meth)acrylate, hydroxyethyl (meth)acrylate, etc.

[0051]

By introducing a glycidyl group into the (meth)-acrylic resin by copolymerizing glycidyl methacrylate, etc., compatibility to the epoxy resin which is a thermosetting type adhesive component mentioned later is improved, and a glass transition temperature (T<sub>g</sub>) after curing becomes high so that heat resistance is also improved. In addition, by introducing a hydroxyl group(s) into an acrylic type polymer with hydroxyethyl acrylate, etc., adhesiveness or tacky property to the chip can be easily controlled.

[0052]

A weight average molecular weight of the (meth)acrylic resin is preferably 100,000 or more, more

preferably 150,000 to 1,000,000. Also, a glass transition temperature of the (meth)acrylic resin is preferably 20°C or lower, more preferably -70 to 0°C or so, and it has an adhesion at normal temperature (23°C).

[0053]

#### (B) Epoxy resin

The epoxy resin is a resin different from the above-mentioned Component (A), and preferably has an epoxy equivalent of 50 to 5,000 g/eq, more preferably 100 to 500 g/eq.

Such an epoxy resin may be mentioned a bisphenol A type epoxy resin, a bisphenol F type epoxy resin (particularly, a liquid bisphenol A type epoxy resin or a liquid bisphenol F type epoxy resin); a glycidyl ether of a phenol such as resorcinol, phenol novolac, cresol novolac, etc.; a glycidyl ether of an alcohol such as butane diol, polyethylene glycol, polypropylene glycol, etc.; a glycidyl ether of a carboxylic acid such as phthalic acid, isophthalic acid, tetrahydrophthalic acid, etc.; a glycidyl type or an alkyl glycidyl type epoxy resin in which an active hydrogen bonded to a nitrogen atom of aniline isocyanurate, etc., has been substituted by a glycidyl group; the so-called alicyclic type epoxide in which an epoxy has been introduced by, for example, oxidizing an intramolecular carbon-carbon double bond such as vinyl cyclohexane diepoxide, 3,4-epoxycyclohexylmethyl-3,4-dicyclohexane carboxylate and 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane. As the others, an epoxy resin having a biphenyl skeleton, a dicyclohexadiene skeleton, or a naphthalene skeleton may be used.

[0054]

Among these, a bisphenol A type epoxy resin, a bisphenol F type epoxy resin (particularly, a liquid

bisphenol A type epoxy resin or a liquid bisphenol F type epoxy resin), o-cresol novolac type epoxy resin and phenol novolac type epoxy resin are preferably used. Two or more kinds of these epoxy resins may be used in combination.

[0055]

(B) The epoxy resin is blended in an amount of 5 to 200 parts by mass, preferably 10 to 200 parts by mass, more preferably 50 to 150 parts by mass based on 100 parts by mass of Component (A). When Component (A) and Component (B) are formulated with such a ratio, the composition shows suitable tack before curing, an attaching operation to the wafer can be carried out stably, and after curing, a protect film excellent in strength can be obtained.

[0056]

The combination of Component (A) and Component (B) is preferred when the phenoxy resin of Component (A) is a bisphenol A type phenoxy resin or a bisphenol F type phenoxy resin, and the epoxy resin of the above-mentioned Component (B) is a liquid bisphenol A type epoxy resin or a liquid bisphenol F type epoxy resin.

[0057]

(C) Filler other than fibrous inorganic filler

As the filler of Component (C), there may be used an inorganic filler other than the fibrous inorganic filler (non-fibrous inorganic filler), for example, silica, alumina, titanium oxide, conductive particles such as carbon black, silver particles, etc., and silicone resin powder, for example, cross-linked type spherical dimethylpolysiloxane fine powder having a structure in which dimethylpolysiloxanes have been cross-linked (JP H3-93834A), cross-linked type spherical polymethylsilsesquioxane fine powder (JP H3-47848A), fine

powder in which the cross-linked type spherical polysiloxane rubber surface has been coated by polymethylsilsesquioxane particles (JP H7-196815A, JP H9-20631A).

[0058]

A blending amount of the filler is 100 to 400 parts by mass, preferably 150 to 350 parts by mass based on 100 parts by mass of Component (A). If the blending amount is the above-mentioned lower limit value or more, low water absorption property, low linear expansion property, etc., which are objects to blend the filler can be sufficiently accomplished. If low water absorption property cannot be accomplished, the semiconductor device is not passed in the water absorption reliability test, while if low linear expansion coefficient cannot be accomplished, mismatch in linear expansion coefficients occurs at the time of curing the combined material of the protective film for a semiconductor wafer and the silicon wafer, which causes remarkable warpage, and dicing thereafter becomes impossible. On the other hand, if the blending amount is the above-mentioned upper limit value or less, there is no fear of heightening the viscosity of the composition for forming the protect layer, no fear of worsening fluidity at the time of coating to the base film, and no fear of becoming difficult to attach the protect film to the silicon wafer at low temperature, whereby remarkable warpage of the combined material of the wafer and the protective film for the semiconductor wafer can be prevented. A content ratio of the filler is preferably 30 to 80 % by mass of the protect film.

[0059]

As the silica, fused silica or crystalline silica is used. An average particle diameter of the silica is

preferably 0.1 to 10  $\mu\text{m}$ , more preferably 0.5 to 7  $\mu\text{m}$ . If the average particle diameter of the silica is within the range, good smoothness of the surface of the coated protect film (adhesive layer) can be obtained. Also, in recent years, as the thickness of the adhesive layer, 15 to 50  $\mu\text{m}$  is required in many cases, and if the average particle diameter of the silica is within the above-mentioned range, the requirement can be easily satisfied even when secondary aggregated particles are present.

[0060]

Silicone rubber fine particles whose surfaces have been coated by a polyorganosilsesquioxane resin can be prepared by the methods described in the above-mentioned publications (JP H7-196815A, JP H9-20631A), or commercially available products sold as hybrid silicone powder KMP600 series (available from Shin-Etsu Chemical Co., Ltd.) can be used. KMP600 is preferably used in the point of particle diameter.

[0061]

As (C) the filler, preferably an inorganic filler, more preferably silica, most preferably silica manufactured by the deflagration method is used. The silica becomes easily wet by the resin component, and is surface treated according to the conventional manner. As the surface treatment agent, a silane series one (silane coupling agent) is preferred in the points of its versatility and advantage of cost, etc. The silane coupling agent preferably used may be mentioned, as the alkoxysilane, including a trialkoxysilane such as glycidoxymethyltrimethoxysilane, glycidoxymethyltriethoxysilane,  $\alpha$ -glycidoxyethyltrimethoxysilane,  $\alpha$ -glycidoxyethyltriethoxysilane,  $\beta$ -glycidoxyethyltrimethoxysilane,  $\beta$ -glycidoxyethyltriethoxy-

silane,  $\alpha$ -glycidoxypropyltrimethoxysilane,  $\alpha$ -glycidoxypropyltriethoxysilane,  $\beta$ -glycidoxypropyltrimethoxysilane,  $\beta$ -glycidoxypropyl-glycidoxypropyltriethoxysilane,  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropylmethyldiethoxysilane,  $\alpha$ -glycidoxybutyltrimethoxysilane,  $\alpha$ -glycidoxybutyltriethoxysilane,  $\beta$ -glycidoxybutyltrimethoxysilane,  $\beta$ -glycidoxybutyltriethoxysilane,  $\gamma$ -glycidoxybutyltrimethoxysilane,  $\gamma$ -glycidoxybutyltriethoxysilane,  $\delta$ -glycidoxybutyltrimethoxysilane,  $\delta$ -glycidoxybutyltriethoxysilane, (3,4-epoxycyclohexyl)methyltrimethoxysilane, (3,4-epoxycyclohexyl)methyltriethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltriethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltripropoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltributoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltriphenoxysilane,  $\gamma$ -(3,4-epoxycyclohexyl)propyltrimethoxysilane,  $\gamma$ -(3,4-epoxycyclohexyl)propyltriethoxysilane,  $\delta$ -(3,4-epoxycyclohexyl)butyltrimethoxysilane,  $\delta$ -(3,4-epoxycyclohexyl)butyltriethoxysilane, etc., N- $\beta$ -(aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane, N- $\beta$ -(aminoethyl)- $\gamma$ -aminopropylmethyldiethoxysilane,  $\gamma$ -aminopropyltrimethoxysilane, N-phenyl- $\gamma$ -aminopropyltrimethoxysilane, trimethoxysilylpropyl nadic acid anhydride, etc.,  $\gamma$ -mercaptopropyltrimethoxysilane,  $\gamma$ -mercaptopropyltriethoxysilane.

[0062]

#### (D) Epoxy resin curing catalyst

As the epoxy resin curing catalyst, preferred is a type of curing by heating, the so-called heat-activatable latent epoxy resin curing agent. There may be used, for example, dicyandiamide, an imidazole compound, various kinds of onium salts, a dibasic acid dihydrazide compound, etc., and two or more kinds thereof may be used in

combination. An amount of the curing catalyst may be an amount effective as a catalyst (a catalytic amount), and in general, it is used in an amount of 0.1 to 20 parts by mass, preferably 1 to 12 parts by mass based on 100 parts by mass of the epoxy resin.

[0063]

(E) Fibrous inorganic filler

As the fibrous inorganic filler, there may be mentioned glass fiber, calcium silicate fiber, potassium titanate fiber, carbon fiber, ceramics whisker such as silicon nitride and potassium titanate, etc., or ceramic fiber, metal fiber, etc. Among these, glass fiber is most preferred. Also, the form of the glass fiber is not particularly specified, and may be either of roving, strand, chopped strand, milled fiber, or a crushed product of the strand called glass powder, etc.

[0064]

A shape, etc., of the fibrous inorganic filler of Component (E) are not particularly limited and, for example, in the case of the glass fiber and the carbon fiber, those having a fiber diameter of 10 to 100  $\mu\text{m}$  are preferred, and those having 15 to 60  $\mu\text{m}$  are more preferred. In addition, those having an aspect ratio (a ratio of fiber length/fiber diameter) in the molded product of 3 or more are preferred, and those having 5 or more are more preferred.

If the fiber diameter is 10  $\mu\text{m}$  or more, there is no fear that manufacture thereof becomes difficult, while if it is 100  $\mu\text{m}$  or less, there is no fear that mechanical properties of the molded product, particularly impact strength is lowered so that the range is preferred. Also, if the aspect ratio is 3 or more, the reinforcing effect can be obtained sufficiently so that it is preferred.

[0065]

As a method for improving the reinforcing effect of the protect film, rather than using a material in which fibrous inorganic filler is distributed in the protect film at random, a nonwoven glass fabric in which fibrous inorganic fillers are distributed in a plain randomly (nonwoven glass fabric, Cumulus, available from Japan Vilene Company, Ltd.), or a material in which long fiber are woven in a mesh shape (IPC standard 3313 glass cloth, etc., available from Nitto Boseki Co., Ltd.) is preferably used. As the matrix resin, since the protect film contains the epoxy resin as Component (B), an epoxy resin, a polyamide resin, a phenol resin, etc., are preferably used.

[0066]

The fibrous inorganic filler may be dispersed in the protect film at random, but it is preferred that the protect film has a two-layered structure of an adhesive layer and a reinforcing layer, and the fibrous inorganic filler is dispersed in the reinforcing layer alone. As the matrix resin of the reinforcing layer, a resin of the adhesive layer may be used.

When the fibrous inorganic filler is to be dispersed in the protect film, an amount thereof is preferably 25 to 5,000 parts by mass based on 100 parts by mass of at least one selected from the group consisting of a phenoxy resin, a polyimide resin and a (meth)acrylic resin of the above-mentioned Component (A), more preferably 40 to 3,000 parts by mass. If the blending amount thereof is the above-mentioned lower limit value or more, there is no fear that the protect film has a high linear expansion coefficient to cause remarkable warpage, and no fear of lowering bending strength as it becomes a cause of chipping at the

dicing whereby it is preferred. While if the blending amount is the above-mentioned upper limit value or less, there is no fear of lowering smoothness of the adhesive surface of the protect film to the silicon wafer and no fear of lowering adhesion, and bending strength becomes high.

[0067]

#### Other components

The protect film of the present invention may contain a curing agent for the epoxy resin, and various kinds of additives in addition to the above-mentioned components. As the curing agent, a phenol resin, for example, a condensate of a phenol such as an alkylphenol, a polyvalent phenol, naphthol, etc., and an aldehyde is used, and preferably a phenol novolac resin, an o-cresol novolac resin, a p-cresol novolac resin, a t-butylphenol novolac resin, a dicyclopentadiene cresol resin, a polyparavinyphenol resin, a bisphenol A type novolac resin, a bisphenol F type novolac resin, or a modified product thereof, etc., are used.

[0068]

As the additives, there may be mentioned a pigment, a dye, etc., and when the protect film of the present invention is colored by formulating these materials, laser mark property is improved. Further, for the purpose of improving adhesion property and bonding property of the protect film and the back surface of the chip, a silane coupling agent may be added. And others, a flame retardant, an antistatic agent, etc., may be blended.

[0069]

A modulus of elasticity after curing of the protective film for a semiconductor wafer of the present invention is preferably 10 to 100 GPa. If the modulus of

elasticity after curing is 10 GPa or more, the protective film for a semiconductor wafer can sufficiently endure to the bending stress at the time of bending, and there is no fear to be a cause of lowering bending strength. Also, if the modulus of elasticity is 100 GPa or less, when a combined cured product of the protective film for a semiconductor wafer and the silicon wafer is warped, there is no fear of generating many chippings by generating large stress at the silicon wafer side, and no fear that leads to lower bending strength.

[0070]

#### Protective film for semiconductor wafer

The protective film for a semiconductor wafer in the present invention is a protective film for a semiconductor wafer 10, as shown in Fig. 1 to Fig. 3, having a base film 1, and a protect film 2 formed over the base film 1. And the protect film 2 contains the above-mentioned Components (A) to (E).

Fig. 1 shows a protective film for a semiconductor wafer 10 in which the fibrous inorganic filler 3 of Component (E) is dispersed in the protect film 2 randomly.

Fig. 2 shows a material in which the protect film 2 comprises a reinforcing layer 3' and an adhesive layer 4, the adhesive layer 4 contains Components (A) to (D), and the reinforcing layer 3' contains Component (E). As the reinforcing layer 3', glass cloth, etc., is preferred. In this case, a content of the fibrous inorganic filler is preferably 25 to 1000 parts by mass based on 100 parts by mass of Component (A).

Fig. 3 shows a material in which the protect film 2 comprises a reinforcing layer 3'' and an adhesive layer 4, the adhesive layer 4 contains Components (A) to (D), and the reinforcing layer 3'' contains Component (E). As the

reinforcing layer 3", a prepreg (for example, glass cloth into which an epoxy resin has been impregnated, etc.) is preferred. In this case, a content of the fibrous inorganic filler is preferably 1,000 to 5,000 parts by mass based on 100 parts by mass of Component (A). As an arrangement to the semiconductor wafer, an arranging method in which the linear expansion coefficient becomes small is preferred for the purpose of preventing warpage, and the order of the semiconductor wafer (not shown in the drawing), the adhesive layer 4 and the reinforcing layer 3" is preferred.

[0071]

As the preparation method of the protective film for a semiconductor wafer of the present invention, the following (Process 1) to (Process 3) may be mentioned, but the invention is not limited by these processes.

(Process 1) A fibrous inorganic filler (Component (E)) is mixed and dispersed in the adhesive layer composition containing the above-mentioned Components (A) to (D), which have been dispersed by a solvent, according to the conventional manner, and the resultant material is coated on a base film 1 according to the method mentioned below to form a protect film 2, whereby a protective film for a semiconductor wafer 10 in which the adhesive layer and the reinforcing layer are integrally unified is prepared (Fig. 1).

(Process 2) On the base film 1, a reinforcing layer 3' comprising a network state fibrous inorganic filler

(Component (E)) is provided, and the adhesive layer composition containing the above-mentioned Components (A) to (D) which have been dispersed by a solvent is coated thereon, to prepare a protective film for a semiconductor wafer 10 having a two-layered structure protect film 2 in

which an adhesive layer 4 and a reinforcing layer 3' are provided with an inclination (Fig. 2).

(Process 3) A protective film for a semiconductor wafer 10 having a two-layered structure protect film 2 in which a film state reinforcing layer 3" comprising a network state fibrous inorganic filler (Component (E)) into which a matrix resin has been impregnated, and a film state adhesive layer 4 prepared from an adhesive layer composition (Components (A) to (D)) according to the following method have been adhered is prepared (Fig. 3).

[0072]

The protect film 2 in (Process 1) or the adhesive layer 4 in (Process 2) and (Process 3) can be obtained by applying the composition obtained by mixing the components corresponding to the above on the base film 1 so that a thickness becomes 5 to 100  $\mu\text{m}$ , preferably 10 to 60  $\mu\text{m}$ , according to the conventionally known method such as gravure coater, etc. Incidentally, the above-mentioned composition can be coated depending on necessity, by dispersing in a solvent, for example, cyclohexanone.

[0073]

As Base film 1, a polyethylene film, a polypropylene film, a polyvinyl chloride film, a polyethylene terephthalate film, a polyimide film, etc., may be used. When Base film 1 is delaminated after curing protect film 2, a polyethylene terephthalate film or a polyimide film which is excellent in heat resistance is preferably used. Also, at that time, a releasing processing may be applied by coating a silicone resin, etc., on the surface of the base film, or a peelable layer may be formed between the base film 1 and the protect film 2.

[0074]

A film thickness of the base film 1 is 5 to 200  $\mu\text{m}$ ,

preferably 10 to 150  $\mu\text{m}$ , particularly preferably 20 to 100  $\mu\text{m}$  or so.

[0075]

The protective film for a semiconductor wafer is used, for example, by the following method.

- (1) a step of attaching the protect film in the protective film for a semiconductor wafer of the present invention to the back surface of the semiconductor wafer whose front surface has been formed a circuit,
- (2) a step of delaminating the base film of the protective film for a semiconductor wafer,
- (3) a step of curing the protect film by heating,
- (4) a step of dicing the semiconductor wafer and the protect film.

Here, the processes (3) and (4) may be in a reverse order.

[0076]

The above-mentioned dicing process of (4) can be carried out according to the conventional manner by using a dicing sheet. By the dicing, a semiconductor chip having a protect film at the back surface can be obtained. The chip is picked up according to the general purpose means such as collet, etc., to arrange on a substrate. By using the protective film for a semiconductor wafer of the present invention, minor damage is difficultly generated at the chip dicing surface, whereby the semiconductor device can be manufactured with a high yield.

#### EXAMPLES

[0077]

In the following, the present invention is explained by referring to Examples, but the present invention is not limited by the following Examples.

[0078]

Preparation of composition for forming protect layer

Into about 50 parts by mass of cyclohexanone was dissolved Component (A) with an amount of parts by mass shown in Table 1. The obtained solution and the other components with amounts shown in Table 1 were mixed to obtain the composition with the solid content of about 70 % by mass.

[0079]

Each component shown in Table 1 and the component used below are as follows.

Component (A)

Phenoxy resin: Mw about 60,000, JER 1256 (available from Japan Epoxy Resin Co., Ltd.)

Polyimide resin 1: Synthetic method is mentioned later.

Acrylic resin 1: Copolymer (Weight average molecular weight: 900,000, Glass transition temperature: -28°C) obtained by 55 parts by mass of butyl acrylate, 15 parts by mass of methyl methacrylate, 20 parts by mass of glycidyl methacrylate, and 15 parts by mass of 2-hydroxyethyl acrylate

Component (B)

Epoxy resin: RE310S (available from Nippon Kayaku Co., Ltd.), viscosity at 25°C: 15 Pa.s

Component (C)

Silica: SC2050, average particle diameter 0.5  $\mu\text{m}$ , maximum particle size: 5  $\mu\text{m}$ , KBM-403 treated product, available from Admatechs Co., Ltd.

Component (D)

Dicyandiamide (DICY-7): available from Japan Epoxy Resin Co., Ltd.

Component (E)

Epoxy impregnated glass cloth EG tape Type S:  
available from Arisawa Manufacturing Co., Ltd.

Glass cloth: IPC standard 3313 glass cloth available  
from Nitto Boseki Co., Ltd.

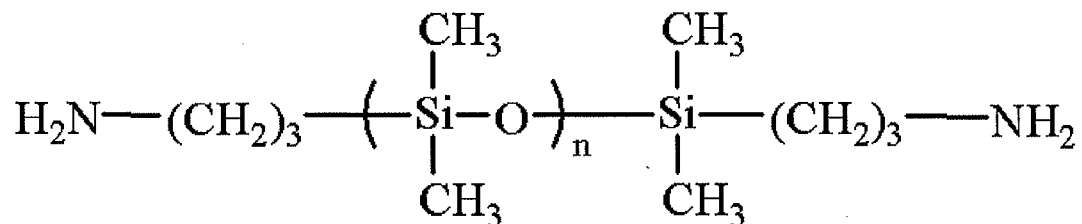
Glass fiber: milled fiber GP-10MA available from  
Nippon Electric Glass Co., Ltd. (fiber diameter: 10  $\mu\text{m}$ ,  
average fiber length: 70  $\mu\text{m}$ , Aspect ratio: 7)

[0080]

#### Synthesis of Polyimide resin 1

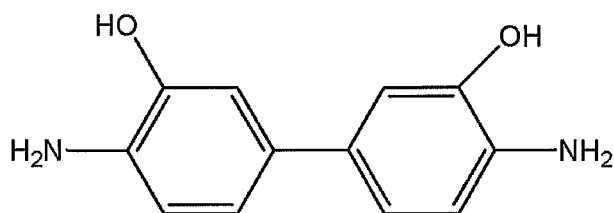
In a 1 liter separable flask equipped with a 25 ml  
of a distillation receiver with a cock, to which a reflux  
condenser has been connected, a thermometer and a stirrer  
were charged 49.01 parts by mass of diaminosiloxane (KF-  
8010, available from Shin-Etsu Chemical Co., Ltd.)  
represented by the following structural formula and 100  
parts by mass of 2-methylpyrrolidone as a reaction  
solvent, and the mixture was stirred at 80°C to disperse  
the diamine therein. To the mixture was added dropwise a  
solution comprising 42.68 parts by mass of 6FDA (2,2-  
bis(3,4-dicarboxyphenyl)hexafluoropropane) as an acid  
anhydride and 100 parts by mass of 2-methylpyrrolidone,  
and the reaction was carried out at room temperature for 2  
hours under stirring to synthesize an acid anhydride  
enriched amic acid oligomer,

[Chemical Formula 15]



Next, 8.31 parts by mass of a diamine (HAB,  
available from Wakayama Seika Corporation) having phenolic  
hydroxyl groups represented by the following formula,

[Chemical Formula 16]



and 100 parts by mass of 2-methylpyrrolidone were charged in a 1 liter separable flask equipped with a 25 ml distillation receiver with a cock, to which a reflux condenser has been connected, a thermometer and a stirrer to disperse the diamine therein, and after adding the above-mentioned acid anhydride enriched amic acid oligomer to the dispersion, the resulting mixture was stirred at room temperature for 16 hours to synthesize a polyamic acid solution. Thereafter, 25 ml of xylene was poured into the mixture and then the temperature of the mixture was raised, and the mixture was refluxed at about 180°C for 2 hours. After confirming that a predetermined amount of water was collected in the distillation receiver and outflow of water was no longer seen, xylene was removed at 180°C while removing the effluent accumulated in the distillation receiver. After completion of the reaction, the obtained reaction mixture was added dropwise to a largely excessive amount of methanol to educe a polymer, and dried under reduced pressure to obtain a polyimide resin having a phenolic hydroxyl group in the skeleton.

When infrared absorption spectrum of the obtained polyimide resin was measured, no absorption based on the polyamic acid which means the presence of an unreacted functional group was appeared, but absorptions based on the imide group were confirmed at 1780  $\text{cm}^{-1}$  and 1720  $\text{cm}^{-1}$ , and an absorption based on the phenolic hydroxyl group was

observed at  $3500\text{ cm}^{-1}$ . A weight average molecular weight of the obtained resin in terms of a polystyrene was 55,000, and the functional group equivalent was 760 g/eq. [0081]

Preparation of protective film for semiconductor wafer  
(Examples 1 to 5 and Comparative Example 1)

Adhesive layer composition liquids (Coating liquids 1 to 5) shown in Table 1 were prepared, and the respective liquids were each coated on an epoxy prepreg reinforcing layer with a thickness of  $115\text{ }\mu\text{m}$  in Examples, or on a SUS304 reinforcing layer with a thickness of  $50\text{ }\mu\text{m}$  in Comparative Example so that the adhesive layer has a layer thickness of  $20\text{ }\mu\text{m}$ , and dried under heating at  $110^{\circ}\text{C}$  for 10 minutes to form protect films with thicknesses of  $135$  and  $70\text{ }\mu\text{m}$ .

[0082]

(Example 6)

A glass cloth IPC standard 3313 with a thickness of  $75\text{ }\mu\text{m}$  was provided on a PET film with a thickness of  $38\text{ }\mu\text{m}$  and the surface of which has been treated by a silicone, and Coating liquid 1 shown in Table 1 was coated thereon so that the adhesive layer became a thickness of  $15\text{ }\mu\text{m}$ , dried under heating at  $110^{\circ}\text{C}$  for 10 minutes to form a protect film with a thickness of  $90\text{ }\mu\text{m}$ .

[0083]

(Example 7)

Coating liquid 6 containing glass fiber shown in Table 2 was coated on a PET film with a thickness of  $38\text{ }\mu\text{m}$  and the surface of which has been treated by a silicone, so that the thickness of the protect film became  $50\text{ }\mu\text{m}$ , dried under heating at  $110^{\circ}\text{C}$  for 10 minutes to form a

protect film with a thickness of 50  $\mu\text{m}$ .

(Incidentally, Coating liquid 6 has a composition in which glass fiber has been added to Coating liquid 1.)

[0084]

(Comparative Examples 2 and 3)

Protect films both having 135  $\mu\text{m}$  were formed according to the same process as in Example 7 except for using Coating liquid 4 or 5.

[0085]

#### Tensile modulus

The obtained protect films were cured at 175°C/4 hours, and a strip shaped sample with a width of 5 mm, and a length of 40 mm was prepared which was made a sample for measurement. By using Seiko Instruments DMA6100, datum at 25°C when the sample was raised from 0°C to 200°C with 3°C/min under 1 Hz and a strain range of 10  $\mu\text{m}$  were made tensile modulus.

[0086]

#### Dicing test

The obtained protect films were attached to a silicon wafer (a wafer in which 8 inches unpolished wafer was subjected to poligrind polishing using DAG-810 manufactured by DISCO Corporation to make a thickness 75  $\mu\text{m}$ ) with a thickness of 75  $\mu\text{m}$  at 50°C by using Technovision FM-114. The protect film-attached silicon wafer was cured in a dryer at 175°C for 4 hours to cure the protect film. The protect film-attached silicon wafer was subjected to dicing to a chip with 10 mm×10 mm square under the following conditions, and cut end surfaces of the obtained 40 chips were observed. When no chipping with 50  $\mu\text{m}$  or more was observed, it was made passed.

[0087]

Dicing conditions

Device: DISCO dicer DAD-341

Cutting method: Single

Dicing blade: ZH05-SD3500-N1-70EE

Rotation number of blade: 30,000 rpm

Blade speed: 30 mm/sec

Thickness of dicing film: 110  $\mu\text{m}$ , Depth of cut to dicing film: 50  $\mu\text{m}$

[0088]

Bending strength measurement test

Bending strength of 40 chips each having 10 mm $\times$ 10 mm square obtained by the previous dicing test was measured by the following conditions, and the average value was shown as the measurement result. The results are shown in Table 3.

[0089]

Bending strength measurement conditions

Apparatus: Autograph manufactured by Shimadzu

Bending jig: 4 mm width wedge-shaped

Inter-fulcrum distance: 6 mm

Wedge-shaped jig speed: 0.01 m/min

[0090]

[Table 1]

|     |                        |                   | Adhesive layer composition |                  |                  |                  |                  |
|-----|------------------------|-------------------|----------------------------|------------------|------------------|------------------|------------------|
|     |                        |                   | Coating liquid 1           | Coating liquid 2 | Coating liquid 3 | Coating liquid 4 | Coating liquid 5 |
| (A) | Phenoxy resin          | JER1256           | 100                        |                  |                  | 100              | 100              |
|     | Polyimide resin        | Polyimide resin 1 |                            | 100              |                  |                  |                  |
|     | Acrylic resin          | Acrylic resin 1   |                            |                  | 100              |                  |                  |
| (B) | Epoxy resin            | RE310S            | 95                         | 95               | 95               | 95               | 95               |
| (C) | Filler (silica filler) | SC2050 KBM-403    | 300                        | 300              | 300              | 100              | 600              |
| (D) | Curing catalyst        | DICY-7            | 5                          | 5                | 5                | 5                | 5                |
|     | Dilution solvent       | Cyclo-hexanone    | 333                        | 333              | 333              | 200              | 400              |

[0091]

[Table 2]

|     |                        |                | Protect film composition |
|-----|------------------------|----------------|--------------------------|
|     |                        |                | Coating liquid 6         |
| (A) | Phenoxy resin          | JER1256        | 100                      |
| (B) | Epoxy resin            | RE310S         | 95                       |
| (C) | Filler (silica filler) | SC2050 KBM-403 | 300                      |
| (D) | Curing catalyst        | DICY-7         | 5                        |
|     | Dilution solvent       | Cyclohexanone  | 366                      |
| (E) | Glass fiber            | GP-10MA        | 50                       |

[0092]

[Table 3]

|                              |               | Example          |                  |                  |                  |                  |                  |                  | Comparative Example |                  |                  |
|------------------------------|---------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|---------------------|------------------|------------------|
|                              |               | 1                | 2                | 3                | 4                | 5                | 6                | 7                | 1                   | 2                | 3                |
| Adhesive layer               |               | Coating liquid 1 | Coating liquid 2 | Coating liquid 3 | Coating liquid 4 | Coating liquid 5 | Coating liquid 1 | Coating liquid 6 | Coating liquid 1    | Coating liquid 4 | Coating liquid 5 |
| Reinforcing layer 1          | EG tape       | ○                | ○                | ○                | ○                | ○                |                  |                  |                     |                  |                  |
| layer 2                      | Type S        |                  |                  |                  |                  |                  |                  |                  |                     |                  |                  |
| layer 3                      | 115 $\mu$ m   |                  |                  |                  |                  |                  |                  |                  |                     |                  |                  |
| Reinforcing layer 2          | SUS304        |                  |                  |                  |                  |                  |                  |                  | ○                   |                  |                  |
| layer 3                      | 50 $\mu$ m    |                  |                  |                  |                  |                  |                  |                  |                     |                  |                  |
| Reinforcing layer 3          | IPC           |                  |                  |                  |                  |                  | ○                |                  |                     |                  |                  |
| Glass cloth                  | Standard 3313 |                  |                  |                  |                  |                  |                  |                  |                     |                  |                  |
| Protect film characteristics |               |                  |                  |                  |                  |                  |                  |                  |                     |                  |                  |
| Film thickness ( $\mu$ m)    |               | 135              | 135              | 135              | 135              | 135              | 90               | 50               | 70                  | 135              | 135              |
| Filler content               | wt%           | 60%              | 60%              | 60%              | 33%              | 75%              | 60%              | 33%              | 60%                 | 33%              | 67%              |
| Tensile modulus              | GPa           | 25               | 25               | 25               | 20               | 30               | 35               | 25               | 190                 | 3                | 15               |
| Dicing property              | Single cut    | Possible         | Possible         | Possible         | Possible         | Possible         | Possible         | Possible         | Not possible        | Possible         | Possible         |
| Bending strength (N)         |               | 8.0              | 7.5              | 7.5              | 7.5              | 8.5              | 9.5              | 7.5              | —                   | 4.5              | 4.8              |

[0093]

The protective films for a semiconductor in which the protect films contain the fibrous inorganic filler of Examples 1 to 7 showed high tensile modulus, dicing property and bending strength, and high productivity of the semiconductor chip can be realized. On the other hand, the protective films for a semiconductor containing no fibrous inorganic filler of Comparative Examples 1 to 3 showed low dicing property, and bending strength was also inferior.

[0094]

It must be stated here that the present invention is not restricted to the embodiments shown by the above-mentioned embodiments. The above-mentioned embodiments are merely examples so that any embodiments composed of substantially the same technical concept as disclosed in the claims of the present invention and expressing a similar effect are included in the technical scope of the present invention.

## CLAIMS

1. A protective film for a semiconductor wafer having a base film, and a protect film formed over the base film, wherein the protect film comprises Components (A) to (E) mentioned below:

(A) 100 parts by mass of at least one selected from the group consisting of a phenoxy resin, a polyimide resin and a (meth)acrylic resin;

(B) 5 to 200 parts by mass of an epoxy resin;

(C) 100 to 400 parts by mass of a filler other than fibrous inorganic fillers;

(D) a catalytic amount of an epoxy resin-curing catalyst;  
and

(E) 25 to 5,000 parts by mass of a fibrous inorganic filler.

2. The protective film for a semiconductor wafer according to claim 1, wherein the protect film comprises a reinforcing layer and an adhesive layer,

the adhesive layer comprises the following Components (A) to (D), and the reinforcing layer comprises the following Component (E):

(A) 100 parts by mass of at least one selected from the group consisting of a phenoxy resin, a polyimide resin and a (meth)acrylic resin;

(B) 5 to 200 parts by mass of an epoxy resin;

(C) 100 to 400 parts by mass of a filler other than fibrous inorganic fillers;

(D) a catalytic amount of an epoxy resin-curing catalyst;  
and

(E) 1,000 to 5,000 parts by mass of a fibrous inorganic filler.

3. The protective film for a semiconductor wafer according to claim 1 or 2, wherein the phenoxy resin of Component (A) is a bisphenol A type phenoxy resin or a bisphenol F type phenoxy resin, and the epoxy resin of Component (B) is a liquid bisphenol A type epoxy resin or a liquid bisphenol F type epoxy resin.

4. A method for manufacturing a semiconductor chip by dicing a semiconductor wafer, which comprises  
attaching the protective film for a semiconductor wafer according to any one of claims 1 to 3 to the semiconductor wafer, and dicing the same collectively, to manufacture a semiconductor chip having a protect film with the same size as that of the semiconductor chip at the back surface thereof.