

DESCRIPTION

TITLE OF THE INVENTION: SURFACE PROTECTION METHOD AND
TEMPORARY FIXING METHOD FOR MATERIAL TO BE PROCESSED

5 TECHNICAL FIELD

The present invention relates to a surface protection method and a temporary fixing method for a material to be processed in processing various materials. More specifically, in processing an optical material, a semiconductor wafer or the like, the present invention provides a method for protecting the surface of a material to be
10 processed for the purpose of protecting a portion not to be processed from scratching or deposition of foreign matters during the processing, by forming a protective film (hereinafter sometimes referred to as a cured product) made of a curable composition on the surface of the material to be processed. Further, the present invention provides a method for temporarily fixing a material to be processed, which comprises
15 bonding such a material to be processed to a substrate, processing the material to be processed and then immersing the bonded portion in warm water to remove the protective film thereby to recover the processed material.

BACKGROUND ART

20 In processing, particularly precision processing such as cutting, grinding or polishing, of engineering components such as metal plates, molds, aluminum sashes, plastic plates, semiconductor wafers, circuit boards, ceramics, glass and quartz, and electric and electronic components such as sensors, a surface protective film to temporarily protect components has been widely used so as to prevent scratching or
25 deposition of foreign matters on the processed surface of such a component, a circuit or a sensor portion. As such a surface protective film, a pressure-sensitive adhesive sheet has been mainly used.

For example, in a case where e.g. a semiconductor wafer or an optical component is to be made thin, a so-called backgrinding method is used for processing.
30 The backgrinding method is a method to protect a circuit surface of a wafer or a non-processed surface of an optical component by a surface protective sheet, to temporarily fix the component to a substrate via the surface protective sheet and to

grind the back side opposite to the circuit surface.

However, a pressure-sensitive adhesive surface protective sheet presently used, has limited capability to follow recesses and protrusions of a circuit on a semiconductor wafer. Accordingly, contamination due to e.g. infiltration of an abrasive fluid between the wafer and the surface protective layer, frequently becomes problematic. Further, also at the time of dicing a semiconductor wafer, a typical semiconductor surface protective sheet has had a problem such that it cannot follow protrusions of at least 100 μm represented by bumps, thus leading to contamination or chipping.

A conventional surface protective sheet is usually a sheet having an adhesive layer as a surface protective layer on a polymer film material, and the adhesive is designed to have a low elastic modulus so as to follow the recesses and protrusions on the circuit surface. However, if the elastic modulus is too low, a great stress will be applied to the wafer when the sheet is removed by peeling from the wafer, thus leading to breakage.

Accordingly, a protective sheet which will be easily removed by energy rays has been developed, such that the adhesive is cured by irradiation with energy rays such as ultraviolet rays before peeling of the sheet to reduce the adhesive force between the wafer and the protective sheet. However, during the grinding, the adhesive layer is in an uncured state and is thus too soft, whereby there has been a problem that the wafer is likely to be broken during the grinding.

Patent Document 1 discloses a wafer grinding method which comprises bonding the above protective sheet which will be easily removed by energy rays, to a wafer on which a circuit is formed, curing the adhesive layer with energy rays, and then carrying out backgrinding of the wafer. However, the adhesive is not a fluid and thus does not have sufficient capability to follow the recesses and protrusions on the wafer circuit surface.

On the other hand, Patent Document 2 discloses a hot-melt type semiconductor surface protective sheet. A hot-melt type sheet which is melted by heating at from 60 to 100°C to show fluidity, follows the recesses and protrusions on the circuit surface and exhibits excellent grinding properties. However, this sheet has such a nature that it undergoes melting every time when the temperature exceeds the

melting point.

In order to solve the above problems, the present inventors have previously proposed a resin composition comprising a resin made of specific (meth)acryl monomers, as a composition which is a material having a sufficient capability to follow
5 recesses and protrusions on a circuit surface of an optical component and which has sufficient rigidity as a supporting material in grinding (Patent Documents 3 and 4). Such a resin composition is effective for the surface protection during backgrinding. However, a resin composition is desired whereby the surface is completely cured at the time of the surface protection. That is, if the polymerization is inhibited by oxygen
10 at the time of the surface protection for the surface grinding or cutting, the surface may not sometimes completely be cured.

On the other hand, separately from the surface protective film, a method has been studied to protect the surface of a material to be processed from e.g. cutting wastes during processing, by coating the surface of the material with an ultraviolet-
15 curable adhesive which is soluble in a specific organic solvent, followed by curing with ultraviolet rays for covering. However, since an organic solvent is used, the cleaning step is complicated, and there is a problem in view of working environment. Further, in the case of fine recesses and protrusions, the organic solvent cannot sufficiently infiltrate to completely remove the protective film, thus causing problems in the outer
20 appearance of the material to be processed.

As a composition which has a sufficient capability to follow recesses and protrusions on a circuit surface of e.g. a wafer or optical component and which has sufficient rigidity as a supporting material in grinding, a resin composition has been proposed which contains, as a component, a resin comprising a (meth)acrylate
25 monomer and a cyclopentadiene skeleton (Patent Document 5).

PRIOR ART DOCUMENTS

PATENT DOCUMENT

Patent Document 1: JP-A-11-026406

Patent Document 2: JP-A-2000-038556

Patent Document 3: WO2007/004620

Patent Document 4: WO2006/100788

DISCLOSURE OF THE INVENTION

However, the above Patent Document 5 does not disclose to provide a
5 protective film on the surface of a material to be processed by means of the above
resin composition and to provide a heating step of heat treatment at from 80 to 150°C.
Further, it discloses nothing about the fact that when such a heating step is provided,
the protective film does not detach during the processing even when subjected to
dicing.

10 The present inventors have conducted an extensive study to solve the above-
mentioned problems and as a result, have found that by carrying out heat treatment of
a protective film after forming the protective film made of the above-mentioned curable
composition on the surface of a material to be processed and then carrying out the
processing of the material to be processed, it is possible to protect the surface of the
15 material to be processed without detachment of the protective film during the
processing, and thus have accomplished the present invention.

That is, the present invention provides a surface protection method for a
material to be protected by forming a protective film made of a curable composition on
the surface of the material to be processed, wherein after forming a protective film on
20 the surface of the material to be processed, via a step of heat-treating the protective
film, processing of the material to be processed is then carried out.

Further, the present invention provides a method for temporarily fixing a
material to be processed, which comprises forming a protective film made of a curable
composition on the surface of the material to be processed, followed by heat treatment,
25 and then carrying out processing of the material to be processed, and then, immersing
it in warm water of at most 90°C to remove the protective film made of the curable
composition from the processed material.

Specifically, the present invention is as follows.

The present invention is a method for protecting the surface of a material to be
30 processed by forming a protective film on the surface of the material to be processed,
which comprises a forming step of forming the protective film made of a cured product
formed from a curable composition comprising the following (A), (B) and (C), on the

surface of the material to be processed, a heating step of heat treatment at a temperature of from 80 to 150°C after the forming step, and a processing step of processing the material to be processed after the heating step:

- (A) a polyfunctional (meth)acrylate,
- 5 (B) a monofunctional (meth)acrylate, and
- (C) a photopolymerization initiator.

Further, it is the method for protecting the surface of a material to be processed according to Claim 1, wherein the protective film contains (D) a resin having a cyclopentadiene skeleton.

10 Further, it is the method for protecting the surface of a material to be processed, wherein (D) the resin containing a cyclopentadiene skeleton contains ester groups or hydroxy groups in its molecule.

Further, it is the method for protecting the surface of a material to be processed, wherein each of (A) the polyfunctional (meth)acrylate and (B) the monofunctional
15 (meth)acrylate is hydrophobic.

Further, it is the method for protecting the surface of a material to be processed, wherein the curable composition contains from 5 to 50 parts by mass of (A) the polyfunctional (meth)acrylate and from 50 to 95 parts by mass of (B) the monofunctional (meth)acrylate per 100 parts by mass of the total amount of (A) and (B),
20 and contains from 0.1 to 20 parts by mass of (C) the photopolymerization initiator and from 0.1 to 50 parts by mass of (D) the resin having a cyclopentadiene skeleton per 100 parts by mass of the total amount of (A) and (B).

Further, it is a method for temporarily fixing a material to be processed by forming a protective film on the surface of the material to be processed, which
25 comprises a forming step of forming the protective film made of a cured product formed from a curable composition comprising the following (A), (B) and (C), on the surface of the material to be processed, a heating step of heat treatment at a temperature of from 80 to 150°C after the forming step, a processing step of processing the material to be processed after the heating step, and a removal step of
30 immersing the processed material in warm water of at most 90°C to remove the protective film from the processed material after the processing step:

- (A) a polyfunctional (meth)acrylate,

- (B) a monofunctional (meth)acrylate, and
- (C) a photopolymerization initiator.

ADVANTAGEOUS EFFECTS OF THE INVENTION

5 According to the method for protecting the surface of a material to be processed of the present invention, it is possible to obtain such an effect that even when subjected to processing such as dicing, the protective film will not be detached, and it is possible to prevent scratching or deposition of foreign matters on the processed surface of the material, the circuit or the sensor portion.

BEST MODE FOR CARRYING OUT THE INVENTION

10 The present invention is a method for protecting the surface of a material to be processed which is characterized in that after forming a protective film formed from a curable composition on the surface of the material to be processed, the protective film
15 is heat-treated at from 80 to 150°C and then processing of the material to be processed is carried out, whereby detachment of the protective film during the processing can be prevented.

 The temperature for the heat treatment is preferably from 80 to 150°C, more preferably from 90 to 120°C with a view to maintaining the releasability of the
20 protective film. When it is at least 80°C, the effect by the heat treatment can be obtained, and when it is at most 150°C, the releasability will be good.

 The curable composition to be used for a protective film in the present invention preferably comprises (A) a polyfunctional (meth)acrylate, (B) a monofunctional (meth)acrylate, (C) a photopolymerization initiator and (D) a resin
25 containing a cyclopentadiene skeleton, in order to obtain the effects of the present invention.

 As (A) the polyfunctional (meth)acrylate to be used for the above curable composition, it is possible to use a polyfunctional (meth)acrylate oligomer/polymer/monomer having at least two (meth)acryloyl groups. The
30 polyfunctional (meth)acrylate oligomer/polymer may, for example, be 1,2-polybutadiene-terminated urethane (meth)acrylate (e.g. "TE-2000" or "TEA-1000", manufactured by NIPPON SODA CO., LTD.), a hydrogenated product thereof (e.g.

“TEAI-1000”, manufactured by NIPPON SODA CO., LTD.), 1,4-polybutadiene-terminated urethane (meth)acrylate (e.g. “BAC-45”, manufactured by OSAKA ORGANIC CHEMICAL INDUSTRY LTD.), polyisoprene-terminated (meth)acrylate or polyurethane acrylate (e.g. “UV-7000B”, manufactured by Nippon Synthetic Chemical Industry Co., Ltd), polyester urethane (meth)acrylate (e.g. “UV-3000B”, manufactured by Nippon Synthetic Chemical Industry Co., Ltd), polyether urethane (meth)acrylate, polyester (meth)acrylate or bisphenol A epoxy (meth)acrylate (e.g. “Biscoat #540” manufactured by OSAKA ORGANIC CHEMICAL INDUSTRY LTD., or “Biscoat VR-77” manufactured by SHOWA HIGHPOLYMER CO., LTD.). Among these, at least one material selected from the group consisting of 1,2-polybutadiene-terminated urethane (meth)acrylate, polyurethane acrylate oligomer and polyester urethane acrylate oligomer is preferred, and 1,2-polybutadiene-terminated urethane (meth)acrylate is more preferred, in that the effect for releasability is high.

Further, a bifunctional (meth)acrylate monomer may, for example, be 1,3-butylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, dicyclopentanyl di(meth)acrylate, 2-ethyl-2-butyl-propanediol (meth)acrylate, neopentyl glycol-modified trimethylol propane di(meth)acrylate, stearic acid-modified pentaerythritol diacrylate, polypropylene glycol di(meth)acrylate, 2,2-bis(4-(meth)acryloxy diethoxyphenyl)propane, 2,2-bis(4-(meth)acryloxy propoxyphenyl)propane or 2,2-bis(4-(meth)acryloxy tetraethoxyphenyl)propane.

A trifunctional (meth)acrylate monomer may, for example, be trimethylolpropane tri(meth)acrylate or tris[(meth)acryloxyethyl]isocyanurate.

A tetrafunctional or higher-functional (meth)acrylate monomer may, for example, be dimethylolpropane tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate, pentaerythritolethoxy tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate or dipentaerythritol hexa(meth)acrylate.

Among these, dicyclopentanyl di(meth)acrylate and/or 1,6-hexanediol di(meth)acrylate is preferred, and dicyclopentanyl di(meth)acrylate is more preferred, in that the effect for releasability is high.

Among (A) polyfunctional (meth)acrylates, it is preferred to use a polyfunctional (meth)acrylate oligomer/polymer having at least two (meth)acryloyl groups and a

bifunctional (meth)acrylate monomer in combination, since the effect for releasability is thereby high. The mixing ratio (mass ratio) of the polyfunctional (meth)acrylate oligomer/polymer having at least two (meth)acryloyl groups to the bifunctional (meth)acrylate monomer is preferably 30-100:70-0, more preferably 50-65:50-35, since
 5 the effect for releasability is thereby high.

(A) The polyfunctional (meth)acrylate to be used in the present invention is preferably hydrophobic one. In the case of hydrophobic one, it is possible to prevent an adverse phenomenon which is likely to occur in the case of water-soluble one such that a cured product of a curable composition will swell during the processing to cause
 10 displacement thereby to deteriorate the processing precision. Here, the hydrophobic polyfunctional (meth)acrylate means a (meth)acrylate having no hydroxy group. For example, the above-mentioned polyfunctional (meth)acrylates may be mentioned. Among them, at least one material selected from the group consisting of 1,2-polybutadiene-terminated urethane (meth)acrylate, 1,6-hexanediol di(meth)acrylate
 15 and dicyclopentanyl di(meth)acrylate is preferred. Even a hydrophilic one may be used unless a cured product of its curable composition will not substantially be swelled or partially dissolved by water.

The amount of (A) the polyfunctional (meth)acrylate is preferably from 5 to 50 parts by mass, more preferably from 20 to 40 parts by mass, per 100 parts by mass of
 20 the total amount of (A) and (B) the after-mentioned monofunctional (meth)acrylate component. When it is at least 5 parts by mass, it is possible to prevent deterioration of the releasability or prevent the cured product of the curable composition from not forming a film, and when it is at most 50 parts by mass, it is possible to avoid too much shrinkage upon curing or deterioration of the initial adhesion.

(B) The monofunctional (meth)acrylate to be used for the curable composition may, for example, be methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, dicyclopentanyl (meth)acrylate,
 25 dicyclopentenyl (meth)acrylate, dicyclopentenyl oxyethyl (meth)acrylate, isobornyl (meth)acrylate, methoxylated cyclodecatriene (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 4-

hydroxybutyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, glycidyl (meth)acrylate, ω -carboxy-polycaprolactone mono(meth)acrylate, caprolactone-modified tetrahydrofurfuryl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, t-butylaminoethyl (meth)acrylate, ethoxycarbonylmethyl (meth)acrylate, phenol ethylene oxide-modified (meth)acrylate, phenol(2-mol ethylene oxide-modified) (meth)acrylate, phenol(4-mol ethylene oxide-modified) (meth)acrylate, paracumylphenol ethylene oxide-modified (meth)acrylate, nonylphenol ethylene oxide-modified (meth)acrylate, nonylphenol (4-mol ethylene oxide-modified) (meth)acrylate, nonylphenol (8-mol ethylene oxide-modified) (meth)acrylate, nonylphenol (2.5-mol propylene oxide-modified) (meth)acrylate, 2-ethylhexyl carbitol (meth)acrylate, ethylene oxide-modified phthalic acid (meth)acrylate, ethylene oxide-modified succinic acid (meth)acrylate, trifluoroethyl (meth)acrylate, acrylic acid, methacrylic acid, maleic acid, fumaric acid, ω -carboxy-polycaprolactone mono(meth)acrylate, phthalic acid monohydroxyethyl (meth)acrylate, (meth)acrylic acid dimer, β -(meth)acroyloxyethyl hydrogen succinate, n-(meth)acryloyloxyalkyl hexahydrophthalimide or 2-(1,2-cyclohexanedicarboxyimido)ethyl (meth)acrylate.

Among these, at least one material selected from the group consisting of 2-(1,2-cyclohexanedicarboxyimido)ethyl (meth)acrylate, phenol(2-mol ethylene oxide-modified) (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, benzyl (meth)acrylate, ω -carboxy-polycaprolactone mono(meth)acrylate and 2-hydroxy-3-phenoxypropyl (meth)acrylate is preferred, and 2-(1,2-cyclohexanedicarboxyimido)ethyl (meth)acrylate and/or phenol(2-mol ethylene oxide-modified) (meth)acrylate is more preferred, since the effects for releasability is thereby high. The mixing ratio (mass ratio) of phenol(2-mol ethylene oxide-modified) (meth)acrylate to 2-(1,2-cyclohexanedicarboxyimido)ethyl (meth)acrylate is preferably 20-70:80-30, more preferably 30-45:70-55, since the effect for releasability is thereby high.

Like component (A), (B) the monofunctional (meth)acrylate is preferably hydrophobic one.

Here, hydrophobic one means a (meth)acrylate having no hydroxy group. In the case of hydrophobic one, it is possible to prevent an adverse phenomenon which is

likely to occur in the case of a water-soluble one such that a cured product of a curable composition will swell during the processing to cause displacement thereby to deteriorate processing precision. Further, even a hydrophilic one may be used unless a cured product of its curable composition will not be swelled or partially dissolved by water.

The amount of (B) the monofunctional (meth)acrylate to be used is preferably from 50 to 95 parts by mass, more preferably from 60 to 80 parts by mass, per 100 parts by mass of the total amount of components (A) and (B). When it is at least 50 parts by mass, there will be no deterioration in the initial adhesion, and when it is at most 95 parts by mass, the releasability will not be deteriorated, and a cured product of the curable composition can be obtained in a film form.

The adhesion to a metal surface can be further improved by using, in combination with components (A) and (B) of the above composition, a phosphate having a vinyl group or a (meth)acryloyl group, such as (meth)acryloyloxyethyl acid phosphate, dibutyl 2-(meth)acryloyloxyethyl acid phosphate, dioctyl 2-(meth)acryloyloxyethyl phosphate, diphenyl 2-(meth)acryloyloxyethyl phosphate or (meth)acryloyloxyethyl polyethylene glycol acid phosphate.

(C) The photopolymerization initiator to be used for the curable composition is incorporated in order to effect sensitization with active energy rays such as visible light or ultraviolet rays to enhance the photocuring property of the curable composition, and can be one of various known photopolymerization initiators. Specifically, it may, for example, be benzophenone or its derivative; benzyl or its derivative; anthraquinone or its derivative; benzoin or a benzoin derivative such as benzoin methyl ether, benzoin ethyl ether, benzoin propyl ether, benzoin isobutyl ether or benzyl dimethyl ketal; an acetophenone derivative such as diethoxyacetophenone, or 4-*t*-butyltrichloroacetophenone; 2-dimethylaminoethyl benzoate, *p*-dimethylaminoethyl benzoate, diphenyl disulfide, thioxanthone or their derivatives; camphor quinone or a camphor quinone derivative such as 7,7-dimethyl-2,3-dioxobicyclo[2.2.1]heptane-1-carboxylic acid, 7,7-dimethyl-2,3-dioxobicyclo[2.2.1]heptane-1-carboxy-2-bromoethylester, 7,7-dimethyl-2,3-dioxobicyclo[2.2.1]heptane-1-carboxy-2-methyl ester or 7,7-dimethyl-2,3-dioxobicyclo[2.2.1]heptane-1-carboxylic acid chloride; an α -amino alkylphenone derivative such as 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino

propan-1-one or 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)-butanone-1; or an acyl phosphine oxide derivative such as benzoyl diphenyl phosphine oxide, 2,4,6-trimethyl benzoyl diphenyl phosphine oxide, benzoyl diethoxyphosphine oxide, 2,4,6-trimethyl benzoyl dimethoxyphenyl phosphine oxide or 2,4,6-trimethyl benzoyl

5 diethoxyphenyl phosphine oxide. (C) The photopolymerization initiators can be used alone or in combination as a mixture of two or more of them.

The amount of (C) the photopolymerization initiator to be used is preferably from 0.1 to 20 parts by mass, more preferably from 3 to 10 parts by mass, per 100 parts by mass of the total amount of components (A) and (B). When the amount is at
10 least 0.1 part by mass, it is possible to certainly obtain the effect of promoting the curing. On the other hand, when the amount is at most 20 parts by mass, a sufficient curing rate can be obtained. A more preferred embodiment is such that component (C) is used in an amount of at least 3 parts by mass, whereby the composition becomes curable regardless of the light irradiation level.

15 (D) The resin having a cyclopentadiene skeleton to be used in the present invention may be any resin so long as it is a resin having a cyclopentadiene skeleton. However, the softening point is preferably from 50 to 200°C, and further, the number average molecular weight (Mn) is preferably from 300 to 600, from the viewpoint of the solubility in components (A) and (B). The softening point is measured in accordance
20 with JIS K2207 ring and ball method. The number average molecular weight is measured in accordance with GPC (gel permeation chromatography) polystyrene-calculated value. (D) may be a petroleum resin produced by using, as the main material, cyclopentadiene extracted from a C5 fraction. Specifically, e.g. "Quintone 1700", "Quintone 1500" or "Quintone 1325", manufactured by ZEON CORPORATION
25 may, for example, be mentioned.

The amount of (D) the resin having a cyclopentadiene skeleton to be used is preferably from 0.5 to 50 parts by mass, more preferably from 5 to 30 parts by mass, per 100 parts by mass of the total amount of components (A) and (B). When it is at
30 least 0.5 part by mass, a film will be formed without adhesive residue, and when it is at most parts by mass, the adhesion will not be deteriorated.

In order to improve the storage stability, the curable composition of the present invention may contain a small amount of a polymerization inhibitor. The

polymerization inhibitor may, for example, be methyl hydroquinone, hydroquinone, 2,2-methylene-bis(4-methyl-6-tertiary-butylphenol), catechol, hydroquinone monomethyl ether, monotertiary butyl hydroquinone, 2,5-ditertiary butyl hydroquinone, p-benzoquinone, 2,5-diphenyl-p-benzoquinone, 2,5-ditertiary-butyl-p-benzoquinone, 5 picric acid, citric acid, phenothiazine, tertiary-butyl catechol, 2-butyl-4-hydroxyanisole or 2,6-ditertiary-butyl-p-cresol.

Among these, at least one material selected from the group consisting of 2,2-methylene-bis(4-methyl-6-tertiary-butylphenol), hydroquinone monomethyl ether and p-benzoquinone is preferred, and 2,2-methylene-bis(4-methyl-6-tertiary-butylphenol) is 10 more preferred.

The amount of the polymerization inhibitor is preferably from 0.001 to 3 parts by mass, more preferably from 0.01 to 2 parts by mass, per 100 parts by mass of the total amount of components (A) and (B). When it is at least 0.001 part by mass, the storage stability will be sufficient, and when it is at most 3 parts by mass, secure 15 adhesion can be obtained, and the composition will not be uncured.

To the curable composition to be used in the present invention, various elastomers such as acryl rubber, urethane rubber, acrylonitrile-butadiene-styrene rubber, etc. which are commonly used, and additives such as an inorganic filler, a solvent, a bulking agent, a reinforcing material, a plasticizer, a thickener, a dye, a 20 pigment, a flame retardant, a silane coupling agent, a surfactant, etc. may be incorporated within a range not to impair the purpose of the present invention.

The present invention is a method for protecting the surface of a material to be processed, which comprises forming a protective film made of the above curable composition on the surface of the material to be processed, heat-treating the protective 25 film and then carrying out processing of the material to be processed, thereby to prevent detachment of the protective film during the processing and to protect the surface of the material to be processed.

The forming step of forming the protective film on the surface of the material to be processed is preferably a step wherein the curable composition is applied in a 30 thickness of from 20 to 200 μm , preferably from 50 to 150 μm , on the surface of the material to be processed, to form a protective film, which is then cured under such conditions that the wavelength is 365 nm and the irradiation is from 1,000 to 4,000

mJ/cm², preferably from 1,500 to 3,000 mJ/cm².

The heating step of heat treatment after the forming step is preferably a step wherein the protective film is heat-treated at a temperature of from 80 to 150°C, preferably from 80 to 120°C, for from 5 to 30 minutes.

5 The processing step of processing the material to be processed after the heating step is preferably a step of carrying out dicing under such conditions that the rotational speed is from 5,000 to 40,000 rpm, preferably from 10,000 to 35,000 rpm, the feed speed is from 0.2 to 50 mm/sec, preferably from 0.5 to 30 mm/sec and the chip size is from 0.5 to 15 mm square.

10 Further, the present invention is a method for temporarily fixing a material to be processed, which comprises forming a protective film made of the curable composition on the surface of the material to be processed, carrying out the heat treatment, then carrying out the processing of the material to be processed, and then, a removal step of immersing the processed material in warm water of from 70 to 90°C, preferably from
15 75 to 85°C, to remove the protective film made of the curable composition from the processed material.

When the cured product of the curable composition is removed, it can be recovered in the form of a film from the material whereby it is possible to obtain such an effect that the operation efficiency is excellent. Further, as a method for contacting
20 the cured product with warm water, a method of immersing it together with the processed material in warm water is simple and recommended.

EXAMPLES

Now, the present invention will be described in further detail with reference to
25 Examples, but it should be understood that the present invention is by no means restricted by such Examples.

Here, Examples I-1 to I-15 are Examples of the present invention, and Examples II-1 to II-5 are Comparative Examples.

EXAMPLE I-1

30 A curable composition was prepared by blending 6 parts by mass of 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one ("IRGACURE 907", manufactured by Ciba Specialty Chemicals, hereinafter referred to as "I-907") as (C)

photopolymerization initiator, 10 parts by mass of a cyclopentadiene skeleton resin ("Quintone 1700" manufactured by ZEON CORPORATION), containing hydroxy groups, softening point: 100°C, number average molecular weight: 380, hereinafter referred to as "Quintone 1700") as (D) resin containing a cyclopentadiene skeleton, and 0.1 part by mass of 2,2-methylene-bis(4-methyl-6-tertiary-butylphenol) (hereinafter referred to as "MDP") as polymerization inhibitor, to 100 parts by mass of a composition comprising 20 parts by mass of "TE-2000" manufactured by NIPPON SODA CO., LTD. (1,2-polybutadiene-terminated urethane methacrylate, hereinafter referred to as "TE-2000") and 15 parts by mass of dicyclopentanyl diacrylate ("KAYARAD R-684" manufactured by Nippon Kayaku Co, Ltd., hereinafter referred to as "R-684"), as (A) polyfunctional (meth)acrylate, and 40 parts by mass of 2-(1,2-cyclohexanedicarboxyimide)ethyl acrylate ("ARONIX M-140" manufactured by TOAGOSEI CO., LTD., hereinafter referred to as "M-140") and 25 parts by mass of phenol 2-mol ethylene oxide-modified acrylate ("ARONIX M-101A" manufactured by TOAGOSEI CO., LTD., hereinafter referred to as "M-101A"), as (B) monofunctional (meth)acrylate. Using the obtained curable composition, measurement of the tensile shear bond strength, the adhesion test and the removing test were carried out by the following evaluation methods. The results are shown in Table 1.

(EVALUATION METHODS)

Bond strength (tensile shear bond strength):

The bond strength (tensile shear bond strength) was measured in accordance with JIS K6850. Specifically, heat resistant Pyrex (registered trademark) glass (25 mm × 25 mm × 2.0 mm) (length × width × thickness)) was used as an adherend. Two sheets of the heat resistant Pyrex (registered trademark) glass were bonded by a prepared curable composition with a bonding area of a circular shape with a diameter of 8 mm and with a thickness of 100 μm. Then, the composition was cured by a curing apparatus using an electrodeless discharge lamp manufactured by Fusion UV Systems Inc., under a condition of an accumulated quantity of light of 2,000 mJ/cm² at a wavelength of 365 nm, to prepare a test piece for tensile shear bond strength. The test piece thus prepared was subjected to measurement of tensile shear bond strength by means of a tensile testing machine at a temperature of 23°C under a relative humidity of 50% at a pulling rate of 10 mm/min.

Retention state of protective film after dicing (adhesion test):

A test on the adhesion was carried out at a temperature of 23°C under a relative humidity of 50%. A curable composition was applied in a thickness of 100 µm on a silicon wafer, and the curable composition was cured by a curing apparatus using an electrodeless discharge lamp manufactured by Fusion UV Systems Inc., under a condition of an accumulated quantity of light of 2,000 mJ/cm² at a wavelength of 365 nm to prepare a protective film. Then, the protective film was heat-treated at 100°C for 10 minutes, and then, dicing was carried out under such conditions that a rotational speed was 30,000 rpm, the feed speed was 1.0 mm/sec and the chip size was 1 mm square, whereupon whether or not the protective film was retained after the dicing, was observed. Out of 25 chips, the number of chips on which the protective film was retained, was counted.

Removal time with warm water of 80°C (removing test):

The test piece on which the protective film was retained even after the above dicing, was immersed in warm water (80°C), whereby the time until the protective film was removed from the silicon wafer, was measured.

Observation of removal state (removing test):

After the test on the removal time with warm water of 80°C (removing test), the removed protective film was inspected.

TABLE 1-1

Ex. No.	Ex. I-1	Ex. I-2	Ex. I-3	Ex. I-4	Ex. I-5	Ex. I-6	Ex. I-7	Ex. I-8
Component (A) (parts by mass)	TE-2000	20	20	20	-	-	30	20
	R-684	15	15	15	-	-	-	15
	UV-7000B	-	-	-	20	-	-	-
	UV-3000B	-	-	-	-	20	-	-
	1,6HX-A	-	-	-	15	15	-	-
Component (B) (parts by mass)	M-101A	25	25	25	25	25	-	-
	M-140	40	40	40	40	40	40	40
	QM	-	-	-	25	-	-	-
	BZ	-	-	-	-	-	-	25
	M-5300	-	-	-	-	-	-	-
Component (C) (parts by mass)	M-5710	-	-	-	-	-	30	-
	I-907	6	6	6	6	6	6	6
	BDK	-	-	-	-	-	-	-
	Quintone1700	10	10	10	10	10	10	10
	Quintone1500	-	-	-	-	-	-	-
Polymerization inhibitor	MDP	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Temperature for heat treatment (°C)	-	100	80	150	100	100	100	100
Bond strength (MPa)	-	13.7	13.7	18.1	14.5	13.1	18.0	17.2
Retention state of protective film after dicing (number of sheets among 25 sheets)	-	25	25	25	25	25	25	25
Removal time in warm water at 80°C (min.)	-	18	15	41	22	20	40	33
Removal state	-	Film form Present invention	Film form Present invention	Film form Present invention	Film form Present invention	Film form Present invention	Film form Present invention	Film form Present invention
Note	-							

EXAMPLE I-2, I-3, I-11 and I-12

A curable composition was prepared in the same manner as in Example I-1 except that the heat treatment was carried out at a temperature shown in Table 1. With respect to the obtained curable composition, evaluation was carried out in the same manner as in Example I-1. The results are shown in Table 1.

EXAMPLE I-4 to I-10 and I-13 to I-15

A curable composition was prepared in the same manner as in Example I-1 except that raw materials of types shown in Table 1 were used in a composition shown in Table 1. With respect to the obtained curable composition, evaluation was carried out in the same manner as in Example I-1. The results are shown in Table 1.

(MATERIALS USED)

QM: dicyclopentenylloxyethyl methacrylate ("QM-657", manufactured by Rohm & Haas)

BZ: benzyl methacrylate ("LIGHT-ESTER BZ", manufactured by KYOEISHA CHEMICAL CO., LTD.)

UV-7000B: polyurethane acrylate oligomer ("UV-7000B", manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.)

UV-3000B: polyester urethane acrylate oligomer ("UV-3000B", manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.)

1,6-HX-A: 1,6-hexanediol diacrylate ("LIGHT ACRYLATE 1,6-HX-A", manufactured by KYOEISHA CHEMICAL CO., LTD.)

M-5300: ω -carboxy-polycaprolactone monoacrylate ("ARONIX M-5300", manufactured by TOAGOSEI CO., LTD.)

M-5710: 2-hydroxy-3-phenoxypropyl acrylate ("ARONIX M-5710", manufactured by TOAGOSEI CO., LTD.)

Quintone 1500: cyclopentadiene skeleton resin ("Quintone 1500", manufactured by ZEON CORPORATION, containing ester groups, softening point: 125°C, number average molecular weight: 470)

BDK: benzyl dimethyl ketal ("IRGACURE 651", manufactured by Ciba Specialty Chemicals)

EXAMPLE II-1 and II-2

A curable composition was prepared in the same manner as in Example I-1

except that the heat treatment was carried out at a temperature shown in Table 2.

With respect to the obtained curable composition, evaluation was carried out in the same manner as in Example I-1. The results are shown in Table 2. Here, "-" for the heat treatment temperature in Example II-1 means that no heat treatment was carried out.

EXAMPLE II-3 to II-5

A curable composition was prepared in the same manner as in Example I-1 except that raw materials of types shown in Table 2 were used in a combination shown in Table 2. With respect to the obtained curable composition, evaluation was carried out in the same manner as in Example I-1. The results are shown in Table 2.

TABLE 2

Ex. No.	Ex. II-1	Ex. II-2	Ex. II-3	Ex. II-4	Ex. II-5
Component (A) (parts by mass)	20	20	-	20	20
	15	15	-	15	80
	25	25	-	25	-
Component (B) (parts by mass)	QM	-	-	-	-
	BZ	-	-	-	-
	M-140	40	100	40	-
	IBX	-	-	-	-
Component (C) (parts by mass)	6	6	6	-	6
Component (D) (parts by mass)	10	10	10	10	10
Polymerization inhibitor	MDP	0.1	0.1	0.1	0.1
Temperature for heat treatment (°C)	-	180	100	100	100
Bond strength (MPa)	13.7	10.7	5.6	Not cured	3.8
Retention state of protective film after dicing (number of sheets among 25 sheets)	0	25	Dissolved	Not measurable	25
Removal time in warm water at 80°C (min.)	Not measurable	Not removed	Not measurable	Not measurable	Not removed
Removal state	Not measurable	Not measurable	Not measurable	Not measurable	Not measurable
Note	Comparative Example	Comparative Example	Comparative Example	Comparative Example	Comparative Example

(MATERIALS USED)

IBX: isobornyl methacrylate ("LIGHT-ESTER IB-X", manufactured by KYOEISHA CHEMICAL CO., LTD.)

As a result, in Example II-1, the protective film was peeled during dicing, since the dicing was carried out without heat treatment. Further, in Example II-2, although the protective film was maintained without peeling during the dicing, the releasability was deteriorated, since the temperature for heat treatment was too high, and its removal was impossible in the subsequent warm water treatment.

Further, in Example II-3, since (A) a polyfunctional (meth)acrylate was not incorporated, the cured product of the curable composition became thermoplastic, and the protective film underwent melting in the heat treatment before processing, and it was not possible to protect the surface. Further, in Example II-4, since (C) a photopolymerization initiator was not incorporated, the composition was not cured even after irradiation with light. In Example II-5, since (B) a monofunctional (meth)acrylate was not incorporated, distortion due to shrinkage upon curing was substantial, and cracking was observed on the surface of the cured product. In Example II-5, the cured product of the curable composition could not be peeled from the wafer.

Whereas, in Examples I-1 to I-14, dicing was carried out after the heat treatment, and in each case, the protective film did not come off during dicing, and it was possible to protect the surface. Further, in Examples I-1 to I-14, (A) a polyfunctional (meth)acrylate and (B) a monofunctional (meth)acrylate were blended in good balance together with a photopolymerization initiator, in each case, the bond strength of the curable composition after photopolymerization was sufficient, and the releasability at the time of peeling the cured product of the curable composition from a silicon wafer after dicing, was good. Further, the surface of the silicon wafer after the dicing was protected well. Further, in Example I-15, (D) a cyclopentadiene skeleton resin was not incorporated, whereby the surface was not completely cured, and stickiness was observed, but the bond strength was good.

INDUSTRIAL APPLICABILITY

According to the present invention, the above-described protective film is

formed on the surface of the material to be processed, and the protective film is heat-treated, followed by processing of the material to be processed, whereby it is possible to prevent detachment of the protective film during the processing, and it is possible to protect the surface of the material to be processed from scratching or contamination.

5 Further, the curable composition of the present invention has a sufficient capability to follow recesses and protrusions on the surface such as a circuit surface, whereby it is possible to protect the surface from scratching or contamination, not only for a flat surface but also for a surface having recesses and protrusions.

By immersing it in warm water of at most 90°C after processing the material to
10 be processed, the protective film of the present invention can be recovered in a film form from the processed material, whereby it is possible to obtain such an effect that the working efficiency is excellent. Further, it is not required to use an organic solvent, which was essentially required by a conventional adhesive, and thus, it is possible to obtain such an effect that the environment burden can be reduced.

15 The present invention is one to provide a protective film on the surface of a material to be processed, by means of the above-described curable composition. According to the present invention, it is possible to obtain such an effect that the protective film will not come off during the processing, even when subjected to dicing under such a condition that the feed speed is for example at most 2 mm/sec.

20 According to the surface protection method of the present invention, the protective film made of the curable composition has a photopolymerizability by virtue of its composition and is curable by visible light or ultraviolet rays, and accordingly, as compared with a conventional hot melt adhesive, it is possible to obtain remarkable effects in the aspects of power saving, energy saving and shortening of the operation.
25 Further, by way of the heat treatment step after forming the above protective film on the surface of the material to be processed, it is possible to relax the internal strain of the protective film thereby to prevent detachment of the protective film in the subsequent step of processing the material to be processed. Further, by using such a method, it is possible to obtain a high bond strength without being influenced by e.g. a
30 cutting liquid to be used for processing of the protective film and it is possible to protect the surface of the material to be processed from infiltration of the cutting fluid or from scratching or deposition of foreign matters due to e.g. cutting wastes.

Since the effects as described above are obtainable, the present invention is useful in industry for e.g. processing of engineering components or electronic or electric components such as sensors, particularly for precision processing such as cutting, grinding or polishing.

5

The entire disclosure of Japanese Patent Application No. 2008-125321 filed on May 12, 2008 including specification, claims, drawings and summary is incorporated herein by reference in its entirety.

CLAIMS:

1. A method for protecting the surface of a material to be processed by forming a protective film on the surface of the material to be processed, which comprises a forming step of forming the protective film made of a cured product formed from a curable composition comprising the following (A), (B) and (C), on the surface of the material to be processed, a heating step of heat treatment at a temperature of from 80 to 150°C after the forming step, and a processing step of processing the material to be processed after the heating step:
 - (A) a polyfunctional (meth)acrylate,
 - (B) a monofunctional (meth)acrylate, and
 - (C) a photopolymerization initiator.
2. The method for protecting the surface of a material to be processed according to Claim 1, wherein the protective film contains (D) a resin having a cyclopentadiene skeleton.
3. The method for protecting the surface of a material to be processed according to Claim 2, wherein (D) the resin having a cyclopentadiene skeleton has ester groups or hydroxy groups in its molecule.
4. The method for protecting the surface of a material to be processed according to any one of Claims 1 to 3, wherein each of (A) the polyfunctional (meth)acrylate and (B) the monofunctional (meth)acrylate is hydrophobic.
5. The method for protecting the surface of a material to be processed according to any one of Claims 2 to 4, wherein the curable composition contains from 5 to 50 parts by mass of (A) the polyfunctional (meth)acrylate and from 50 to 95 parts by mass of (B) the monofunctional (meth)acrylate per 100 parts by mass of the total amount of (A) and (B), and contains from 0.1 to 20 parts by mass of (C) the photopolymerization initiator and from 0.1 to 50 parts by mass of (D) the resin having a cyclopentadiene skeleton per 100 parts by mass of the total amount of (A) and (B).
6. A method for temporarily fixing a material to be processed by forming a protective film on the surface of the material to be processed, which comprises a forming step of forming the protective film made of a cured product formed from a curable composition comprising the following (A), (B) and (C), on the surface of the material to be

processed, a heating step of heat treatment at a temperature of from 80 to 150°C after the forming step, a processing step of processing the material to be processed after the heating step, and a removal step of immersing the processed material in warm water of at most 90°C to remove the protective film from the processed material after

5 the processing step:

- (A) a polyfunctional (meth)acrylate,
- (B) a monofunctional (meth)acrylate, and
- (C) a photopolymerization initiator.