PROTECTIVE FILM-FORMING FILM AND PROTECTIVE FILM-FORMING COMPOSITE SHEET

TECHNICAL FIELD

[0001]

The present invention relates to a protective layer-forming film capable of forming the protective layer on the semiconductor wafer or the semiconductor chip, and capable of improving the production efficiency of the semiconductor chip. Particularly, the present invention relates to the protective layer-forming film used for the production of the semiconductor chip which is mounted by so called "face down" method.

DESCRIPTION OF THE RELATED ART

[0002]

Recently, the production of a semiconductor device is carried out by the mounting method of so called "face down method". In the face down method, the semiconductor chip (hereinafter, it will be simply referred as "chip") comprising the electrode such as bumps or so on the circuit face is used, and the electrode is bonded to the substrate. Therefore, the opposite face (the chip backside) of the circuit face of the chip will be exposed.

[0003]

This chip backside being exposed may be protected by the organic film in some cases. Conventionally, for the chip comprising the protective film made of this organic film, a liquid resin is coated to the wafer backside by a spin coat method, then dried and cured, and it is obtained by cutting the protective film with the wafer. However, the accuracy of the protective film thickness formed as such is not sufficient, thus the product yield may decline in some cases.

[0004]

In order to solve the above problem, a protective layer-forming sheet for chip comprising a curable protective film forming layer including a curable component by heat or energy ray is disclosed (the patent document 1).

[0005]

Conventionally, when the wafer itself was thick enough, the warpage of the wafer did not take place; however as the wafer become thinner, the warpage of the thinned wafer occurred due to the difference of the shrinkage ratio between the wafer surface formed with the circuit and the wafer backside which is not formed with the circuit.

The wafer with large warpage has a risk to cause the transportation malfunction during the subsequent chip production step. Also, due to such warpage of the wafer, the dicing of the wafer may become difficult. In order to solve such problems caused by the warpage of the wafer, the protective layer-forming film which is adhered on the wafer backside is demanded to have the function to correct the wafer warpage.

[0006]

In the patent document 2, the flip chip type semiconductor backside film wherein the volume shrinkage rate in the rage of 23°C to 165°C when heat curing is 100 ppm/°C or more and 400 ppm/°C or less, and the modulus storage elasticity at 23°C after the heat curing is 1 GPa or more and 5 GPa or less is used; thereby the warpage of the semiconductor element such as the semiconductor wafer or the semiconductor chip or so is suppressed or prevented.

Also, in the patent document 3, the flip chip type semiconductor backside film wherein the amount of the shrinkage by the heat curing with respect to the entire volume of before the heat curing is 2 vol% or more and 30 vol% or less is used; thereby the warpage of the semiconductor element is suppressed or prevented.

PRIOR ART DOCUMENT

[0007]

Patent document 1: JP Patent Application Laid Open No.2004-214288

Patent document 2: JP Patent Application Laid Open No.2012-33554

Patent document 3: JP Patent Application Laid Open No.2011-228499

DISCLOSURE OF THE INVENTION

MEANS FOR SOLVING THE PROBLEMS

[0008]

Recently, the circuit patterns formed on the wafer surface has diversified, and the wafer with large warpage caused by the circuit forming has increased. Therefore, the protective layer-forming film capable of correcting the larger wafer warpage is in demand; however the flip chip type semiconductor backside film of the patent documents 2 and 3 were unable to sufficiently solve the warpage of the wafer in some case. Also, the present inventors have carried out keen examination in order to further enhance the correction function of the warpage, then the obtained chip with the protective layer was released from the bonding part between the protective layer and the chip, or cracked at the protective layer; thus in some case the reliability was not sufficient.

[0009]

The object of the present invention is to provide the protective layer-forming film capable of suppressing the wafer warpage and also capable of forming the protective layer with high reliability to the chip.

MEANS FOR SOLVING THE OBJECT

[0010]

The gist of the present invention is as described in below.

[1] A protective layer-forming film having a heat curable property,

a glass transition temperature after heat curing of 150 to 300°C, and a modulus of elasticity at a temperature of 23°C after heat curing of 0.5 to 10 GPa.

[0011]

[2] The protective layer-forming film as set forth in [1] comprising a heat curable component comprising an epoxy compound and an amine based curing agent.

[0012]

[3] The protective layer-forming film as set forth in [2] further comprising either one or both of a polymer component and a heat curable polymer component, and comprises 135 parts by weight or less of the heat curable component with respect to 100 parts by weight of total of the polymer component and the heat curable polymer component.

[0013]

[4] The protective layer-forming film as set forth in any one of [1] to [3], wherein said protective layer-forming film comprise an inorganic filler, and a content of the inorganic filler is 10 to 70 parts by weight with respect to 100 parts by weight of entire solid portion constituting the protective layer-forming film.

[0014]

[5] The protective layer-forming film as set forth in [4], wherein an average molecular weight of the inorganic filler is 0.02 to 5 μm.

[0015]

[6] The protective layer-forming film as set forth in any one of [1] to [5], wherein the heat curable polymer component is comprised in the protective layer-forming film, and the heat curable polymer component is an acrylic polymer comprising epoxy group containing monomer as a constituting monomer.

[0016]

[7] A protective film-forming composite sheet wherein a support sheet is formed in a releasable manner on one side of the protective layer-forming film according to any one of [1] to [6].

THE EFFECT OF THE INVENTION

[0017]

According to the present invention, in regards with the wafer warpage due to the shrinkage caused during the circuit formation of the wafer surface side, by adhering the protective layer-forming film to the wafer backside and then heat curing, the wafer warpage can be corrected by the stress caused by the curing and shrinking of the protective layer-forming film, and the chip with the protective layer having high reliability can be obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

[Fig.1] Fig.1 shows the first embodiment of the protective layer-forming composite sheet formed by using the protective layer-forming film according to the present invention.

[Fig.2] Fig.2 shows the second embodiment of the protective layer-forming composite sheet formed by using the protective layer-forming film according to the present invention.

[Fig.3] Fig.3 shows the third embodiment of the protective layer-forming composite sheet formed by using the protective layer-forming film according to the present invention.

[Fig.4] Fig.4 shows the fourth embodiment of the protective layer-forming composite sheet formed by using the protective layer-forming film according to the present invention.

[Fig.5] Fig.5 is the figure describing "the amount of the warpage" which is evaluated in the examples.

[0019]

Hereinafter, the detail of the protective layer-forming film of the present invention will be described.

[0020]

[The protective layer-forming film]

The protective layer-forming film of the present invention has the heat curable property, and the glass transition temperature (Tg) after heat curing of 150 to 300°C, preferably 170 to 280°C, and more preferably 220 to 270°C. In the present invention, the glass transition temperature (Tg) of after heat curing the protective layer-forming film refers to the temperature wherein a loss tangent tan δ showing the maximum value at the low temperature range -50 to 30°C during the dynamic viscoelasticity measurement of the protective layer-forming film (the protective layer) after heat curing which is measured at the frequency of 11 Hz.

If Tg after the heat curing of the protective layer-forming film is less than 150°C, the fluidity of the protective layer-forming film rises during the heat curing step of the protective layer-forming film which is usually carried out at 120 to 150°C or so, and the stress caused by the curing shrinkage of the protective layer-forming film is relieved and is reduced. As a result, the correction of the wafer warpage becomes insufficient.

On the other hand, if Tg of after the heat curing of the protective layer-forming film exceeds 300°C, then the protective layer-forming film or the protective layer obtained by heat curing said film may be released from the wafer or the chip; thus as a result, the reliability of the chip with the protective layer declines.

By setting Tg after heat curing the protective layer-forming film within the above range, during the heat curing step of said film, since the protective layer-forming

film comprises the predetermined rigidity, the stress caused by the curing shrinkage of said film is not relieved, and the warpage of the wafer or the chip, which is obtained by separating the wafer, can be corrected.

[0021]

Also, the protective layer-forming film has the modulus of elasticity at 23°C after heat curing of 0.5 to 10 GPa, preferably 1 to 10 GPa, and more preferably more than 5 GPa and 8 GPa or less.

If the modulus of elasticity at 23°C after heat curing the protective layer-forming film is less than 0.5 GPa, the stress caused by the curing shrinkage of the protective layer-forming film cannot be maintained, and the stress is relieved; hence the correction of the wafer warpage becomes insufficient. On the other hand, if the modulus of elasticity at 23°C after the heat curing of the protective layer-forming film exceeds 10 GPa, the protective layer-forming film or the protective layer obtained by heat curing said film may be released from the wafer or the chip.

By setting the modulus of elasticity at 23°C after the heat curing of the protective layer-forming film within the above mentioned range, the warpage of the wafer or the chip can be corrected, and also the reliability of the chip with the protective layer can be improved.

[0022]

Also, the heat shrinkage ratio when heating the protective layer-forming film at 130°C for 2 hours is preferably 0.1 to 10%, and more preferably 0.5 to 5%. By setting the heat shrinkage ratio when heating the protective layer-forming film at 130°C for 2 hours within the above mentioned range, the effect of correcting the warpage of the wafer (the warpage correction function) improves. Note that, the heat shrinkage ratio when heating the protective layer-forming film at 130°C for 2 hours is obtained from

the below formula based on the area of the protective layer-forming film of before and after introducing the protective layer-forming film in the environment of 130°C.

[0023]

The heat shrinkage ratio (%) = {(the area of the protective layer-forming film before introduction) – (the area of the protective layer-forming film after the introduction)} / the area of the protective layer-forming film before introduction x 100

[0024]

The functions at least required to the protective layer-forming film are the sheet form maintaining property (1), the initial adhesiveness (2) and the curability (3). Note that, the protective layer-forming film of the present invention comprises the heat curable property as mentioned in the above, but it may also have the property to cure by the means other than the heat.

[0025]

The protective layer-forming film can be provided with the sheet form maintaining property (1) and the curability (3) by adding the binder component; and as the binder component, the first binder component comprising the polymer component (A) and the heat curable component (B), or the second binder component comprising the heat curable polymer component (AB) which has the properties of both the component (A) and the component (B) can be used.

Note that, the initial adhesiveness (2) which is the property to temporarily adhere the protective layer-forming film to the adherend until the curing may be a pressure sensitive property or it may be a property to adhere by softening by heat. The initial adhesiveness (2) is usually controlled by various characteristics of the binder component or by the blending amount of the inorganic filler (C) which will be described in below.

[0026]

(The first binder component)

The first binder component provides the sheet form maintaining property and the heat curable property to the protective layer-forming film by comprising the polymer component (A) and the heat curable component (B). Note that, the first binder component does not comprise the heat curable polymer component (AB) in order to differentiate from the second binder component.

[0027]

The polymer component (A)

The polymer component (A) is added to the protective layer-forming film mainly for the purpose to provide the sheet form maintaining property to the protective layer-forming film.

In order to achieve the above object, the weight average molecular weight (Mw) of the polymer component (A) is usually 20,000 or more, and preferably 20,000 to 3,000,000. The value of the weight average molecular weight (Mw) is the value measured by gel permeation-chromatography method (GPC method) (polystyrene standard). As the measurement according to such method, for example those connecting the high speed GPC device "HLC-8120GPC" made by TOSOH CORPORATION with the high speed GPC column "TSK gurd column H_{XL}-H", "TSK Gel GMH_{XL}", "TSK Gel G2000 H_{XL}" (all made by TOSOH CORPORATION) is used, then the measurement is carried out under the column temperature of 40°C, the liquid sending speed: 1.0 mL/min, and using the detector as differential refractometer.

Note that, in order to differentiate from the heat curable polymer component (AB) which will be described in below, the polymer component (A) does not comprise the curable functional group.

[0028]

As the polymer component (A), acrylic polymer, polyester, phenoxy resin (in order to differentiate from the heat curable polymer component (AB), it is limited to those which does not comprise the epoxy group), polycarbonate, polyether, polyurethane, polysiloxane, rubber based polymer or so can be used. Also, those which bonds two or more thereof, for example it may be acrylic urethane resin or so obtained by reacting acrylic polyol which is the acrylic polymer comprising hydroxyl group, with the urethane prepolymer comprising isocyanate group at the molecular terminal. Further, those combining two or more may be used as well including the polymer binding two or more thereof.

[0029]

The acrylic polymer (A1)

As the acrylic polymer (A), the acrylic polymer (A1) is preferably used. The glass transition temperature (Tg) of the acrylic polymer (A1) is preferably -60 to 50°C, more preferably -50 to 40°C, and further preferably -40 to 30°C. When the glass transition temperature of the acrylic polymer (A1) is high, the initial adhesiveness of the protective layer-forming film declines and it may not be able to transfer to the adherend. Also, if the glass transition temperature of the acrylic polymer (A1) is low, the release force of protective layer-forming film and the support sheet which will be described in following becomes large, and the transfer malfunction of the protective layer-forming film may occur.

Note that, Tg of the acrylic polymer is the value obtained from FOX formula.

[0030]

The weight average molecular weight (Mw) of the acrylic polymer (A1) is preferably 100,000 to 1,500,000. If the weight average molecular weight of the acrylic polymer is high, the initial adhesiveness of the protective layer-forming film declines and it may not be able to transfer to the adherend. Also, if the weight average molecular

weight of the acrylic polymer (A1) is low, the adhesiveness between the protective layer-forming film and the support sheet becomes high, and the transfer malfunction of the protective layer-forming film may occur.

[0031]

The acrylic polymer (A1) includes (meth)acrylate at least in the monomer constituting thereof.

As (meth)acrylate, alkyl (meth)acrylate comprising the carbon atoms of 1 to 18, specifically, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, lauryl (meth)acrylate, tetradecyl (meth)acrylate, octadecyl (meth)acrylate or so; (meth)acrylate comprising cyclic backbone, specifically cycloalkyl (meth)acrylate, benzyl (meth)acrylate, isobornyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentenyloxyethyl (meth)acrylate, imide (meth)acrylate or so may be mentioned. Also, among those described as the example of the monomer comprising the hydroxyl group, the monomer comprising the carboxyl group, and the monomer comprising the amino group, those which are (meth)acrylate may be mentioned as example as well.

[0032]

In the present invention, by using (meth)acrylate comprising the hydroxyl group, (meth)acrylate comprising the carboxyl group or (meth)acrylate comprising the amino group as the monomer constituting the acrylic polymer (A1), the modulus of elasticity at 23°C after heat curing the protective layer-forming film can be easily controlled within the predetermined range.

[0033]

Note that, (meth)acryl in the present specification is used to encompass both acryl and methacryl.

[0034]

The monomer comprising the hydroxyl group may be used as the monomer constituting the acrylic polymer (A1). As the monomer comprising the hydroxyl group; (meth)acrylate comprising the hydroxyl group such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate or so; vinyl alcohol, N-methylol (meth)acrylic amide or so may be mentioned.

[0035]

The monomer comprising the carboxyl group may be used as the monomer constituting the acrylic polymer (A1). As the monomer comprising the carboxyl group; (meth)acrylate comprising the carboxyl group such as 2-(meth)acryloyloxyethylphthalate, 2-(meth)acryloyloxypropylphthalate or so; (meth)acrylic acid, maleic acid, fumaric acid, itaconic acid or so may be mentioned. In case of using the epoxy based heat curable component as the heat curable component (B) which will be described in following, the used amount of the monomer comprising the carboxyl group is preferably low because the carboxyl group and the epoxy group in the epoxy based heat curable component reacts.

[0036]

The monomer comprising the amino group may be used as the monomer constituting the acrylic polymer (A1). As the monomer comprising the amino group, (meth)acrylate comprising the amino group such as monomethylamino (meth)acrylate, monoethylamino (meth)acrylate, diethylamino (meth)acrylate or so may be mentioned.

[0037]

As the monomer constituting the acrylic polymer (A1), vinyl acetate, styrene, ethylene, α-olefin or so may be used besides the above mentioned.

[0038]

The acrylic polymer (A1) may be crosslinked. The acrylic polymer (A1) before crosslinking comprises the crosslinkable functional group such as hydroxyl group or so, and by adding the crosslinking agent to the composition for forming the protective layer-forming film, the crosslinkable functional group and the functional group comprised in the crosslinking agent reacts; thereby the crosslinking is carried out. By crosslinking the acrylic polymer (A1), the cohesive strength of the protective layer-forming film can be regulated. Also, by regulating the crosslinking density of the acrylic polymer (A1), the glass transition temperature or the modulus of elasticity at 23°C after heat curing the protective layer-forming film can be controlled. The crosslinking density can be controlled by the added amount of the crosslinking agent which will be described in below.

[0039]

As the crosslinking agent, the organic polyvalent isocyanate compounds and the organic polyvalent imine compounds or so may be mentioned.

[0040]

As the organic polyvalent isocyanate compounds, aromatic polyvalent isocyanate compounds, aliphatic polyvalent isocyanate compounds, alicyclic polyvalent isocyanate compounds and trimer of the organic polyvalent isocyanate compounds thereof, and also terminal isocyanate urethane polymer or so obtained by reacting these organic polyvalent isocyante compounds and polyol compounds or so may be mentioned.

[0041]

As for specific example of the organic polyvalent isocyanate compound, 2,4-tolylenediisocyanate, 2,6-tolylenediisocyanate, 1,3-xylylenediisocyanate, 1,4-xylenediisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, 3-methyldiphenylmethanediisocyanate, hexamethylenediisocyanate, isophoronediisocyanate, dicyclohexylmethane-4,4'-diisocyanate, dicyclohexylmethane-2-4'-diisocyanate, lysine isocyanate and polyvalent alcohol adducts thereof or so may be mentioned.

[0042]

As for the above mentioned organic polyvalent imine compounds, N-N'-diphenylmethane-4,4'-bis(1-aziridinecarboxyamide), trimethylolpopane-tri-β-aziridinylpropionate, tetramethylolmethane-tri-β-aziridinylpropionate, and N,N'-toluene-2,4-bis(1-aziridinecarboxyamide) triethylenemelamine or so may be mentioned.

[0043]

The crosslinking agent before the crosslinking is usually 0.01 to 20 parts by weight, preferably 0.1 to 10 parts by weight and more preferably 0.5 to 5 parts by weight with respect to 100 parts by weight of the acrylic polymer (A1).

[0044]

In the present invention, in case the content of the component constituting the protective layer-forming film is determined based on the content of the polymer component (A), if the polymer component (A) is the crosslinked acrylic polymer, the content to be based on is the content of the acrylic polymer before the crosslinking.

[0045]

(B) The heat curable component

The heat curable component (B) is added to the protective layer-forming film mainly for the purpose to provide the heat curable property to the protective layer-forming film.

The heat curable component (B) comprises the compound having the functional group which reacts at least by applying the heat. The functional groups comprised in the heat curable component (B) reacts with each other, and the three dimensional network structure is formed; thereby curing is done. The heat curable component (B) is used by combining with the polymer component (A), hence from the point of suppressing the viscosity of the composition for coating which is to form the protective layer-forming film, and to improve the handling property, the weight average molecular weight (Mw) thereof is usually 10,000 or less and preferably 100 to 10,000.

[0046]

As the heat curable component (B), for example, the epoxy based heat curable component is preferable.

The epoxy based heat curable component comprises the compound (B11) comprising the epoxy group (hereinafter, it may be referred as "epoxy compound (B11)"); and it is preferable to use those which combines the compound (B11) comprising the epoxy group and the heat curing agent (B12), and more preferably those further combining the curing catalyst (B13) is used.

[0047]

The compound (B11) comprising the epoxy group

As the epoxy compound (B11), those already known can be used. Specifically, the epoxy compound comprising two or more functional groups in molecule such as polyfunctional epoxy resins, bisphenol A diglycidyl ether and the hydrogenated product, o-cresolnovolac type epoxy resins, dicyclopentadiene type epoxy resin, biphenyl type epoxy resins, bisphenol A type epoxy resins, bisphenol F type epoxy resins, phenylene

backbone epoxy resins or so may be mentioned. These may be used alone, or by combining two or more thereof.

[0048]

The curing agent (B12)

The curing agent (B12) functions as the curing agent against the epoxy compounds (B11). As the preferable heat curing agent, the compound comprising two or more functional group capable of reacting with the epoxy group in one molecule may be mentioned. As the functional groups, a phenolic hydroxyl group, an alcoholic hydroxyl group, an amino group, a carboxyl group and acid anhydride or so may be mentioned. Among these, the phenolic hydroxyl group, the amino group and the acid anhydride are preferable; and the phenolic hydroxyl group and amino group are more preferable; and particularly preferably it is amine based curing agent comprising amino group. The amine based curing agent can easily regulate the glass transition temperature of after the heat curing of the protective layer-forming film within the above mentioned range even by small blended amount. On the other hand, for the curing agent other than the amine based curing agent such as the phenol based curing agent or so; it is difficult to regulate the glass transition temperature of after the heat curing of the protective layer-forming film within the above mentioned range unless more heat curing agent is blended. If the content of the heat curing agent (B12) is too much, the entire content of the heat curable component (B) must be increased, thus there is a risk that the content of the heat curable component (B) becomes too much.

[0049]

As specific examples of the phenol based curing agent, polyfunctional phenol resins, biphenol, novolac phenol resins, dicyclopentadiene based phenol resins, XYLOK type phenol resins, aralkyl phenol resins or so may be mentioned. As for specific

examples of the amine based curing agent, DICY (dicyandiamide) may be mentioned. These may be used alone or by mixing two or more thereof.

[0050]

The content of the heat curing agent (B12) is usually 0.1 to 500 parts by weight or so with respect to 100 parts by weight of the epoxy compound (B11). In the present invention, by regulating the content of the epoxy compound (B11), the heat curing agent (B12) and the curing catalyst (B13), the glass transition temperature after heat curing the protective layer-forming film can be controlled. Particularly, in case the amine based curing agent is used as the heat curing agent (B12), the glass transition temperature of after the heat curing the protective layer-forming film becomes easy to regulate within the above mentioned range. when the amount of the epoxy group comprised by the epoxy compound (B11) and the amount of the active hydrogen comprised by the amine based curing agent is preferably 0.4 to 1.5, more preferably 0.5 to 1.3, and particularly preferably 0.6 to 1.1 in terms of mol ratio (active hydrogen/ epoxy group). From the point of regulating the mol ratio (active hydrogen/ epoxy group) regarding the amount of the epoxy group comprised by the epoxy compound (B11) and the amount of the active hydrogen comprised by the amine based curing agent, the amine based curing agent is included in the protective layer-forming film preferably by 5 to 20 parts by weight, and more preferably 5 to 15 parts by weight, with respect to 100 parts by weight of the epoxy compound (B11).

[0051]

The curing catalyst (B13)

The curing catalyst (B13) may be used to regulate the speed of the heat curing of the protective layer-forming film. The heat curing catalyst (B13) is preferably used particularly when the epoxy based heat curable component is used as the heat curable component (B).

[0052]

As the preferable curing catalyst, tertiary amines such as triethylene diamine, benzyldimethyl amine, triethanol amine, dimethylamino ethanol, tris(dimethylaminomethyl) phenol or so; imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole, 2-phenyl-4-methyl-5-hydroxymethylimidazole or so; organic phosphine such as tributylphosphine, diphenylphosphine, triphenylphosine or so; tetraphenylboron salt such as tetraphenylphosphoniumtetraphenylborate, triphenylphosphinetetraphenylborate or so may be mentioned. These may be used alone or by mixing two or more thereof.

[0053]

The curing catalyst (B13) is included preferably by 1 to 10 parts by weight and further preferably by 5 to 10 parts by weight with respect to 100 parts by weight of total of the epoxy compound (B11) and the heat curing agent (B12). By comprising the curing catalyst (B13) within the above mentioned range, an excellent adhesiveness can be exhibited even when exposed under high temperature and high humidity condition, and also high reliability can be attained even in case of being exposed under harsh reflow condition. By adding the curing catalyst (B13), the adhesiveness after curing the protective layer-forming film can be improved. The larger the content of the curing catalyst (B13) is, the more enhanced such effect is.

[0054]

(The second binder component)

The second binder component provides the sheet form maintaining property and the heat curable property to the protective layer-forming film by comprising the heat curable polymer component (AB).

[0055]

The heat curable polymer component (AB)

The heat curable polymer component is the polymer comprising the curable functional group. The curable functional group is the functional group capable of constituting the three dimensional network structures by reacting with each other, and the functional group which reacts by applying heat may be mentioned.

The curable functional group may be added in the unit of the continuous structure which is the backbone of the heat curable polymer component (AB), or it may be added to the terminal thereof. In case the curable functional group is added in the unit of the continuous structure which is the backbone of the heat curable polymer component (AB), the curable functional group may be added to the side chain, or it may be added directly to the main chain. The weight average molecular weight (Mw) of the heat curable polymer component (AB) is usually 20,000 or more from the point of providing the sheet form maintaining property to the protective layer-forming film.

[0056]

As the functional group which reacts by applying the heat, the epoxy group may be mentioned. As the heat curable polymer component (AB) comprising the epoxy group, the phenoxy resin comprising the epoxy group may be mentioned.

Also, it may be the same polymer as the above mentioned acrylic polymer (A1), wherein the monomer comprising the epoxy group is used as the monomer, then polymerizing it (epoxy group comprising acrylic polymer). As such monomers, the epoxy group containing (meth)acrylate or a non-acrylic epoxy group containing monomer may be mentioned. As the epoxy group containing (meth)acrylate, for example glycidyl(meth)acrylate, β-methylglycidyl(meth)acrylate, (3,4-epoxycyclohexyl)methyl(meth)acrylate, 3-epoxycyclo-2-hydroxypropyl(meth)acrylate or so may be mentioned; and as the non-acrylic epoxy group containing monomer, for example, glycidylcrotonate,

allylglycidylether or so may be mentioned. As the epoxy group containing monomer, epoxy group containing (meth)acrylate is preferable, and among these glycidyl(meth)acrylate is preferable.

In case of using the epoxy group containing acrylic polymer, the preferable embodiment is as same as the acrylic polymer (A1).

In case of using the epoxy group containing acrylic polymer, and using the amine based curing agent is used as the following described heat curing agent which is included in the second binder component, the epoxy group and the active hydrogen comprised in the amine based curing agent reacts, thereby it contributes to the glass transition temperature of the protective layer-forming film after the heat curing, and the glass transition temperature can be easily controlled with in the above range. Also, the modulus of elasticity of the protective layer-forming film at 23°C after the heat curing can be easily controlled as well.

[0057]

In case of using the heat curable polymer component (AB) comprising the epoxy group, as similar to the case of using the epoxy based heat curable component as the heat curable component (B), it is preferable to together use the heat curing agent (B12) or the curing catalyst (B13).

[0058]

The second binder component may comprise the above mentioned polymer component (A) or the heat curable component (B) together with the heat curable polymer component (AB).

[0059]

In case the protective layer-forming film comprises either or both of the heat curable component (B) and the heat curable polymer component (AB), the protective layer-forming film will have the heat curable property. In order to provide further

enhanced heat curable property to the protective layer-forming film, and also to improve the warpage correction function of the adherend, the protective layer-forming film preferably at least comprises the heat curable component (B). However, in case the protective layer-forming film only comprises the heat curable component (B), the sheet form maintaining property of the protective layer-forming film may deteriorate. Thus, the protective layer-forming film preferably comprises the heat curable component (B), and either one or both of the polymer component (A) and the heat curable polymer component (AB).

[0060]

In this case, the protective layer-forming film includes the heat curable component (B) of preferably more than 70 parts by weight, and more preferably more than 85 parts by weight with respect to 100 parts by weight of total of the polymer component (A) and the heat curable polymer component (AB). When the lower limit of the content of the heat curable component (B) is within such range, the glass transition temperature of the protective layer-forming film after the heat curing and the modulus of elasticity of the protective layer-forming film at 23°C after the heat curing can be easily regulated within the above mentioned range.

Note that, in the present invention, for the embodiment of the content of the components constituting the protective layer-forming film, in case it is determined based on the content of the heat curable polymer component (AB), and when the heat curable polymer component (AB) is the crosslinked epoxy group containing acrylic polymer, the content to be based on is the content of the epoxy group containing acrylic polymer before crosslinking.

[0061]

Also, as the upper limit of the content, the heat curable component (B) is included preferably by 135 parts by weight or less with respect to 100 parts by weight

of total of the polymer component (A) and the heat curable polymer component (AB). By having the upper limit of the content of the heat curable component (B) within such range, the sheet form maintaining property or the flexibility of the protective layer-forming film tends to be maintained in good condition. Particularly, in case the protective layer-forming film comprises the inorganic filler (C) which will be described in the following, when the content of the inorganic filler (C) is too much, the sheet form maintaining property or the flexibility of the protective layer-forming film declines, and the resistance against the bending or the handling property tends to decline. Thus, the upper limit of the content of the heat curable component (B) is preferably within such range.

[0062]

Further, in case the heat curable polymer (B) is the epoxy based curable component, the protective layer-forming film includes the epoxy compounds (B11) of preferably 70 parts by weight or more, more preferably 85 to 130 parts by weight and further preferably 85 to 120 parts by weight with respect to 100 parts by weight of total of the polymer component (A) and the heat curable polymer component (AB). Thereby, the glass transition temperature of the protective layer-forming film after the heat curing and the modulus of elasticity of the protective layer-forming film at 23°C after the heat curing can be easily regulated within the above mentioned range.

[0063]

The protective layer-forming film may comprise the following components besides the binder component.

[0064]

The inorganic filler (C)

The protective layer-forming film preferably comprises the inorganic filler (C). By blending the inorganic filler (C) to the protective layer-forming film, the modulus of

elasticity at 23°C after the heat curing can be easily regulated within the above mentioned range. Further, by carrying out the laser marking to the protective layer, thereby the inorganic filler (C) is exposed at the part which was ground off by the laser beam, and the reflection light is scattered which show a color close to white. Thereby, in case the protective layer-forming film comprises the coloring agent which will be described in below, the contrast between the laser marking part and other part is generated thereby there is an effect to make the printing clearer.

[0065]

As the preferable inorganic filler, powders such as silica, alumina, talc, calcium carbonate, titanium oxide, iron oxide, silicon carbide, boron nitride or so, a beads of which these has been made into spherical form, a single crystal fiber and glass fiber or so may be mentioned. Among these, silica filler and alumina filler are preferable. The above mentioned inorganic filler (C) may be used alone or by mixing two or more thereof.

In order to ensure the above effect, as the range of the content of the inorganic filler (C), it is preferably 10 to 70 parts by weight, more preferably 40 to 70 parts by weight and particularly preferably 55 to 65 parts by weight, with respect to the entire solid portion 100 parts by weight constituting the protective layer-forming film. By setting the content of the inorganic filler (C) within the above mentioned range, the modulus of elasticity at 23°C after the heat curing is easily regulated within the above mentioned range, and the warpage correction function is improved; thereby the protective layer-forming film having high reliability can be obtained.

Also, the average particle diameter of the inorganic filler (C) is preferably 0.02 to 5 μm, more preferably 0.05 to 4.5 μm, and particularly preferably 0.1 to 4 μm. By having the average particle diameter of the inorganic filler (C) within the above mentioned range, the warpage correction function improves. The average particle

diameter of the inorganic filler (C) is the number average particle diameter wherein 20 inorganic fillers (C) are arbitrary selected in the electron microscope to measure the long axis diameter, then calculating an arithmetic mean value.

[0066]

The coloring agent (D)

The protective layer-forming film can be blended with the coloring agent (D). By blending the coloring agent, when the semiconductor devices are incorporated to the machines, the infrared ray or so generated by the surrounding devices can be blocked, thus the malfunction of the semiconductor device caused thereby can be prevented. Also, if the protective layer is marked by means of laser marking or so, there is an effect that the marks such as the letters and symbols or so become visible. That is, for the semiconductor device or the semiconductor chip formed with the protective film, usually the product number is printed on the surface of the protective layer by laser marking method (the method of printing by grinding the surface of the protective film by the laser light), however since the protective film comprises the coloring agent (D), the sufficient contrast between the area of the protective film which is ground off by the laser, and those not ground off can be generated, hence the visibility is improved.

[0067]

As the coloring agent, the organic or inorganic pigment and die are used. Among these, a black pigment is preferable from the point of the blocking property of the electromagnetic wave or the infrared ray. As for the black pigment, carbon black, iron oxide, manganese dioxide, aniline black, and activated carbon or so may be used, but it is not limited thereto. The carbon black is particularly preferable from the point of improving the reliability of the semiconductor device. The coloring agent (D) may be used alone, or by combining two or more thereof.

The blending amount of the coloring agent (D) is preferably 0.1 to 35 parts by weight, more preferably 0.5 to 25 parts by weight and particularly preferably 1 to 15 parts by weight with respect to 100 parts by weight of the entire solid portion constituting the protective layer-forming film.

[0068]

The coupling agent (E)

The coupling agent (E) comprising the functional group reacting with the inorganic compound and the functional group reacting with the organic functional group may be used to improve the adhesiveness and the contact of the protective layer-forming film against the adherend, and/or the cohesiveness of the protective layer. Also, by using the coupling agent (E), without compromising the heat resistance of the protective layer obtained by curing the protective layer-forming film, the water resistance thereof can be improved. As such coupling agent, a titanate based coupling agent, an aluminate based coupling agent, and a silane coupling agent or so may be mentioned. Among these, the silane coupling agent is preferable.

[0069]

As the silane coupling agent, the silane coupling agent is preferably used wherein the functional group which reacts with the organic functional group thereof is the group which reacts with the functional group comprised in the polymer component (A), the heat curable component (B) and the heat curable polymer component (AB).

As such silane coupling agent, γ-glycidoxypropyltrimethoxy silane, γ-glycidoxypropylmethyldiethoxy silane, β-(3,4-epoxycyclohexyl)ethyltrimethoxy silane, γ-(methacryloxypropyl)trimethoxy silane, γ-aminopropyltrimethoxy silane, N-6-(aminoethyl)-γ-aminopropyltrimethoxy silane, N-6-(aminoethyl)-γ-aminopropylmethyldiethoxy silane, N-phenyl-γ-aminopropyltrimethoxy silane, γ-ureidepropyltriethoxy silane, γ-melcaptopropyltrimethoxy silane,

γ-melcaptopropylmethyldimethoxy silane, bis(3-triethoxysilylpropyl)tetrasulphone, methyltrimethoxy silane, methyltriethoxy silane, vinyltrimethoxy silane, vinyltriacetoxy silane, imidazole silane or so may be mentioned. These may be used alone or by mixing two or more thereof.

[0070]

The silane coupling agent is included in the ratio usually of 0.1 to 20 parts by weight, more preferably 0.2 to 10 parts by weight and further preferably 0.3 to 5 parts by weight with respect to 100 parts by weight of total of the polymer component (A), the heat curable component (B) and the heat curable polymer component (AB). If the content of the coupling agent is less than 0.1 parts by weight, there is a chance that the above mentioned effect cannot be obtained, and if it exceeds 20 parts by weight, it may become a cause of the outgas generation.

[0071]

The general additives (F)

Various additives may be blended depending on the needs into the protective layer-forming film besides the above described. As for the various additives, a leveling agent, a plasticizer, an antistatic agent, an antioxidizer, an ion scavenger, a gettering agent, a chain transfer agent, a release agent or so may be mentioned.

[0072]

The protective layer-forming film has the initial bonding property and the heat curable property, and at the non-cured condition, it is easily bonded to the semiconductor wafer or chip or so by pressing. When pressing, the protective film-forming layer may be applied with heat. By going through the heat curing, at the end, a protective film having high impact resistance can be provided, and having excellent bonding strength, further sufficient protection function can be maintained even under the harsh condition of the high temperature and high humidity. Note that, the

protective layer-forming film can be a single layer structure, or it may be multilayer structure.

[0073]

The protective layer-forming film is obtained for example by using the composition (the protective layer-forming composition) obtained by mixing the above mentioned each component in appropriate ratio. The protective layer-forming composition may be diluted with the solvent in advance, or the solvent may be added during the mixing. Also, when using the protective layer-forming composition, it may be diluted with the solvent.

As such solvent, ethyl acetate, methyl acetate, diethyl ether, dimethyl ether, acetone, methylethyl ketone, acetonitrile, hexane, cyclohexane, toluene, heptane or so may be mentioned.

[0074]

The thickness of the protective layer-forming film is not particularly limited, however preferably it is 3 to 30 μm, more preferably 5 to 250 μm, and particularly preferably 7 to 200 μm.

[0075]

The maximum transmittance rate at the wavelength of 300 to 1200 nm, which is the scale to indicate the transmittance of the visible light and/or the infrared ray and the ultraviolet ray of the protective layer-forming film, is preferably 20% or less, more preferably 0 to 15%, even more preferably more than 0% and 10% or less, and particularly preferably 0.001 to 8%. By having the maximum transmittance rate of the protective layer-forming film at the wavelength of 300 to 1200 nm within the above mentioned range, the effects of reducing the transmittance at the visible light wavelength and/or the infrared ray range, the prevention of the malfunction caused by the infrared ray of the semiconductor wafer, and the improvements of visibility of the

printings can be obtained. The maximum transmittance rate of the protective film forming layer at the wavelength of 300 to 1200 nm can be regulated by the above mentioned coloring agent (D). Note that, the maximum transmittance rate of the protective layer-forming film is determined by measuring the total light transmittance rate at the 300 to 1200 nm of the cured protective layer-forming film (the thickness of 25 μm), using UV-vis spectroscopy (made by Shimadzu Corporation), then the highest value of the transmittance rate was determined as the maximum transmittance rate.

[0076]

The protective layer-forming film of the present invention is used as the protective layer of the adherend such as semiconductor wafer or chip which uses silicon or galium·arsenic or so as the material.

[0077]

The production method of the protective layer-forming film is not particularly limited.

For example, the protective layer-forming film can be formed on the casting film. The protective layer-forming film can be formed on the casting film by coating and drying the composition for forming the protective layer-forming film using a generally known method such as a roll knife coater, a gravure coater, a die coater, a reverse coater or so.

The casting film can be used as the support sheet or cover film which will be described in following. Also, after it is formed, the protective layer-forming film may be transferred to the support sheet or to the cover film from the casting film. The casting film may be either of the support sheet or the cover film, and also the material which is to be transferred may be other one of the support sheet or the cover film.

[0078]

[The protective layer-forming composite sheet]

The protective layer-forming composite sheet is obtained by forming the support sheet in a releasable manner on one face of the protective layer-forming film. The shape of the protective layer-forming composite sheet is not limited to sheet shape, but it may be a belt shape, or these may be rolled up. As the support sheet, the release sheet may be mentioned, and the adhesive sheet which will be described in the following can be used.

[0079]

The protective layer-forming composite sheet is adhered to various adherends, and in some case a predetermined processing such as dicing or so may be carried to the adherend on the protective layer-forming composite sheet. Then, the support sheet is released while the protective layer-forming film is adhered to the adherend. That is, the protective layer-forming film is used for the process including the step of transferring to the adherend from the support sheet.

[0080]

The protective layer-forming film can have the same shape as the support sheet. Also, the protective layer-forming composite sheet may take pre-forming constitution wherein the protective layer-forming film is prepared to have roughly the same shape as the wafer or the shape which can completely include the shape of the wafer, and stacked on the support sheet having larger size than the protective layer-forming film.

[0081]

As the release sheet, for example polyethylene film, polypropylene, film, polybutene film, polybutadiene film, polymethylpentene film, polyvinyl chloride film, vinyl chloride copolymer film, polyethylene terephthalate film, polyethylene naphthalate film, polybutyleneterephthalate film, polyurethane film, ethylene vinyl acetate copolymer film, ionomer resin film, ethylene·(meth)acrylic acid copolymer film, ethylene·(meth)acrylate copolymer film, polystyrene film, polycarbonate film,

polyimide film, fluorine resin film or so is used. Also, the crosslinked film thereof may be used as well. Further, it may be a laminated film thereof.

[0082]

The surface tension of the face of the release film contacting with the protective layer-forming film is preferably 40 mN/m or less, more preferably 37 mN/m or less, and particularly preferably 35 mN/m or less. The lower limit is usually 25 mN/m or so. The release sheet with such low surface tension can be obtained by selecting the material appropriately, or by carrying out the release treatment by coating the release agent to the surface of the release sheet.

[0083]

As the release agent used for the release treatment, the release agent of an alkyd based, a silicone based, a fluorine based, an unsaturated polyester based, a polyolefin based, a waxed based or so may be used; and the alkyd based, the silicone based, and the fluorine based release agent are preferable since these have heat resistance.

[0084]

In order to carry out the release treatment to the surface of the film or so which becomes the base of the release sheet using the above mentioned release agent, the release agent may be used without the solvent, or by diluting with the solvent or by emulsifying, then coating by a gravure coater, a Meyer bar coater, an air knife coater, a roll coater or so; then the release agent layer may be formed by curing by placing the release sheet coated with the release agent under the ambient temperature or under a heating condition, or applying the electron beam.

[0085]

Also, the surface tension of the release film may be regulated by stacking the films using a wet lamination or dry lamination, a thermofusion lamination, a melt extrusion lamination, and a coextrusion processing or so. That is, the release sheet may

be made by producing the multilayered body stacked with other films so that the film having the surface tension of at least one face within the above mentioned preferable range as the face contacting with the protective layer-forming film of the release sheet, is the face contacting the protective layer-forming film.

[0086]

In case the predetermined processing such as dicing or so is carried out to the adherend on the protective layer-forming composite sheet, the adhesive sheet formed with the adhesive agent layer on the base is preferably used as the support sheet. In such embodiment, the protective layer-forming film is stacked on the adhesive agent layer provided on the support sheet. As the base of the adhesive sheet, the films described as the examples mentioned in the above may be mentioned. As the adhesive agent layer, those which is weak adhesive type having the adhesive force which can release the protective layer-forming film may be used, or those which is energy ray curable type wherein the adhesive force declines by energy ray irradiation may be used.

[0087]

The adhesive agent layer can be formed by conventionally known various adhesive agents (for example, a general adhesive agent such as a rubber based, an acrylic based, a silicone based, an urethane based, and vinylether based, the surface roughness formable adhesive agent, an energy ray curing adhesive agent, the thermal expansion component containing adhesive agent or so).

If the constitution of the protective layer-forming composite sheet has such constitution, when the protective layer-forming composite sheet function as the dicing sheet for supporting the adherend during the dicing step, the adhesiveness between the support sheet and the protective layer-forming film is maintained, and the chip with the protective layer-forming film is suppressed from being released during the dicing step. When the protective layer-forming composite sheet function as the dicing sheet for

supporting the adherend during the dicing step, there is no need to separately attach the dicing sheet to the wafer with the protective layer-forming film during the dicing step, thus the production steps of the semiconductor device can be simplified.

[0088]

In case the protective layer-forming composite sheet takes such pre-forming constitution, the protective layer-forming composite sheet may take the first, second and third constitution mentioned in following. Hereinafter, each constitution of the protective layer-forming composite sheet will be explained based on Fig.1 to Fig.3.

[0089]

In the first embodiment, as shown in Fig.1, the adhesive sheet 3 formed with the adhesive agent layer 2 on the base 1 is formed in a releasable manner on one face of the protective layer-forming film 10. In case of employing the first embodiment, the adhesive agent layer is constituted by the energy ray curing adhesive agent, and the energy ray is irradiated in advance to the area where the protective layer-forming film is to be stacked in order to reduce the adhesiveness, while other area is not irradiated with the energy ray; thereby the adhesive force may be kept high. In order to prevent the energy ray irradiation to other area, the energy ray blocking layer is provided by printing or so to other area of the support sheet, then the energy ray may be irradiated from the support sheet side.

[0090]

In the second constitution, as shown in Fig.2, the a jig adhesive layer 4 is separately provided to area which does not overlap with the protective layer-forming film 10 on the adhesive agent layer 2 of the protective layer-forming composite sheet 100. As the jig adhesive layer, the both sided adhesive sheet with the core material or the layer made of single layer of the adhesive agent or so can be used.

[0091]

In the third constitution, as shown in Fig.3, the interface bond regulating layer 5 having the shape which can completely include the shape of the protective layer-forming film is provided between the protective layer-forming film 10 and the adhesive agent layer 2. The interface bond regulating layer may be a predetermined film, or an interface bond regulating adhesive agent layer. In case the interface bond regulating layer is the interface bond regulating adhesive agent layer, it is preferably cured by irradiating the energy ray in advance to the adhesive agent layer having the energy ray curable property.

[0092]

By the protective layer-forming composite sheet taking these first to third constitutions, in the area surrounded by the protective layer-forming film, the protective layer-forming composite sheet can be adhered to the jig due to the sufficient adhesiveness of the adhesive agent layer or the jig adhesive layer. Also, the adhesiveness at the interface between the protective layer-forming film and the adhesive agent layer or the interface bond regulating layer is regulated, thus the pickup of the chip adhered to the protective layer-forming film or the protective layer can be easily done.

[0093]

In case the protective layer-forming composite sheet does not take the pre-forming constitution, that is as shown in Fig.4, when the protective layer-forming film 10 and the support sheet (in Fig.4, the adhesive sheet 3 formed with the adhesive agent layer 2 on the base 1) have the same shape, the jig adhesive layer 4 may be provided at the outer peripheral part of the surface of the protective layer-forming film 10. As the jig adhesive layer, the same mentioned in the above may be used.

[0094]

The thickness of the support sheet is usually 10 to 500 μm, preferably 15 to 300 μm, and particularly preferably 20 to 250 μm. In case the support sheet is the adhesive sheet formed with the adhesive agent layer on the base, the thickness of the adhesive agent layer is 3 to 50 μm in the support sheet.

[0095]

On the opposite face which is the face where the support sheet of the protective layer-forming film is adhered, the cover film may be temporarily adhered. The cover film may cover the jig adhesive layer or the adhesive agent layer when the support sheet is the adhesive sheet. As the cover sheet, the same as the release sheet mentioned in the above can be used.

[0096]

The thickness of the cover film is usually 5 to 300 μm, preferably 10 to 200 μm, and particularly preferably 20 to 150 μm.

[0097]

The protective layer-forming film of such protective layer-forming composite sheet can be the protective layer of the adherend. The protective layer-forming film is adhered to the backside of the semiconductor wafer for chip or to the semiconductor chip by face down method, then it is cured by appropriate means thereby it comprises the function to protect the semiconductor wafer or semiconductor chip in place of the sealing resin. In case of adhering to the semiconductor wafer, the protective layer has a function to reinforce the wafer hence the breakage of the wafer can be prevented.

[0098]

[The production method of the semiconductor device]

Next, the method of using the protective layer-forming film of the present invention will be described using the case of applying the protective layer-forming composite sheet for the production of the semiconductor device.

[0099]

The production method of the semiconductor device in the present invention preferably includes the step of adhering the protective layer-forming film of the above mentioned protective layer-forming composite sheet to the semiconductor wafer thereby obtaining the semiconductor chip comprising the protective layer.

Specifically, the protective layer-forming film of the above mentioned protective layer-forming composite sheet is adhered to the backside of the semiconductor wafer formed with the circuit on the surface, then obtaining semiconductor chip comprising the protective layer on the backside. The protective layer preferably is the protective layer of the semiconductor wafer or the semiconductor chip. Also, the production method of the semiconductor device of the present invention preferably includes the following steps (1) to (3), and in order to exhibit the warpage correction function of the wafer comprising the protective layer-forming film, the step (2) is carried out prior to the step (3). Note that, as discussed in the above, in case the protective layer-forming composite sheet functions as the dicing sheet for supporting the adherend during the dicing step, from the point of simplifying the production step of the semiconductor device, it is preferable to carry out the step (3) prior to the step (1).

Step (1): releasing the support sheet, and the protective layer-forming film or the protective layer,

Step (2): obtaining the protective layer by curing the protective layer-forming film,

Step (3): dicing the semiconductor wafer, and the protective layer-forming film or the protective layer.

[0100]

Also, the production method of the semiconductor wafer in the present invention may include the following step (4) besides the above mentioned steps (1) to (3).

Step (4): laser printing on the protective film.

[0101]

The semiconductor wafer may be a silicon wafer, or it may be a compound semiconductor wafer such as galium·arsenic or so. The formation of the circuit to the wafer surface can be carried out by various methods including the method conventionally used such as etching method, liftoff method or so. Next, the opposite face (the backside) of the circuit surface of the semiconductor wafer is ground. The method of grinding is not particularly limited, and the known means using the grinder or so may be used for grinding. During the backside grinding, to the circuit face for protecting the circuit of the surface, the adhesive sheet called surface protection sheet is adhered. The backside grinding is carried out by fixing the circuit face side of the wafer (that is the surface protection sheet side) to the chuck table or so, then grinding using the grinder the backside which is the side not formed with the circuit. The thickness of the wafer after the grinding is not particularly limited, however, usually it is 50 to 500 μm or so.

[0102]

Then, depending on the needs, the fracture layer caused during the backside grinding is removed. The removal of the fracture layer is done by chemical etching, plasma etching or so.

[0103]

Next, on the backside of the semiconductor wafer, the protective layer-forming film of the above mentioned protective layer-forming composite sheet is adhered. Then, the steps (1) to (3) are carried in the order of, step (1), (2), (3); step (2), (1), (3); or step (2), (3), (1). The detail of this process is discussed in Japanese Patent Application Laid Open No.2002-280329. As an example, the case of carrying out in the order of (1), (2) (3) will be described.

[0104]

First, the protective layer-forming film of the above mentioned protective layer-forming composite sheet is adhered to the backside of the semiconductor wafer to which the circuit is formed on the surface. Next, the support sheet is released from the protective layer-forming film, and the multilayered body of the semiconductor wafer and the protective layer-forming film is obtained. Next, the protective layer-forming film is cured, and the protective layer is formed on the entire face of the wafer. Specifically, the protective layer-forming film is cured by heat curing. As a result, the protective layer formed of cured resin is formed to the wafer backside; hence the strength is improved compared to the case of wafer alone, thereby the breakage when handling the thinned wafer can be reduced. Also, compared to the coating method wherein the coating solution for the protective layer is directly coated or made into film to the backside of the wafer or chip, the thickness of the protective layer has excellent uniformity.

[0105]

Next, the multilayered body of the semiconductor wafer and the protective layer is diced for each circuit formed on the wafer surface. The dicing is carried out by cutting the wafer and the protective layer. The dicing of the wafer is carried out by usual method using the dicing sheet. As a result, the semiconductor chip group comprising the protective layer on the backside which is separated on the dicing sheet is obtained.

[0106]

Next, it is preferable to laser print to the protective layer. The laser printing is carried out by a laser marking method, the product number is marked to the protective layer by grinding off the surface of the protective layer by irradiating the laser beam.

[0107]

Lastly, by picking up the semiconductor chip comprising the protective layer on the backside (the chip with the protective layer) using the general means such as collet or so, the chip with the protective layer is obtained. Further, the semiconductor device can be produced by mounting the chip with the protective layer on the predetermined base by face down method. Also, the semiconductor device can be produced by adhering the semiconductor chip comprising the protective layer on the backside to other members (on the chip mounting member) such as the die pad part or other semiconductor chip or so. According to the present invention as such, the protective layer having highly uniform thickness can be easily formed on the chip backside, and the cracks caused during the dicing step or packaging becomes difficult to occur.

[0108]

Note that, in case the protective layer-forming film of the above mentioned protective layer-forming composite sheet is adhered on the backside of the semiconductor wafer, and then the step (3) is done before step (1) (in the case of carrying out in order of the steps (2), (3), (1)); in such case, the protective layer-forming composite sheet can function as the dicing sheet. That is, it can be used as the sheet to support the semiconductor wafer during the dicing step. In this case, the semiconductor wafer is adhered to the inner peripheral part of the protective layer-forming composite sheet via the protective layer-forming film, and the outer peripheral part of the protective layer-forming composite sheet is bonded to other jigs such the ring flames or so, thereby the protective layer-forming composite sheet adhered to the semiconductor wafer is fixed and diced.

[0109]

The protective layer-forming film of the present invention or the protective layer-forming composite sheet using said film can be used for the protection of the

semiconductor compound, glass, ceramics and metals or so other than the method of use mentioned in above.

EXAMPLES

[0110]

Herein below, the present invention will be described based on the examples; however it is not to be limited thereto. Note that, in the following examples and comparative examples, <the glass transition temperature after the heat curing>, <the modulus of elasticity at 23°C after the heat curing>, <the warpage correction function evaluation>, <the reliability evaluation> and <the wafer warpage evaluation> were measured/evaluated.

[0111]

<The glass transition temperature after the heat curing >

Four of the protective layer forming films having the thickness of 45 μm were stacked, and heat cured (for 2 hours at 130°C) in the oven under the atmospheric environment, then the test samples were produced by cutting in a strip form having the width of 4.5 mm, the length of 20.0 mm, and the thickness of 0.18 mm. Using the viscoelasticity measurement device (DMA Q800 made by TA instruments), tan δ (the ratio between the loss modulus and the storage elasticity) of the test sample was measured at the tensile mode, under the frequency of 11 Hz, the temperature rising speed of 3°C/min, and the atmospheric environment of 0 to 300°C. Within this temperature range, the maximum value of tan δ was read, then the glass transition temperature (Tg) after the heat curing of the protective layer-forming film was determined.

[0112]

<The modulus of elasticity at 23°C after the heat curing>

The modulus of elasticity at 23°C of the measured data obtained from the measurement of the above mentioned <the glass transition temperature after the heat curing> was read, and the modulus of elasticity at 23°C after the heat curing of the protective layer-forming film was determined.

[0113]

<The warpage correction function evaluation>

The test sample wherein the protective layer-forming film having the thickness of 45 μm adhered to the copper foil having the thickness of 30 μm was heat cured (for 2 hours at 130°C) in the oven under the atmospheric environment.

Then, two points were taken which is the maximum distance in the copper foil rounded up by having the face adhered with the protective layer-forming film to the inner side due to the shrinking of the protective layer-forming film caused by the heat curing, and the distance of the two points was measured. The smaller this distance was, the larger the warpage was, and when the stress by the heat shrinking of the protective layer-forming film was large, then it can be determined that the warpage correction function was high.

[0114]

<The reliability evaluation>

1. The production of the chip with the protective layer

To the polished face of the silicon wafer carried out with #2000 polish (the diameter of 200 mm and the thickness of 350 μm), the protective layer-forming film of the protective layer-forming composite sheet was adhered while heating at 70°C, using the tape mounter (Adwill RAD-3600 F/12 made by Lintec Corporation), then the support sheet was released. Next, the protective layer-forming film was cured by heating for 2 hours at 130°C, thereby the multilayered body of the silicon wafer and the protective layer was obtained.

The protective layer side of the multilayered body obtained in the above was adhered to the dicing tape (Adwill D-686H made by Lintec Corporation), then using the dicing device (DFD651 made by DISCO Corporation), it was diced into the size of 3 mm x 3 mm thereby the chip with the protective layer for the reliability evaluation was obtained.

[0115]

2. The reliability evaluation

The obtained chip with the protective layer was left for 168 hours at 85°C and the relative humidity of 85%RH to allow absorbing the moisture, then IR reflow (Reflow furnace WL-15-20DNX made by Sagami-Rikou Co.,Ltd) of heating time of 1 minute at the maximum temperature of 260°C was carried out for three times. Further, this chip with the protective layer was placed in the thermal shock chamber (TSE-11 made by ESPEC CORP.), and the cycle of maintaining for 10 minutes at -40°C then maintaining 10 minutes at 125°C were carried out for 1000 cycles.

Then, for the chip with the protective layer which was taken out of the thermal shock chamber, the releasing at the bonding part which is between the semiconductor chip and the protective layer, or the presence of the crack at the protective layer were observed by the cross section observation and the scanning ultrasonic flow detection device (Hye-Focus made by Hitachi Construction Machinery Co.,Ltd).

Then, the above mentioned evaluations were carried out to 25 of the chips with the protective layer, and the numbers (the defective numbers) of the releasing of the bonding part between the semiconductor chip and the protective layer, or the presence of the crack at the protective layer were counted. The smaller the number of the defective number is, the higher the reliability of the protection layer-forming film is.

[0116]

<The wafer warpage evaluation>

The wafer having the 8 inch circuit (refer to Fig.5) was prepared wherein the thickness was 200 μm and having the warpage (the amount of the warpage: 10 mm) of the concave shape at the circuit face side (the surface side). Then, the protective layer-forming film was adhered to the backside of the wafer, heat cured for 2 hours at 130°C.

In case the amount of the warpage of the obtained wafer was 2 mm or less, it was evaluated "good", and if the amount of the warpage of the obtained wafer was more than 2 mm, then it was evaluated "poor". As long as the amount of the warpage of the wafer is 2 mm or less, it can be transported by the general wafer mounter.

[0117]

[The protective layer-forming composition]

Each component constituting the protective layer-forming composition is shown in below.

(A1-1) The polymer component: the acrylic polymer (the weight average molecular weight: 900,000, the glass transition temperature: -28°C) made by copolymerizing 55 parts by weight of n-butyl acrylate, 15 parts by weight of methyl acrylate, 20 parts by weight of glycidyl methacrylate, and 10 parts by weight of 2-hydroxyethyl acrylate

(A1-2) The polymer component: the acrylic polymer (the weight average molecular weight: 900,000, the glass transition temperature: -31°C) made by copolymerizing 55 parts by weight of n-butyl acrylate, 35 parts by weight of methyl acrylate, and 10 parts by weight of 2-hydroxyethyl acrylate

(B11-1) Bisphenol A type epoxy resin (jER828, the epoxy equivalent of 184 to 194 g/eq made by Mitsubishi Chemical Corporation)

(B11-2) Bisphenol A type epoxy resin (jER1055, the epoxy equivalent of 800 to 900 g/eq made by Mitsubishi Chemical Corporation)

(B11-3) Dicyclopentadiene type epoxy resin (EPICLON HP-7200HH, the epoxy equivalent of 255 to 260 g/eq made by DIC Corporation)

(B11-4) o-cresolnovolac type epoxy resin (EOCN-104S, the epoxy equivalent of 213 to 233 g/eq made by Nippon Kayaku Co.,Ltd)

(B12) Thermoactive latent epoxy resin curing agent (dicyandiamide (ADEKA HARDNER EH-3636AS, the active hydrogen amount of 21 g/eq made by ADEKA Corporation))

(B13) The curing catalyst (2-phenyl-4,5-dihydroxymethylimidazol (CUREZOL 2PHZ made by SHIKOKU CHEMICALS CORPORATION)

(C-1) Silica filler (SC2050MA, the average particle diameter of 0.5 μm made by Admatechs)

(C-2) Silica filler (the average particle diameter of 3 μm)

(C-3) Silica filler (SV-10, the average particle diameter of 8 μm made by Tatsumori Ltd)

(D) The coloring agent: carbon black (#MA650, the average particle diameter of 28 nm made by Mitsubishi Chemical Corporation)

(E) Silane coupling agent (A-1110 made by NUC Corporation)

[0118]

(The examples and the comparative examples)

The protective layer-forming composition was obtained by blending the above mentioned components in the amount described in Table 1. The blending amount of each component in Table 1 is shown by parts by weight in terms of the solid portion, and in the present invention, the solid portion refers to the entire component except for the solvent.

The protective layer-forming composition of Table 1 was diluted by methylethylketone so that the solid concentration was 61 wt%, then it was coated and

dried (the drying condition: 2 minutes in the oven at 120°C) on the release treated face of the support sheet (SP-PET3811, the thickness of 38 μm, made by Lintec Corporation) so that the thickness after the drying was 45 μm, thereby the protective layer-forming film was formed on the support sheet, thereby the protective layer-forming composite sheet was obtained. Then, the protective layer-forming film and the release treated face of the release sheet (polyethylene terephthalate film (SP-PET381031, the thickness of 38 μm, made by Lintec Corporation) were adhered against each other, thereby the protective layer-forming composite sheet adhered with the release sheet was obtained. The results are shown in Table 2.

[0119]

Table 1

	Examples							Comparative examples		
	1	2	3	4	5	6	7	1	2	3
A1-1	100	100	100	100	100	100		100	100	100
A1-2							100			
B11-1	60	60	60	60	60	20	60	60	20	60
B11-2	10	10	10	10	10		10	10		10
B11-3	30	30	30	30	30		30	30		30
B11-4						80			80	
B12	7.5	12.5	7.5	7.5	7.5	7.5	7.5	2	1	2
B13	7.5	12.5	7.5	7.5	7.5	7.5	7.5	2	1	2
C-1	320					320	320		320	
C-2		320	320	366	411					850
C-3								320		
D	10	10	10	10	10	10	10	10	10	10
E	2	2	2	2	2	2	2	2	2	2
Filler content	58.5	57.5	58.5	61.7	64.4	58.5	58.5	59.7	59.9	79.7
mol amount of entire epoxy group	0.45	0.45	0.45	0.45	0.45	0.47	0.45	0.45	0.47	0.45
mol amount of entire DICY active hydrogen	0.36	0.60	0.36	0.36	0.36	0.36	0.36	0.10	0.05	0.10
hydrogen/epoxy group (mol ratio)	0.80	1.33	0.80	0.80	0.80	0.76	0.80	0.21	0.10	0.21

[0120]

Table 2

	Examples							Comparative examples		
	1	2	3	4	5	6	7	1	2	3
Glass transition temperature after heat curing (°C)	182	198	182	182	182	260	154	121	104	104
Modulus of elasticity at 23°Cafter heat curing (GPa)	3.7	3.9	3.7	5.8	7.9	3.1	2.9	3	7.1	13.5
Warpage correction function evaluation (mm)	39	36	38	31	32	28	46	78	69	35
Reliability evaluation	0	0	0	0	0	0	0	0	0	11
Wafer warpage evaluation	Good	Good	Good	Good	Good	Good	Good	Poor	Poor	Good

Numerical References

[0121]

1: Base

2: Adhesive agent layer

3: Adhesive sheet (Support sheet)

4: Jig adhesive layer

5: Interface bond regulating layer

10: Protective layer-forming film

100: Protective layer-forming composite sheet

CLAIMS

1. A protective layer-forming film having a heat curable property,

a glass transition temperature after heat curing of 150 to 300°C, and a modulus of elasticity at a temperature of 23°C after heat curing of 0.5 to 10 GPa.

2. The protective layer-forming film as set forth in claim 1 comprising a heat curable component comprising an epoxy compound and an amine based curing agent.

3. The protective layer-forming film as set forth in claim 2 further comprising either one or both of a polymer component and a heat curable polymer component, and comprises 135 parts by weight or less of the heat curable component with respect to 100 parts by weight of total of the polymer component and the heat curable polymer component.

4. The protective layer-forming film as set forth in any one of claims 1 to 3, wherein said protective layer-forming film comprise an inorganic filler, and a content of the inorganic filler is 10 to 70 parts by weight with respect to 100 parts by weight of entire solid portion constituting the protective layer-forming film.

5. The protective layer-forming film as set forth in claim 4, wherein an average molecular weight of the inorganic filler is 0.02 to 5 μm.

6. The protective layer-forming film as set forth in any one of claims 1 to 5, wherein the heat curable polymer component is comprised in the protective layer-forming film, and the heat curable polymer component is an acrylic polymer comprising epoxy group containing monomer as a constituting monomer.

7. A protective film-forming composite sheet wherein a support sheet is formed in a releasable manner on one side of the protective layer-forming film according to any one of claims 1 to 6.